List of Research Papers

1. Synthesis of 4H-furo(3,2-c)benzopyran-4-one, a Furocoumarin derived from 4-Hydroxycoumarin. By V.N.Dholakia and K.N.Trivedi, Chem.and Ind. 4, 160 (1966).

2. Studies in the synthesis of Coumarino-α-pyrones and Furocoumarins. Part II. By V.N.Dholakia and K.N.Trivedi, J.Indian Chem. Soc., 43, 804 (1966).

3. Studies in 4-Hydroxycoumarins By V.N.Dholakia, M.G.Parekh and K.N.Trivedi, Aust. J.Chem., 21, 2345-7 (1968).

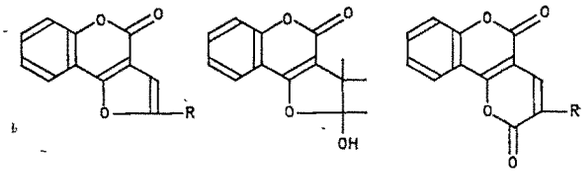
REPRINTED FROM CHEMISTRY AND INDUSTRY, 1966, p. 160

Synthesis of 4-H-Furo-[3,2,-*c*]-benzopyran-4-one, a Furocoumarin Derived from 4-Hydroxycoumarin

By V. N. Dholakia and K. N. Trivedi

Chemistry Department, Faculty of Science, Baroda 2, India

Trivedi and Sethna[1] developed a new approach for the synthesis of furocoumarins. This is now extended for the synthesis of 4*H*-furo[3,2,-*c*]benzopyran-4-one (I*a*) as this compound is likely to possess anticoagulant activity according to the hypothesis of Chmielewska and Cieslak.[2] This furocoumarin is the dehydration product of the hypothetical compound (II) suggested by above workers.



(I *a*, R = H; *b*, R = CO_2H) (II) (III *a*, R = H; *b*, R = Br)

The synthesis starts from 4-hydroxycoumarin which on Pechmann reaction with malic acid gave benzopyranyl[3,2,-*c*]pyran-2,8-dione (III*a*), m.p. 243° (Found C, 67·21; H, 2·65. $C_{12}H_6O_4$ requires C, 67·3; H, 2·8%), which on bromination gave the 9-bromo-derivative (III*b*), m.p. 211° (Found Br, 27·22. $C_{12}H_5BrO_4$ requires Br, 27·30%). This bromo-derivative underwent ring contraction when boiled with 10% sodium carbonate solution and gave 4*H*-furo[3,2-*c*]benzopyran-4-one-2-carboxylic acid (I*b*), m.p. 290° (Found C, 62·44; H, 3·07. $C_{12}H_6O_5$ requires C, 62·62; H, 2·60%). This on decarboxylation afforded compound (I*a*), m.p. 93° (Found C 70·71; H, 3·10. $C_{11}H_6O_3$ requires C, 70·98; H, 3·22%).

This is the first synthesis of an unsubstituted furocoumarin of this type. By this procedure, several 4*H*-furo[3,2-*c*]benzopyran-4-ones, which have substituents like CH_3, C_6H_5, OCH_3, etc. in the benzene as well as the furan part of the furocoumarin ring system, have been synthesised and details will be published elsewhere.

The authors thank Professor S. Sethna for his keen interest in the work and Dr S. S. Lele for microanalyses. One of us (V.N.D.) thanks C.S.I.R., New Delhi, for a Junior Research Fellowship.

Received November 8, 1965

References

1 Trivedi, K. N. & Sethna, S., *J. Ind. Chem. Soc.*, 1963, **40**, 563
2 Chmielewska, I. & Cieslak, J., *Tetrahedron*, 1958, **4**, 135

PRINTED BY RICHARD MADLEY LTD., 54 GRAFTON WAY, LONDON, W 1, ENGLAND

[Jour. Indian Chem. Soc., Vol. 43, No. 12, 1966]

Studies in the Synthesis of Coumarino-α-pyrones and Furocoumarins. Part II*

V. N. Dholakia and K. N. Trivedi

4-Hydroxycoumarin has been condensed with malic acid to yield benzopyranyl (3, 2-c) pyran-2,8-dione which has been brominated to 9-bromo derivative and the latter degraded to 4*H*-furo(3, 2-c)benzopyran-4-one. 4-Hydroxycoumarin, 4-hydroxy-6-methylcoumarin and 4-hydroxy-7-methoxycoumarin have been similarly condensed with ethyl acetoacetate and degraded to corresponding 3-methyl-4*H*-furo(3,2-c) benzopyran-4-ones.

Arora and Mathur[1] reported that coumarino (3′, 4′, 5, 6)-4-methyl-3-phenyl-α-pyrone possesses anticoagulant activity comparable to dicoumarol. 4*H*-furo-(3,2-c)benzopyran-4-one is likely to possess anticoagulant acivity, as it is a dehydrated product of the hypothetical compound (IV), as suggested by Chmielewska and Cieslak[2]. It was thought of interest to synthesise different benzopyranyl (3,2-c) pyran-2, 8-diones and degrade them to 4*H*-furo-(3,2-c) benzopyran-4-one according to the method developed by Trivedi and Sethna[3] which consists of bromination of coumarino-α-pyrones, followed by ring contraction with alkali.

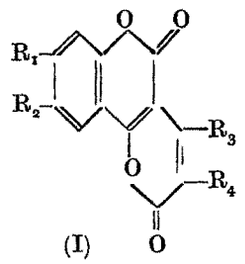
4-Hydroxycoumarin on the Pechmann condensation with malic acid in presence of 80% sulphuric acid gave benzopyranyl (3, 2-c) pyran-2, 8-dione (Ia) which, on bromination, gave 9-bromo derivative (Ie). This 9-bromo derivative on hydrolysis with 10% sodium carbonate solution afforded 4*H*-furo(3,2-c)benzopyran-4-one-2-carboxylic acid (IIIa) which on decarboxylation gave 4*H*-furo (3,2-c) benzopyran-4-one (IIIb).

4-Hydroxycoumarin, 4-hydroxy-6-methylcoumarin and 4-hydroxy-7-methoxycoumarin were condensed with ethyl acetoacetate in presence of 80% sulphuric acid or aluminium chloride to give 10-methylbenzopyranyl (3, 2-c)-pyran-2, 8-dione[4,5] (Ib), 4,10-dimethylbenzopyranyl (3,2-c)-pyran, 2, 8-dione[5] (Ic) and 5-methoxy-10-methylbenzopyranyl (3,2-c) pyran-2,8-dione (Id) respectively. These coumarino-4,3-α-pyrones on bromination gave corresponding 9-bromo derivatives (If, Ig, Ih) respectively. These 9-bromo derivatives when hydrolysed by refluxing 10% sodium carbonate solution gave 2-(o-hydroxyphenyl) furan-3-carboxylic acids (IIa, IIb, IIc) respectively and not the corresponding 4*H*-furan (3,2-c) benzopyran-4-one-2-carboxylic acids. On hydrolysis of the bromo-derivatives (If, Ig, Ih), the compounds must have been degraded to coumarilic acids first, followed by decarboxylation to furocoumarins, the pyrone ring of which must have been opened up to give the above acids. These hydroxyacids were subsequently cyclised by

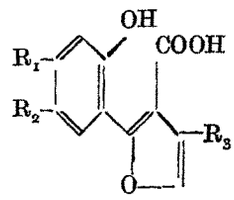
*Part I, *this Journal*, 1963, **40**, 563.

1. Arora and Mathur, *Brit. J. Pharmacol.* 1963. **20**, 29.
2. Chmielewska and Cieslak, *Tetrahedron*, 1958, **4**, 135.
3. Trivedi and Sethna, *this Journal*, 1963, **40**, 563.
4. Mustafa, Hsihmat, Zayed and Ahmed Nawar, *Tetrahedron*, 1963, **19**, 1832.
5. Usgaonker and Patell, *this Journal*, 1965, 217.

refluxing hydrochloric acid to give 3-methyl-4*H*-furo (3,2-c)benzopyran-4-one (IIIc), 3,8-dimethyl-4*H*-furo (3,2-c) benzopyran-4-one (IIId) and 3-methyl-7-methoxy-4*H*-furo (3,2-c) benzopyran-4-one (IIIe) respectively.



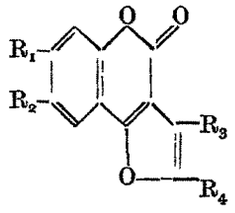
(I)



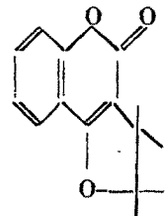
(II)

Ia: $R_1=R_2=R_3=R_4=H$.
b: $R_1=R_2=R_4=H$; $R_3=CH_3$.
c: $R_1=R_4=H$; $R_2=R_3=CH_3$.
d: $R_1=OCH_3$; $R_2=R_4=H$; $R_3=CH_3$.
e: $R_1=R_2=R_3=H$; $R_4=Br$.
f: $R_1=R_2=H$; $R_3=CH_3$; $R_4=Br$.
g: $R_1=H$; $R_2=R_3=CH_3$; $R_4=Br$.
h: $R_1=OCH_3$; $R_2=H$; $R_3=CH_3$; $R_4=Br$.

IIa: $R_1=R_2=H$; $R_3=CH_3$.
b: $R_1=H$; $R_2=R_3=CH_3$.
c: $R_1=OCH_3$; $R_2=H$; $R_3=CH_3$



(III)



(IV)

IIIa, $R_1=R_2=R_3=H$; $R_4=COOH$.
b, $R_1=R_2=R_3=R_4=H$.
c, $R_1=R_2=R_4=H$; $R_3=CH_3$.
d, $R_1=R_4=H$; $R_2=R_3=CH_3$
e, $R_1=OCH_3$; $R_2=R_4=H$; $R_3=CH_3$.

EXPERIMENTAL

Benzopyranyl(3-2-c)*pyran*-2,8 *dione* (I*a*).—A mixture of 4-hydroxycoumarin (5.0 g.) and malic acid (5.0 g.) was heated on a steam bath with gradual addition of 80% H_2SO_4(50 ml) in 45 min. period. Heating was continued for further 4 hr. The reaction mixture was added to ice and the product filtered and washed with sodium bicarbonate solution, dried and crystallised from acetic acid, m.p. 242°; yield 2.0 g. (Found: C, 67.21; H, 2.65. $C_{12}H_6O_4$ requires C, 67.3; H, 2.81%).

9-*Bromobenzopyranyl* (3,2-c)*pyran*-2,8-*dione* (Ie).—Benzopyranyl (3,2-c) pyran-2, 8-dione (2.0 g.) was dissolved in minimum amount of acetic acid and bromine, dissolved in acetic acid (30 ml. 20%, 4 mole), was added and the mixture heated on a water bath for 2 hr. The reaction mixture was then added to ice and the bromo derivative filtered, dried and crystallised from acetic acid, m.p. 211°, yield, 1.0 g. (Found: Br, 27.22. $C_{12}H_5O_4Br$ requires Br, 27.3%).

4H-*Furo* (3,2-c) *benzopyran*-4-*one*-2-*carboxylic Acid* (IIIa).—9-Bromobenzopyranyl (3, 2-c) pyran-2, 8-dione (1.0 g.) was refluxed with sodium carbonate solution (10 ml, 10%) for 45 min. The reaction mixture was allowed to cool and acidified. The product was purified by dissolving it in sodium bicarbonate solution, reprecipitated and crystallised from dilute ethanol, m.p. 290°, yield, 0.4 g. (Found: C, 62.44; H, 3.07. $C_{12}H_6O_5$ requires C, 62.62; H, 2.6%).

4H-*Furo*(3, 2-c)*benzopyran*-4-*one* (IIIb).—4*H*-furo(3,2-c)benzopyran-4-one-2-carboxylic acid (0.4 g.) was heated on a sand bath with quinoline (5 ml) and copper bronze (0.2 g.) for 1 hr. The reaction mixture was filtered hot and the filtrate acidfied with hydrochloric acid and filtered again. The filtrate was diluted with water and extracted with ether. The product obtained after evaporation of the ether was washed with sodium bicarbonate solution and crystallised from petroleum ether, m.p. 93°, yield, 0.1 g. (Found: C, 70.71; H, 3.1. $C_{11}H_6O_3$ requires C, 70.98; H, 3.22%).

9-*Bromo*-10-*methylbenzopyranyl*(3,2-c)*pyran*-2,8-*dione* (If)—10-Methylbenzopyranyl 3,2-c)pyran-2, 8-dione (5.0 g.) was dissolved in hot acetic acid and a solution of bromine in acetic acid (35 ml) 20%, 2 mole) was added with stirring and the mixture left overnight. The separated bromo derivative was filtered, dried and crystallised from acetic acid, m.p. 258°; yield, 2.5 g. (Found: Br, 26.15. $C_{13}H_7O_4Br$ requires Br, 26.06%).

2-(o-*Hydroxyphenyl*)-4-*methylfuro*-3-*carboxylic Acid*(IIa).—9-Bromo-10-methylbenzopyranyl (3,2-c) pyran-2, 8-dione (2.0 g.) was refluxed with 10% sodium carbonate solution (20 ml) for 3 hr. The reaction mixture was allowed to cool and acidified. The separated product was purified by treatment with sodium bicarbonate solution, and crystallised from hot water, m.p. 155°, yield, 0.8 g. (Found: C, 66.27; H, 4.38. $C_{12}H_{10}O_4$ requires C, 66.06; H, 4.58%).

3-*Methyl*-4H-*furo* (3, 2-c)*benzopyran*-4-*one*(IIIc).—2-(o-Hydroxyphenyl)-4-methylfuro-3-carboxylic acid (0.8 g.) was dissolved in ethanol and refluxed with hydrochloric acid for 4 hr. The separated product was filtered (charcoal) and crystallised from dilute acetic acid, m.p. 166°. yield, 0.2 g. (Found: C, 71.89; H, 4.001. $C_{12}H_8O_3$ requires C, 72.0; H, 4.0%).

9-*Bromo*-4,10-*dimethylbenzopyranyl*(3,2-c)*pyran*-2-8-*dione* (Ig).—4,10-Dimethylbenzopyranyl (3, 2-c) pyran-2, 8-dione (5.0 g.) was dissolved in hot acetic acid and bromine in acetic acid (33 ml, 20%, 2 mole) was added with stirring and the mixture kept overnight. The separated bromo derivative was filtered, dried and crystallised from acetic acid; m.p. 250°, yield 2.0 g. (Found: Br, 24.77. $C_{14}H_9O_4Br$ requires Br, 24.92%).

2-(2′-*Hydroxy*-5′-*methylphenyl*)-4-*methylfuro*-3-*carboxylic Acid* (*IIb*).—9-Bromo--4,10-dimethylbenzopyranyl (3,2-c) pyran-2,8-dione (2.0 g.) was refluxed with 10% sodium

carbonate solution (20 ml) for 6 hr. The reaction mixture was allowed to cool and acidified. The separated product was purified by treatment with sodium bicarbonate solution and crystallised from hot water, m.p. 178°, yield, 0.7 g. (Found: C, 67.39; H, 4.75. $C_{13}H_{12}O_4$ requires C, 67.23; H, 5.17%).

3,8-*Dimethyl*-4H-*furo* (3,2-c) *benzopyran*-4-*one*(IIId).—2-(2-Hydroxy-5-methylphenyl) -4-methylfuro-3-carboxylic acid (0.7 g.) was dissolved in and refluxed with hydrochloric acid for 3 hr. The separated product was filtered (charcoal), washed with sodium bicarbonate solution, dried and crystallised from dil acetic acid, m.p. 157°, yield, 0.3 g. (Found: C, 72.59; H, 4.43. $C_{13}H_{10}O_3$ requires C, 72.9; H, 4.67%)

5-*Methoxy*-10-*methylbenzopyranyl* (3,2-c) *pyran*-2,-8-*dione* (Id).—4-Hydroxy-7-methoxycoumarin (5.0 g.) and ethyl acetoacetate (6.5 g.) were heated on steam bath with gradual addition of 80% sulphuric acid (50 ml.) for 45 min. Heating was continued for further 4 hr. The reaction mixture was added to ice and the product was filtered and washed with sodium bicarbonate solution, dried and crystallised from acetic acid, m.p. 237°, yield, 2.0 g.

A mixture of 4-hydroxy-7-methoxycoumarin (5.0 g.) and ethyl acetoacetate (10.0 g.) was added to a solution of anhydrous aluminium chloride (6.5 g.) in dry nitrobenzene (30 ml). The reaction mixture was heated at 130° for 4 hr., then decomposed with ice and hydrochloric acid; nitrobenzene was steam-distilled. The product was washed with sodium bicarbonate solution, dried and crystallised from acetic acid; yield was 4.5 g. (Found: C, 65.16; H, 3.85. $C_{14}H_{10}O_5$ requires C, 65.12; H, 3.87%).

9-*Bromo*-5-*methoxy*-10-*methylbenzopyranyl*(3,2-c)*pyran*-2,8-*dione* (Ih).—5-Methoxy-10-methylbenzopyranyl(3,2-c) pyran-2,8-dione (4.5 g.) was dissolved in acetic acid and bromine in acetic acid (14 ml, 20%, 1 mole) was added with stirring. The bromo derivative separating immediately was filtered, dried, and crystallised from acetic acid, m.p. 278°; yield, 3 g. (Found: Br, 23.6. $C_{14}H_9O_5$ Br requires Br, 23.74%).

2-(2′-*Hydroxy*-4′-*methoxyphenyl*)-4-*methylfuro*-3-*carboxylic Acid* (IIc).—9-Bromo-5-methoxy-10-methylbenxopyranyl(3,2-c)pyran-2,8-dione (2.0 g.) was refluxed with 10% sodium carbonate solution (20 ml) for 5 hr. The reaction mixture was cooled and acidified. The product was filtered and purified by treatment with sodium bicarbonate solution and crystallised from hot water, m.p. 201°; yield 0.8 g. (Found: C 62.77; H, 4.76. $C_{13}H_{10}O_5$ requires C, 63.77; H, 4.45%).

3-*Methyl*-7-*methoxy*-4H-*furo*(3,2-c) *benzopyran*-4-*one* (IIIc).—2-(2′-Hydroxy-4′-methoxyphenyl)-4-methylfuro-3-carboxylic acid (0.8 g.) was dissolved in ethanol and refluxed with hydrochloric acid for 3 hr. The separated product was filtered (charcoal), washed with sodium bicarbonate solution, dried and crystallised from dil, acetic acid. m.p. 173°, yield, 0.2 g. (Found: C, 67.64; H, 4.22. $C_{13}H_{10}O_4$ requires C, 67.82; H,4.34%).

The authors record their thanks to Prof. S.M. Sethna for his keen interest in the work and to Dr. S. S. Lele for microanalysis. One of them (V.N.D.) thanks the C.S.I.R. for a fellowship.

CHEMISTRY DEPARTMENT,
FACULTY OF SCIENCE,
M. S. UNIVERSITY OF BARODA, BARODA.

Received February 24, 1966

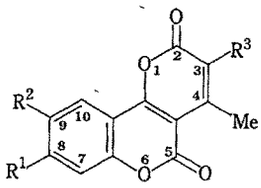
Short Communication reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY

STUDIES IN 4-HYDROXY COUMARINS*

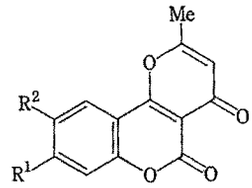
II.† α- AND γ-PYRONES FROM 4-HYDROXY COUMARINS

By V. N. Dholakia,‡ M. G. Parekh,‡ and K. N. Trivedi‡§

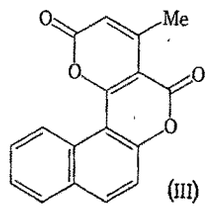
Arora and Mathur[1] reported that a methyldioxophenylpyranobenzopyran (Ia) possesses anticoagulant activity comparable to that of dicoumarol. It was thought of interest to prepare α- and γ-pyrones having different groups in the benzenoid part of the coumarin ring system and to study their anticoagulant activity.



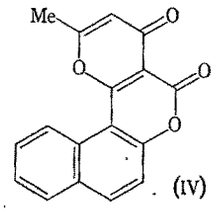
	R^1	R^2	R^3
(Ia)	H	H	Ph
(Ib)	H	H	H
(Ic)	H	Me	H
(Id)	OMe	H	H



	R^1	R^2
(IIa)	H	H
(IIb)	H	Me
(IIc)	OH	H



(III)



(IV)

Woods[2] condensed 4-hydroxycoumarin with ethyl acetoacetate in the presence of trifluoroacetic acid and claimed to have obtained 2-methyl-4,5-dioxo-4*H*,5*H*-pyrano[3,2-*c*]benzopyran (IIa), m.p. 252°, principal absorption bands in the i.r. region, 3344, 1727, 1631, 1613 cm^{-1}. Mustafa *et al.*[3] synthesized (IIa), yellow crystals, m.p.

* Manuscript received March 19, 1968.

† Part I, *J. scient. ind. Res.* B, 1962, **21**, 402.

‡ Chemistry Department, Faculty of Science, Baroda-2, India.

§ Present address: Chemistry Department, Wollongong University College, Wollongong, N.S.W. 2500.

[1] Arora, R. B., and Mathur, C. N., *Brit. J. Pharmac. Chemother.*, 1963, **20**, 29.

[2] Woods, L. L., *J. org. Chem.*, 1962, **27**, 696.

[3] Mustafa, A., Hsihmat, O. H., Zayed, S. M. A. D., and Ahmed Nawar, A., *Tetrahedron*, 1963, **19**, 1831.

246°, carbonyl stretching frequencies, 1754 cm^{-1} and 1667 cm^{-1}, by different routes and claimed that it was identical in all respects with the compound prepared according to Woods.[2] On repeating Woods's work, it has now been found that 4-methyl-2,5-dioxo-2*H*,5*H*-pyrano[3,2-*c*]benzopyran (Ib), colourless crystals, m.p. 243°, carbonyl stretching frequency in the i.r. region, 1740 cm^{-1}, is the only isolable product when the condensation is carried out in the presence of trifluoroacetic acid. The mixed m.p. with an authentic sample of (Ib) prepared by using either concentrated sulphuric acid[3,4] or anhydrous aluminium chloride[4] was not depressed; but the mixed m.p. with an authentic sample of (IIa), yellow crystals, m.p. 246°, carbonyl stretching frequencies in the i.r. region, 1760 cm^{-1} and 1670 cm^{-1}, prepared according to Mustafa *et al.*[3] was depressed by 20°.

This observation is further supported when three substituted 4-hydroxycoumarins are condensed with ethyl acetoacetate in the presence of trifluoroacetic acid: they yield the same known compounds (Ic), (Id), and (III) which were obtained by using either conc. sulphuric acid or anhydrous aluminium chloride as condensing agent. 3-Acetyl-4-hydroxy-6-methylcoumarin, 3-acetyl-4-hydroxy-7-methoxycoumarin, and 3-acetyl-4-hydroxybenzo[*f*]coumarin when subjected to Claisen condensation followed by cyclization with 25% sulphuric acid gave (IIb), (IIc), and (IV) respectively; demethylation took place during cyclization to yield (IIc). (Ic) and (III) differed considerably from the corresponding (IIb) and (IV) in i.r. spectra and melting point. The carbonyl stretching frequencies in the i.r. region of the above compounds are (Ic), 1745; (Id), 1740; (III), 1745; (IIb), 1760, 1672; (IIc), 1760, 1672; and (IV), 1760, 1670 cm^{-1}.

Experimental

Infrared spectra ($CHCl_3$) were determined with a Perkin–Elmer 237 grating spectrophotometer. All melting points were uncorrected.

*4,9-Dimethyl-2,5-dioxo-2*H,5H-*pyrano[3,2-c]benzopyran (Ic)*

4-Hydroxy-6-methylcoumarin (1 g) was heated with ethyl acetoacetate (1 ml) in trifluoroacetic acid (5 ml) on a sand-bath for 15 hr. After the completion of the reaction, a few millilitres of ethanol were added and the mixture kept overnight. The product which separated was filtered off and washed with sodium bicarbonate solution. The residue was crystallized from acetic acid, colourless crystals, m.p. 197–198° (lit.[4] 197–198°), yield 0·3 g. Mixed m.p. with an authentic sample prepared by using conc. sulphuric acid as condensing agent was not depressed.

*8-Methoxy-4-methyl-2,5-dioxo-2*H,5H-*pyrano[3,2-c]benzopyran (Id)*

4-Hydroxy-7-methoxycoumarin was condensed with ethyl acetoacetate in the presence of trifluoroacetic acid using the above procedure. M.p. of the colourless crystals and mixed m.p. with an authentic sample was 237° (lit.[5] 237°).

*4-Methyl-2,5-dioxo-2*H,5H-*pyrano[3,2-c]benzo[f]benzopyran (III)*

4-Hydroxybenzo[*f*]coumarin was condensed with ethyl acetoacetate in the presence of trifluoroacetic acid using the above procedure. M.p. and mixed m.p. with an authentic sample was 246° (lit.[6] 245–246°).

[4] Patell, J., and Usgaonker, R. N., *J. Indian chem. Soc.*, 1965, **42**, 217.
[5] Dholakia, V. N., and Trivedi, K. N., *J. Indian chem. Soc.*, 1966, **43**, 804.
[6] Patell, J., and Usgaonker, R. N., *J. Indian chem. Soc.*, 1966, **43**, 536.

3-Acetoacetyl-4-hydroxy-6-methylcoumarin

A solution of 3-acetyl-4-hydroxy-6-methylcoumarin (1 g) in freshly distilled ethyl acetate (25 ml) was added to pulverized sodium (1 g). The reaction mixture was heated on a water-bath for 6 hr. It was then decomposed with ice and extracted with ether. The aqueous layer on acidification gave *3-acetoacetyl-4-hydroxy-6-methylcoumarin*, which crystallized from dil. acetic acid, yellow needles, m.p. 153°, yield 0·7 g (Found: C, 64·5; H, 4·7. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%).

*2,9-Dimethyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzopyran* (*IIb*)

A solution of 3-acetoacetyl-4-hydroxy-6-methylcoumarin (0·5 g) in 50 ml dil. sulphuric acid (25%) was heated on a sand-bath for 1 hr. The cooled reaction mixture was neutralized with sodium carbonate solution, the separated product was crystallized from dil. acetic acid, yellow needles, m.p. 248°, yield 0 2 g (Found: C, 69·7; H, 3·8. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·2%).

3-Acetoacetyl-4-hydroxy-7-methoxycoumarin

A solution of 3-acetyl-4-hydroxy-7-methoxycoumarin (1 g) in ethyl acetate (25 ml) was added to pulverized sodium (1 g) and the reaction mixture refluxed on a water-bath for 6 hr. The reaction mixture was worked up as before. *3-Acetoacetyl-4-hydroxy-7-methoxycoumarin* crystallized from dil. acetic acid, yellow needles, m.p. 153°, yield 0·8 g (Found: C, 60·9; H, 4·2. $C_{14}H_{12}O_6$ requires C, 60·9; H, 4·4%).

*8-Hydroxy-2-methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzopyran* (*IIc*)

A solution of 3-acetoacetyl-4-hydroxy-7-methoxycoumarin (0·7 g) in 75 ml dil. sulphuric acid (25%) was refluxed on a sand-bath for 1 hr. The cooled reaction mixture was basified with sodium hydroxide solution and filtered. The filtrate on acidification gave *8-hydroxy-2-methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzopyran*, which crystallized from dil. acetic acid, yellow needles, m.p. 221° (Found: C, 63·4; H, 3·8. $C_{13}H_8O_5$ requires C, 63·9; H, 3·3%).

3-Acetyl-4-hydroxybenzo[f]*coumarin*

4-Hydroxybenzo[*f*]coumarin (1 g) was dissolved in acetic acid (5 ml) and phosphorus oxychloride (2 ml) and the reaction mixture was gently refluxed for 40 min and then added to ice-water. *3-Acetyl-4-hydroxybenzo*[f]*coumarin* crystallized from acetic acid, m.p. 201°, yield 0·68 g. It developed a red coloration with alcoholic ferric chloride solution (Found: C, 70·4; H, 4·1. $C_{15}H_{10}O_4$ requires C, 70·8; H, 4·0%).

3-Acetoacetyl-4-hydroxybenzo[f]*coumarin*

3-Acetyl-4-hydroxybenzo[*f*]coumarin (0·5 g) dissolved in ethyl acetate (15 ml) was added to pulverized sodium (0·6 g) and refluxed for 6 hr. On working up the reaction mixture as before, *3-acetoacetyl-4-hydroxybenzo*[f]*coumarin* crystallized from benzene, yellow needles, m.p. 166°, yield 0·2 g (Found: C, 68·9; H, 4·5. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%).

*2-Methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzo*[f]*benzopyran* (*IV*)

3-Acetoacetyl-4-hydroxybenzo[*f*]coumarin (0·4 g) was refluxed with 25 ml of dil. sulphuric acid (25%) on a sand-bath for 2 hr. On working up the reaction mixture as before, *2-methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzo*[f]*benzopyran* crystallized from acetic acid, yellow needles, m.p. 282°, yield 0·1 g (Found: C, 73·1; H, 3·9. $C_{17}H_{10}O_4$ requires C, 73·4; H, 3·6%).

Acknowledgments

The authors thank Professor E. Gellert of Wollongong University College for infrared spectra; Dr Lele for microanalyses; and Professor Sethna for his keen interest. One of us (V.N.D.) thanks C.S.I.R., New Delhi, for a junior research fellowship.