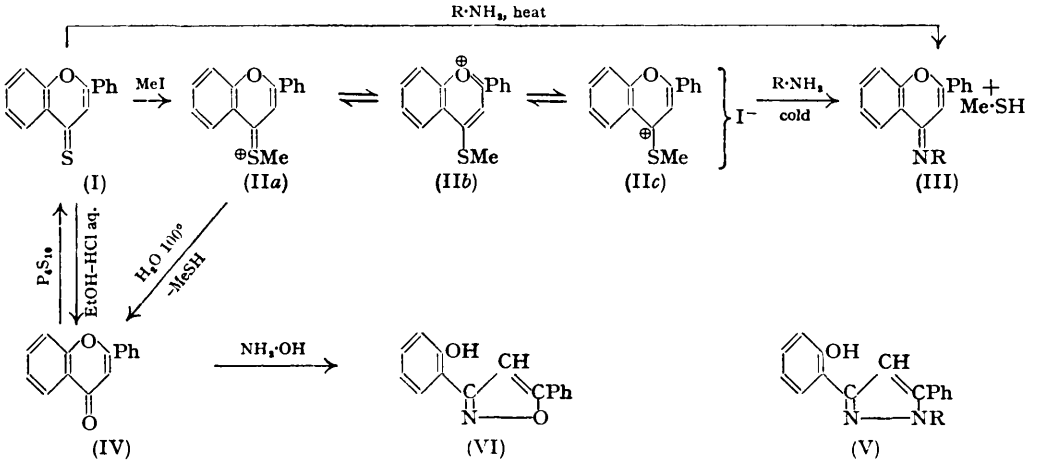
235. *Some Properties of 4-Thionflavone and its Methiodide, and of 4-Thionchromones.*

By Wilson Baker, J. B. Harborne, and W. D. Ollis

4-Thionflavone, prepared from flavone and phosphorus pentasulphide, is slowly hydrolysed by acids to flavone, and reacts with hydroxylamine on heating to give flavone oxime. 4-Thionflavone methiodide is much more reactive; it is hydrolysed by water to flavone, and gives at room temperature with the appropriate reagents, derivatives of flavone imine, including flavone oxime, hydrazone, and semicarbazone. The previously described " flavone oxime," prepared from flavone, is shown to be an *iso*oxazole, and " phenylhydrazones " derived from some 4-thionchromones are proved to be pyrazoles.

4-Thionflavone (I), deep red needles, m. p. 87°, has been little studied, and was first prepared by Schnell (Diss., Berlin, 1921; the method was later published by Schönberg and Nickel, *Ber.*, 1931, **64**, 2325, and by Diesbach and Kramer, *Helv. Chim. Acta*, 1945, **28**, 1404) by heating flavone (IV) with phosphorus pentasulphide. By using purified phosphorus pentasulphide and toluene as solvent at 100°, 4-thionflavone is now readily prepared in 55% yield. Its structure follows from the facts that it differs from 1-thiaflavone (prepared by cyclisation of β-phenylthiocinnamic acid, Ruhemann, *Ber.*, 1913, **46**, 2197), that it shows no phenolic properties, and that it is extremely easily reconverted into flavone by hydrolysis of its methiodide (see p. 1306).



4-Thionflavone is unaffected by hot methanolic barium hydroxide, which converts flavone into *o*-hydroxydibenzoylmethane (Müller, *J.*, 1915, **107**, 872). It is, however, slowly hydrolysed to flavone and hydrogen sulphide by boiling ethanolic hydrochloric acid. It very readily forms a dark, maroon-coloured methiodide, which undoubtedly contains a mesomeric cation derived from canonical forms such as (II*a*), (II*b*), and (II*c*).

4-Thionflavone methiodide (II) is extremely reactive; it is hydrolysed rapidly by boiling water, giving flavone (IV) and methanethiol, and quickly reacts at room temperature with many compounds containing the anionoid amino-group to form methanethiol and derivatives of flavone imine. Form (II*c*) is doubtless the reactive form of the molecule involved in attack by these anionoid reagents. Thus, with the appropriate reagents, it yields flavone benzylimine (III; R = CH_2Ph) (preceding paper), flavone anil (III; R = Ph), flavone hydrazone (III; R = NH_2), flavone benzoylhydrazone (III; R = NH·COPh), flavone semicarbazone (III; R = NH·CO·NH_2), flavone thionsemicarbazone (III; R = NH·CS·NH_2), and flavone oxime (III; R = OH). The flavone hydrazone (III; R = NH_2)

gave an *N*-benzoyl derivative, identical with the product prepared from 4-thionflavone methiodide (II) and benzoylhydrazine, an *N*-acetyl derivative (III; R = NHAc), and a benzylidenehydrazine derivative (III; R = N:CHPh). None of the above compounds containing –N–N– groups shows phenolic properties, and they are, therefore, correctly represented as flavone hydrazones, and not as the isomeric, phenolic pyrazoles (V; R = H, COPh, $CO{\cdot}NH_2$, and $CS{\cdot}NH_2$), one of which (V; R = H) has for comparison been prepared from *o*-hydroxydibenzoylmethane and hydrazine. In addition, flavone hydrazone reacts with a further molecule of 4-thionflavone methiodide to give 4-flavyleneazine; attempts to convert the latter compound into di-4-flavylene by loss of nitrogen were unsuccessful.

It was shown in the preceding paper that the reaction of 4-thionflavone with benzylamine to give flavone benzylimine is reversible, since the benzylimine with excess of hydrogen sulphide in boiling ethanol gave 4-thionflavone. Under the same conditions only a trace of 4-thionflavone is formed from flavone anil, and flavone oxime and flavone phenylhydrazone are unaffected. Flavone hydrazone and hydrogen sulphide gave some 4-flavyleneazine, which must result from interaction of flavone hydrazone and 4-thionflavone.

4-Thionflavone, as might be expected, is much less reactive towards anionoid reagents than its methiodide. It is not affected by boiling water, and reacts only on heating with hydroxylamine (this paper), benzylamine, *n*-butylamine, and *n*-octylamine (preceding paper), to give derivatives of flavone imine (III); it does not react with aniline even on prolonged boiling. It is nevertheless appreciably more reactive towards carbonyl reagents than is flavone, which is as yet known to yield directly only a 2 : 4-dinitrophenylhydrazone. In view of possible alternative, isomeric structures for this compound, for "flavone oxime," and for flavone phenylhydrazone, some comment is desirable.

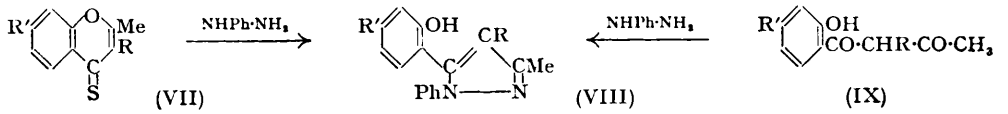
Flavone oxime. Reaction of flavone with hydroxylamine hydrochloride in pyridine gives a compound, $C_{15}H_{11}O_2N$, m. p. 237°, which was regarded as flavone oxime (III; R = OH) (Gulati and Ray, *Current Sci.*, 1936, **5**, 75). Shenoi, Shah, and Wheeler, (*J.*, 1940, 247) obtained a substance, m. p. 231°, with the same molecular formula from *o*-hydroxydibenzoylmethane and hydroxylamine, and proved by an unambiguous, independent synthesis that it was 3-*o*-hydroxyphenyl-5-phenyl*iso*oxazole (VI). We have repeated both preparations and obtained the same compound, m. p. 234°, from each, thus proving that the previously described "flavone oxime" is in reality (VI). The true flavone oxime (III; R = OH), m. p. 184—186°, has now been prepared from hydroxylamine and 4-thionflavone or 4-thionflavone methiodide (see above). It is not converted into the isomeric *iso*oxazole (VI) by boiling alkali, being recovered unchanged [cf. conversion of 2-methyl-3-(1-phenylhydrazonoethyl)chromone into 4-acetyl-5-*o*-hydroxyphenyl-3-methyl-1-phenylpyrazole by reaction with alkali; Baker and Butt, *J.*, 1949, 2150].

Flavone phenylhydrazone (III; R = NHPh). This compound, m. p. 155°, was made by Diesbach and Kramer (*loc. cit.*) by boiling 4-thionflavone with phenylhydrazine in pyridine for two hours, and the structure is now confirmed by the fact that it is not identical with the isomeric 3-*o*-hydroxyphenyl-1 : 5-diphenylpyrazole (V; R = Ph), which has been prepared from *o*-hydroxydibenzoylmethane and phenylhydrazine. It is assumed in this latter reaction that the phenylhydrazine reacts with the carbonyl group attached to the phenolic nucleus as do benzylamine (previous paper) and hydroxylamine (Shenoi, Shah, and Wheeler, *loc. cit.*). Flavone phenylhydrazone is not isomerised to the pyrazole (V; R = Ph) by heating it with alkali.

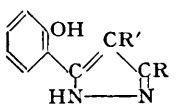
Flavone 2 : 4-*dinitrophenylhydrazone* [III; R = $NH{\cdot}C_6H_3(NO_2)_2$]. Adkins and Mozingo (*J. Amer. Chem. Soc.*, 1938, **60**, 675) prepared a substance, m. p. 282°, from flavone and 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid, and assumed that it was flavone 2 : 4-dinitrophenylhydrazone because it differed from a compound (not analysed), m. p. 119—120°, similarly prepared from *o*-hydroxydibenzoylmethane. In attempting to repeat the latter reaction, we isolated only a 2 : 4-dinitrophenylhydrazone, m. p. 282°, identical with that prepared from flavone, but we would note, in connection with the claim of Adkins and Mozingo, that *o*-hydroxydibenzoylmethane has m. p. 120—122°, and that it is converted into flavone by heating it with acids in alcoholic solution. The possibility remained, therefore, that the derivative, m. p. 282°, might be a pyrazole [V; R = $C_6H_3(NO_2)_2$], but the fact that the same substance has now been prepared in high yield at room temperature

from 4-thionflavone methiodide and 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid, suffices to establish the structure as that of flavone 2 : 4-dinitrophenylhydrazone. The unique carbonyl reactivity of flavone thus disclosed may be ascribed to its probable conversion into the oxonium cation by acceptance of a proton from the ethanolic sulphuric acid; this cation, like the cation of 4-thionflavone methiodide, would be expected to be readily attacked by anionoid reagents.

"Phenylhydrazones" of some 2-methyl-4-thionchromones. Simonis and Rosenberg (*Ber.*, 1914, **47**, 1232) prepared 2 : 3-dimethyl- and 2 : 3 : 5- and 2 : 3 : 8-trimethyl-4-thionchromones and treated them with phenylhydrazine in presence of alkali, obtaining yellow products regarded as the chromone phenylhydrazones. There was reason to doubt, however, whether these reactions had been correctly interpreted, since Baker and Butt (*J.*, 1949, 2147) showed that 7-methoxy-2-methyl-4-thionchromone (VII; R = H, R′ = OMe) reacted with phenylhydrazine and alkali to give the phenolic 5-(2-hydroxy-4-methoxyphenyl)-3-methyl-1-phenylpyrazole (VIII; R = H, R′ = OMe), a compound which was also prepared from phenylhydrazine and 2-acetoacetyl-5-methoxyphenol (IX; R = H, R′ = OMe). It has also been found (see p. 1308) that both 2-methyl-4-thionchromone (VII; R = R′ = H) and 2-acetoacetylphenol (IX; R = R′ = H) react with phenylhydrazine to give the colourless, phenolic 5-*o*-hydroxyphenyl-3-methyl-1-phenylpyrazole (VIII; R = R′ = H).



(VII) (VIII) (IX)



(X)

2 : 3-Dimethyl-4-thionchromone (VII; R = Me, R′ = H) and phenylhydrazine gave, as previously described by Simonis and Rosenberg, a product, m. p. 209°; it was, however, colourless and exhibited phenolic properties, giving an acetyl derivative. This substance is clearly 5-*o*-hydroxyphenyl-3 : 4-dimethyl-1-phenylpyrazole (VIII; R = Me, R′ = H), and it must be concluded that the other products described by Simonis and Rosenberg as chromone phenylhydrazones are in reality the isomeric pyrazoles. The mechanism of pyrazole formation from 2-methyl-4-thionchromones (VII) and phenylhydrazine in presence of aqueous-alcoholic alkali may involve as the first step or addition of phenylhydrazine to the 2 : 3-double bond of (VII) (cf. reaction of benzylamine with, *e.g.*, 3-acetyl-2-methylchromone under anhydrous conditions which proceeds by way of addition of the amine to the 2 : 3-double bond; Baker and Butt, *loc. cit.*, p. 2143).

These results are in harmony with the observation of Koenigs and Freund (*Ber.*, 1947, **80**, 146) that 2-methylchromone reacts with hydrazine hydrate to give 3(5)-*o*-hydroxyphenyl-5(3)-methylpyrazole (X; R = Me, R′ = H). This same pyrazole has now been obtained from hydrazine hydrate and 2-acetoacetylphenol (IX; R = R′ = H) or 2-methyl-4-thionchromone (VII; R = R′ = H), and in a similar manner 2 : 3-dimethyl-4-thionchromone (VII; R = Me, R′ = H) gave 3(5)-*o*-hydroxyphenyl-4 : 5(3 : 4)-dimethylpyrazole (X; R = R′ = Me).

Schönberg and Stolpp (*Ber.*, 1930, **63**, 3116) have shown that chromone and 4-thionchromone react with hydrazine to give the same product, m. p. 96°, which was regarded as chromone hydrazone. The reaction of chromone with hydrazine has been repeated, but the product is phenolic, being soluble in aqueous sodium hydroxide and giving a strong blue ferric chloride reaction, and it must, therefore, be 3(5)-*o*-hydroxyphenylpyrazole (X; R = R′ = H). This conclusion is supported by its ultra-violet absorption spectrum recorded below.

The ultra-violet absorption maxima ($\lambda_{max.}$ mμ) of the pyrazoles described in this paper

are given below. Measurements were made in ethanol, and the values of log $\varepsilon_{max.}$ are given in parentheses.

Pyrazole derivative	$\lambda_{max.}$ (log $\varepsilon_{max.}$)			
(1) 3(5)-*o*-Hydroxyphenyl-	215 (4·32);	248 (4·22);	258 (4·24);	293·5 (3·84)
(2) 3(5)-*o*-Hydroxyphenyl-5(3)-methyl-	211 (4·33);	248 (4·15);	259 (4·16);	294 (3·76)
(3) 3(5)-*o*-Hydroxyphenyl-4 : 5(3 : 4)-dimethyl- ...	211 (4·4);	252 (4·06);	262 (3·96);	292 (3·74)
(4) 3(5)-*o*-Hydroxyphenyl-5(3)-phenyl-	214 (4·58);	250 * (4·46);	256 (4·49);	294 (3·95)
(5) 5-*o*-Hydroxyphenyl-3-methyl-1-phenyl-	213 (4·39);		253 (4·15);	286 † (3·71)
				294 † (3·64)
(6) 5-*o*-Hydroxyphenyl-3 : 4-dimethyl-1-phenyl-	‡		258 (4·09);	No band
(7) 5-*o*-Hydroxyphenyl-2 : 3-diphenyl-	‡	250 (4·48);		296 (4·14)

* Inflexion. † Ill-defined maxima. ‡ Intense absorption, maxima probably at *ca.* 205.

The similarity of the spectra of the compounds (1)—(5) gives additional evidence that they are all of the same type and excludes the possibility that some are derivatives of chromone hydrazone, as has been previously suggested. The spectra of the compounds (1)—(4) show four maxima, and are more complicated than the other three, probably owing to prototropic tautomerism; the compounds (5)—(7) cannot be tautomeric. The band in the 290-mμ region is not shown for (6) and this may be due to steric interference of the phenolic group with the substituents in positions 1 and 4.

Experimental

M.p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford, and Mr. W. M. Eno, Bristol.

4-Thionflavone (I).—A satisfactory product is only obtained when purified phosphorus pentasulphide is used; we have used crystalline material extracted from the technical product with carbon disulphide in a Soxhlet apparatus. Flavone (5 g.), phosphorus pentasulphide (10 g.), and toluene (50 c.c.) were heated on a steam-bath for 3½ hours and the solvent was decanted whilst hot. The residue was extracted with hot toluene (3 × 20 c.c.), and the extracts yielded a residue which was crystallised from ethanol (charcoal). 4-Thionflavone (2·93 g., 55%) was obtained as deep red needles, m. p. 87° (lit., 87° and 89°).

Acid Hydrolysis of 4-Thionflavone.—4-Thionflavone (250 mg.) in ethanol (10 c.c.) and concentrated hydrochloric acid (1 c.c.) were heated on the steam-bath for 40 hours. Hydrogen sulphide was evolved and the deep red colour of the solution faded. The solution was evaporated under reduced pressure, and the residue crystallised twice from light petroleum (b. p. 60—80°), giving needles of flavone, m. p. and mixed m. p. 96—97° (yield, 65%).

4-Thionflavone Methiodide (II).—Methyl iodide (5 c.c.) was added to 4-thionflavone (300 mg.) in chloroform (15 c.c.), and after 18 hours the solid was collected and washed with acetone and ether. *4-Thionflavone methiodide* (460 mg., 96%) was obtained as fine, maroon-coloured needles, m. p. 220—222° (Found: C, 50·5; H, 3·6; S, 8·6; I, 33·1. $C_{16}H_{13}OSI$ requires C, 50·5; H, 3·4; S, 8·4; I, 33·4%).

Hydrolysis of 4-Thionflavone Methiodide.—The methiodide (100 mg.) was boiled with water (10 c.c.) for 10 minutes; dissolution then occurred and methanethiol was evolved. After cooling, the solid was collected and crystallised from light petroleum (b. p. 60—80°), giving flavone (54 mg., 92%), m. p. and mixed m. p. 96—97°.

Flavone Anil (III; R = Ph).—Aniline (1 c.c.) was shaken with a suspension of 4-thionflavone methiodide (250 mg.) in ethanol, and reaction was complete in 15 minutes. The *flavone anil* (160 mg., 82%), obtained on addition of water, separated from ethanol in deep yellow needles, m. p. 121·5—122·5° (Found: C, 84·9; H, 5·0; N, 4·6. $C_{21}H_{15}ON$ requires C, 84·9; H, 5·0; N, 4·7%). The *picrate* formed yellow needles, m. p. 230—240° (decomp.; dependent upon rate of heating) (Found: N, 10·4. $C_{21}H_{15}ON,C_6H_3O_7N_3$ requires N, 10·6%).

Flavone Hydrazone (III; R = NH_2).—Hydrazine hydrate (0·5 c.c.) was added to a solution of 4-thionflavone (200 mg.) in warm ethanol (10 c.c.). The deep red colour rapidly disappeared, hydrogen sulphide was evolved and, after 10 minutes, water was added. The solid (130 mg., 65%) which separated after some time in a refrigerator crystallised from aqueous methanol, giving *flavone hydrazone* as deep yellow needles, m. p. 136° (Found: C, 76·0; H, 5·1; N, 12·0. $C_{15}H_{12}ON_2$ requires C, 76·2; H, 5·1; N, 11·9%). It showed no phenolic properties. The *benzylidene* derivative (III; R = N:CHPh) separated when flavone hydrazone (100 mg.) and benzaldehyde (1 c.c.) in methanol (3 c.c.) were kept at room temperature overnight. The pre-

cipitate (113 mg., 83%) was collected and crystallised from ethanol, giving yellow needles, m. p. 136° (Found: C, 80·7; H, 4·8; N, 8·7. $C_{22}H_{16}ON_2$ requires C, 81·45; H, 4·9; N, 8·7%). The N-*acetyl* derivative (III; R = NHAc) was prepared from flavone hydrazone (100 mg.), acetic anhydride (5 c.c.), and pyridine (2 drops); after being kept at room temperature overnight, the mixture was poured into water, and the solid (112 mg., 96%) crystallised from dioxan, giving almost colourless needles, m. p. 284° (Found: C, 73·3; H, 5·4; N, 9·8. $C_{17}H_{14}O_2N_2$ requires C, 73·4; H, 5·0; N, 10·1%).

Flavone Benzoylhydrazone (III; R = NH·COPh).—(*a*) Benzoylhydrazine (72 mg.) was added to a suspension of 4-thionflavone methiodide (200 mg.) in ethanol (10 c.c.), and after 15 minutes' shaking (methanethiol was evolved), the yellow solid was collected. Crystallisation from ethanol gave *flavone benzoylhydrazone* (85 mg., 47%) as microscopic yellow crystals, m. p. 244° (decomp.) (Found: C, 77·5; H, 4·7; N, 8·35. $C_{22}H_{16}O_2N_2$ requires C, 77·6; H, 4·7; N, 8·2%).

(*b*) Benzoyl chloride (0·049 c.c.) was added to flavone hydrazone (100 mg.) in pyridine (1 c.c.) and after 2·5 hours the mixture was poured into dilute hydrochloric acid. The solid was collected (146 mg., 100%) and crystallised from ethanol (40 c.c.) and water (20 c.c.), giving flavone benzoylhydrazone, m. p. and mixed m. p. 244° (decomp.).

Flavone Semicarbazone (III; R = NH·CO·NH_2).—An aqueous solution of semicarbazide hydrochloride (1 g.) and sodium acetate (1 g.) was added to 4-thionflavone methiodide (200 mg.) suspended in ethanol. The reaction was complete after a few minutes' shaking, and the solid was collected (132 mg., 90%) and crystallised from ethanol (30 c.c.), giving *flavone semicarbazone* as bright yellow, irregular prisms, m. p. 245° (decomp.) (Found: C, 69·0; H, 4·7; N, 15·3. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·05%). It exhibited a brilliant green fluorescence in ultra-violet light.

Flavone Thionsemicarbazone (III; R = NH·CS·NH_2).—4-Thionflavone methiodide (300 mg.) was added to a solution of thionsemicarbazide (300 mg.) in ethanol (50 c.c.) and water (50 c.c.). *Flavone thionsemicarbazone* (226 mg., 97%) separated as deep yellow plates, m. p. 234° (decomp.), from aqueous ethanol (Found: C, 64·2, 63·9, 63·6; H, 4·8, 4·5, 4·7; N, 13·8; S, 11·1. $C_{16}H_{13}ON_3S$ requires C, 65·1; H, 4·4; N, 14·2; S, 10·9%).

Flavone Oxime (III; R = OH).—(*a*) 4-Thionflavone (220 mg.), hydroxylamine hydrochloride (220 mg.), and pyridine (4 c.c.) were heated on a steam-bath for 30 minutes; hydrogen sulphide was evolved. The very pale yellow solution was poured into water and the solid was crystallised from ethanol, giving *flavone oxime* (157 mg., 72%) as colourless needles, m. p. 184—186° (Found: C, 76·1; H, 4·8; N, 6·2. $C_{15}H_{11}O_2N$ requires C, 75·9; H, 4·7; N, 5·9%).

(*b*) 4-Thionflavone methiodide (120 mg.) suspended in pyridine (3 c.c.) was shaken with hydroxylamine hydrochloride (120 mg.); immediate reaction occurred with evolution of methanethiol. After 5 minutes, the colourless solution was poured into 10% aqueous acetic acid, and the solid was crystallised from ethanol, giving flavone oxime (54 mg., 73%), m. p. and mixed m. p. 184°.

This flavone oxime was recovered unchanged after being heated under reflux either for 1 hour with aqueous-alcoholic 2N-sodium hydroxide or overnight with methanolic barium hydroxide.

3(5)-o-*Hydroxyphenyl*-5(3)-*phenylpyrazole* (V; R = H).—*o*-Hydroxydibenzoylmethane (1·1 g.), hydrazine hydrate (1 c.c.), and ethanol (10 c.c.) were heated under reflux for 20 minutes and cooled, water was added, and the solid collected, washed, dried (1·05 g., 97%), and crystallised from ethanol. 3(5)-o-*Hydroxyphenyl*-5(3)-*phenylpyrazole* was obtained as hexagonal plates, m. p. 144° (Found: C, 76·0; H, 5·1; N, 11·7. $C_{15}H_{12}ON_2$ requires C, 76·2; H, 5·1; N, 11·9%). It dissolves in 2N-sodium hydroxide giving a sparingly soluble sodium salt, and gives a deep green colour with aqueous-alcoholic ferric chloride.

4-*Flavyleneazine*.—(*a*) Reaction of flavone hydrazone (100 mg.) with 4-thionflavone methiodide (161 mg.) in ethanol (5 c.c.) yielded after 1 hour at room temperature a product (182 mg., 100%) which was crystallised by dissolving it in cold pyridine and carefully adding water. 4-*Flavyleneazine* separated in orange, microscopic needles, m. p. 298° (decomp.) (Found: C, 81·75; H, 4·7; N, 6·5. $C_{30}H_{20}O_2N_2$ requires C, 81·8; H, 4·6; N, 6·4%).

(*b*) Hydrogen sulphide was passed through a boiling solution of flavone hydrazone (100 mg.) in ethanol (10 c.c.) for 2 hours and, after cooling the solid was collected and crystallised from aqueous pyridine, giving 4-flavyleneazine (23 mg., 25%), m. p. and mixed m. p. 296° (decomp.).

3-o-*Hydroxyphenyl*-1 : 5-*diphenylpyrazole* (V; R = Ph).—*o*-Hydroxydibenzoylmethane (1 g.), phenylhydrazine (0·44 c.c.), and ethanol (10 c.c.) were heated under reflux for 2·5 hours, the solution concentrated to half its volume, and water added. The precipitate

(0·94 g., 72%) was crystallised from ethanol, giving 3-o-*hydroxyphenyl*-1 : 5-*diphenylpyrazole* as fine needles, m. p. 105—106° (Found : C, 80·5; H, 4·7; N, 8·5. $C_{21}H_{16}ON_2$ requires C, 80·8; H, 5·1; N, 9·0%).

Flavone 2 : 4-*Dinitrophenylhydrazone* [III; R = $NH{\cdot}C_6H_3(NO_2)_2$].—(*a*) Flavone and 2 : 4-dinitrophenylhydrazine gave, as described by Adkins and Mozingo (*loc. cit.*), a dark red powder, m. p. 282° (decomp.) after crystallisation from dioxan.

(*b*) 4-Thionflavone (0·5 g.) was added to a solution of 2 : 4-dinitrophenylhydrazine (1 g.) and concentrated sulphuric acid (2 c.c.) in ethanol (40 c.c.). After being heated to its b. p. (hydrogen sulphide evolved), the mixture was left overnight, giving a deep red precipitate (72 mg., 8%). Recrystallisation from dioxan gave flavone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 282° (decomp.).

(*c*) 4-Thionflavone methiodide (190 mg.), 2 : 4-dinitrophenylhydrazine (99 mg.), and concentrated sulphuric acid (3 drops) in ethanol (5 c.c.), were shaken at room temperature for 18 hours; methanethiol was evolved. The deep red powder (161 mg., 79%) was recrystallised from dioxan, giving flavone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 282° (decomp.) (Found : N, 14·2. Calc. for $C_{21}H_{14}O_5N_4$: N, 13·9%).

(*d*) By reaction of *o*-hydroxydibenzoylmethane with 2 : 4-dinitrophenylhydrazine according to method (*b*) (above), only flavone 2 : 4-dinitrophenylhydrazone was obtained, m. p. and mixed m. p. 282° (decomp.), in 18% yield (cf. Adkins and Mozingo).

2-*Methyl*-4-*thionchromone* (VII; R = R′ = H).—2-Methylchromone (2·5 g.), purified phosphorus pentasulphide (4·8 g.), and toluene (50 c.c.) were heated under reflux for 1·5 hours, the toluene was decanted whilst hot, and the residue was extracted with hot toluene (2 × 20 c.c.). The residue (2·0 g.) from the combined extracts was washed with hot ammonium sulphide solution, and crystallised from ethanol, giving 2-*methyl*-4-*thionchromone* (1·53 g., 56%) as very deep red needles, m. p. 96—97° (Found : C, 68·7; H, 4·8; S, 18·0. $C_{10}H_8OS$ requires C, 68·2; H, 4·5; S, 18·2%).

In another experiment, the 2-methyl-4-thionchromone was obtained as light red needles, m. p. 98° (Found : C, 68·3; H, 4·6; S, 18·5%).

5-o-*Hydroxyphenyl*-3-*methyl*-1-*phenylpyrazole* (VIII; R = R′ = H).—2-Methyl-4-thionchromone (200 mg.), phenylhydrazine (0·24 c.c.), 2N-sodium hydroxide (4 drops), and ethanol (10 c.c.) were heated on a steam-bath for 2 hours and cooled, and concentrated hydrochloric acid (2 drops) added. The solid (245 mg., 86%) obtained by addition of water was collected and crystallised from dilute alcohol, giving 5-*o*-hydroxyphenyl-3-methyl-1-phenylpyrazole, m. p. 190—191°. This m. p. was not depressed on admixture with a specimen, m. p. 190—191°, prepared from 2-acetoacetylphenol according to Baker and Butt (*loc. cit.*).

5-o-*Hydroxyphenyl*-3 : 4-*dimethyl*-1-*phenylpyrazole* (VIII; R = Me; R′ = H).—2 : 3-Dimethyl-4-thionchromone (1·5 g.), phenylhydrazine (1·7 c.c.), 2N-sodium hydroxide (15 c.c.), and ethanol (30 c.c.) were heated on a steam-bath for 1 hour. After distillation of the ethanol, water was added to the pale yellow solution, which was then neutralised, and the solid product was crystallised from aqueous methanol, giving 5-o-*hydroxyphenyl*-3 : 4-*dimethyl*-1-*phenylpyrazole* (1·15 g., 55%) as colourless prisms, m. p. 210—211° (Found : C, 77·7; H, 6·1; N, 10·6. $C_{17}H_{16}ON_2$ requires, C, 77·3; H, 6·1; N, 10·6%). Simonis and Rosenberg described their product as weakly yellow prisms, m. p. 209°. This pyrazole is soluble in 2N-sodium hydroxide, but does not give a ferric chloride reaction.

Acetylation with acetic anhydride–pyridine gave 5-o-*acetoxyphenyl*-3 : 4-*dimethyl*-1-*phenylpyrazole* (86% yield) as rectangular prisms, m. p. 96—97·5°, from light petroleum (b. p. 60—80°) (Found : C, 75·3; H, 5·9; N, 9·2. $C_{19}H_{18}O_2N_2$ requires C, 74·5; H, 5·9; N, 9·2%).

3(5)-o-*Hydroxyphenyl*-5(3)-*methylpyrazole* (X; R = Me).—(*a*) 2-Methyl-4-thionchromone (250 mg.), ethanol (5 c.c.), and hydrazine hydrate (0·5 c.c.) were shaken at room temperature for 10 minutes, water was added, and the precipitate (223 mg., 90%) crystallised from dilute ethanol. The pyrazole formed needles, m. p. 132—134°, not depressed on admixture with material prepared by method (*b*).

(*b*) *o*-Acetoacetylphenol (245 mg.), hydrazine hydrate (1 c.c.), and ethanol (5 c.c.) were warmed on a steam-bath for 10 minutes, water was added, and the solid (198 mg., 82%) collected and crystallised from aqueous ethanol. The pyrazole formed colourless needles, m. p. 132—134° (Koenigs and Freund, *loc. cit.*, give m. p. 136°). The picrate, yellow needles from ethanol, had m. p. 190° (Koenigs and Freund give m. p. 160°) (Found : C, 47·9; H, 3·1; N, 17·7. Calc. for $C_{10}H_{10}ON_2,C_6H_3O_7N_3$: C, 47·7; H, 3·2; N, 17·4%).

3(5)-o-*Hydroxyphenyl*-4 : 5(3 : 4)-*dimethylpyrazole*.—2 : 3-Dimethyl-4-thionchromone (0·5 g.), hydrazine hydrate (0·8 c.c.), and ethanol (15 c.c.) were heated on a steam-bath for 0·5 hour.

After removal of the ethanol, water was added, and the solid (320 mg.) was crystallised from aqueous ethanol, giving the *pyrazole* as colourless prisms, m. p. 116—118° (Found : C, 70·0; H, 6·4; N, 15·4. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4; N, 14·9%). It gave an intense purple-green colour with ferric chloride and was soluble in 2N-sodium hydroxide

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