Tetrahedron Vol. 39, No. 9, pp 1523 to 1528, 1983
Printed in Great Britain.

0040-4020/83/091523-06$03.00/0
Pergamon Press Ltd

4, 6-DIMETHYL-2H, 8H-BENZO[1, 2-b: 5, 4-b'] DIPYRAN-2, 8-DIONE. FORMATION OF *LINEAR* AND *ANGULAR* ISOMERS IN THE PECHMANN REACTION

A. G. OSBORNE
Department of Chemistry, The City University, London ECIV OHB, England

(*Received in UK* 16 *August* 1982)

Abstract—The structure of Hantzsch and Zürchers "dimethyldicoumarin" obtained from resorcinol or 7-hydroxy-4-methylcoumarin and ethylacetoacetate has been confirmed as the *linear* title compound **1**. *peri*-Substituent effects in ^1H and ^{13}C NMR spectroscopy have been used to differentiate between the *lin* and *ang* isomers, the *ang* Me groups being deshielded. A set of rules to govern the formation of *lin*/*ang* isomers has been proposed.

In 1887 Hantzsch and Zürcher[1] performed a double Pechmann reaction[2] by the condensation of one mole of resorcinol with two moles of ethylacetoacetate (EAA) in the presence of conc sulphuric acid and obtained, in very low yield, a compound which they termed "dimethyldicoumarin". Sen and Chakravarti[3] later prepared the same compound from the intermediate 7-hydroxy-4-methylcoumarin[4] and one mole of EAA. A yield of 30% was claimed; however, the exact constitution was not established, it was regarded as either the *linear* (*lin*) **1** or *angular* (*ang*) **2a** isomer.

Rangaswami and Seshadri[5] subsequently made a detailed investigation of the constitution of this and similar compounds which they termed coumarinopyrones. The structures of the *lin* and *ang* isomers from the Pechmann reaction of 7-hydroxycoumarin with malic acid were elucidated, that of **3** being confirmed by an unambiguous synthesis as shown in Scheme 1.

Certain observations regarding the *lin*/*ang* isomers were reported:

(i) *lin* isomers were more sparingly soluble and had a higher m.p. than the corresponding *ang* isomers

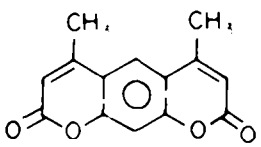
(ii) in the reaction with malic acid, the predominant tendancy was to form the *ang* compound, the *lin* isomer being produced to a small extent only.

Reactions with 7-hydroxy-4-methylcoumarin **5** were then studied, malic acid gave **2b**, the structure of which was substantiated by an unambiguous Perkin synthesis from 7-hydroxy-4-methylcoumarin-8-carboxaldehyde. The preparation of Hantzsch and Zürchers[1] "dimethyldicoumarin" was then examined. Under all conditions, starting from resorcinol or **5**, a single compound (m.p. 333–5°) only was obtained. By analogy with the rules proposed for the malic acid reaction, this was described as the *ang* isomer **2a**.

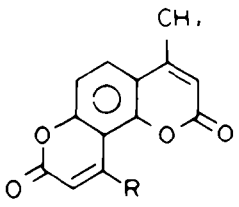
The structure of the *lin* isomer **4** has subsequently been additionally verified by Worden *et al.*[6] The compound was synthesised from 4, 6-dihydroxyisophthaldehyde by a double Perkin reaction, and the structure confirmed by NMR.

Merchant, Patell and Thakkar[7] have recently reported the formation of a neutral substance-A (m.p. 319–20°) during the preparation of **5** by the Pechmann reaction. Their limited spectral data (M$^+$, ν C=O) suggested that the structure was either **1** or **2a**. A compound, designated as the *ang* isomer (m.p. 320–2°), was then obtained by the procedure of Sen and Chakravarti[3] and found to differ from the neutral substance-A, which was accordingly assigned the *lin* structure **1**. These results appear to be very suspect, particularly since it has been previously noted[5] that the m.p.'s of *lin* and *ang* isomers are quite different, as shown by the examples gathered in Table 1; however, in the Indian study,[7] the m.p.'s of the two alleged compounds were almost identical and much lower than the literature value[5] which was not quoted.

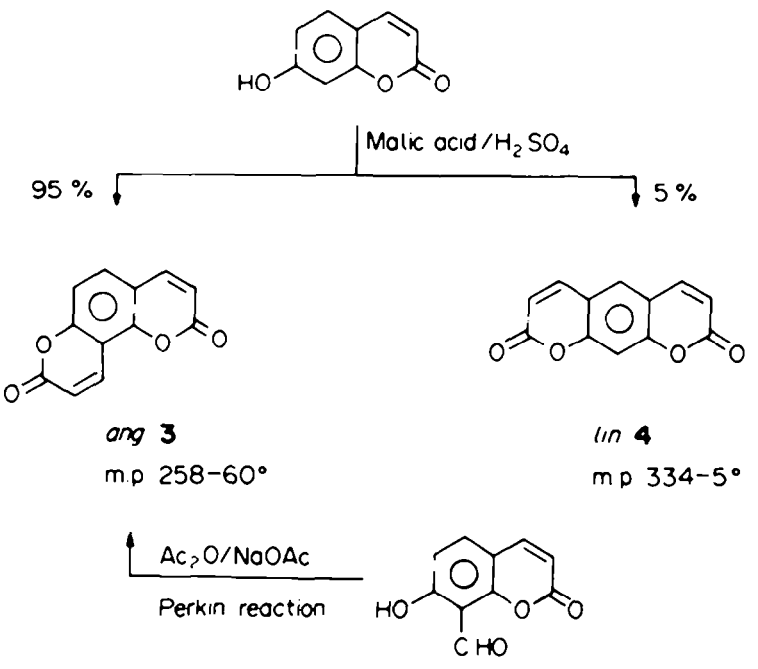
In view of these rather contradictory results, the



1

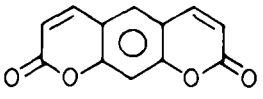
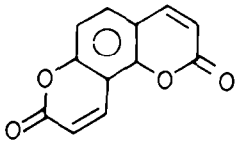
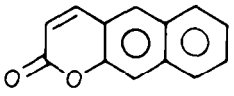
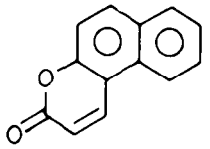
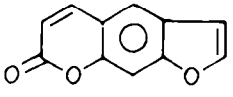
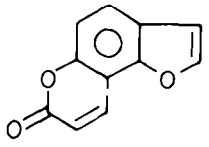
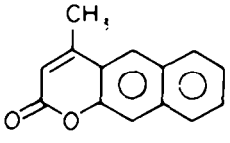
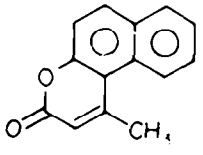


2a R = CH_3
2b R = H



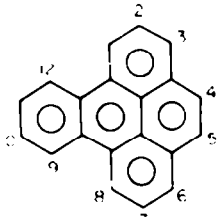
Scheme 1.

Table 1. Comparison of melting points of *linear* and *angular* isomers

Linear m.p (lit.)	*Angular* m.p (lit.)
 334–5° (5) 348–51° (8)	 258–60° (5)
 165° (9)	 118° (9)
 171° (10)	 138–95° (11)
 217–8° (12)	 183° (13)

earlier work has been repeated in order to establish the precise identity of Hantzsch and Zürchers "dimethyldicoumarin" and to obtain a reliable spectroscopic technique to differentiate between such *lin* and *ang* isomers. A further aim of the study was to formulate a set of rules to govern the formation of *lin* and/or *ang* isomers in a given reaction.

For the differentiation of *lin*/*ang* isomers, application of the *peri*-proximity effect in ^{1}H NMR spectroscopy was envisaged as an appropriate technique. This effect causes a deshielding of the high intensity methyl signals,[14] which should render the method particularly appropriate for the sparingly soluble compounds involved. As an illustration of the effect, the recent paper by Harvey *et al.*[15] concerning the monomethylbenzo(e)pyrenes **6** may be considered.



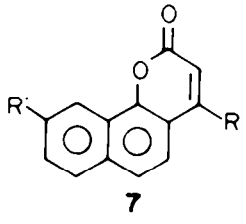
6

For the 2-, 3-, 4- and 10- monomethyl derivatives, the Me signals resonated in the 2.60–2.88 δ range, typical of a methyl group attached to a polycyclic aromatic ring, with no additional *peri*-substituent. In contrast, the Me signals of the *peri*-substituted 1- and 9-monomethyl isomers appeared significantly downfield at 3.17–3.27 δ, an average deshielding effect of *ca.* 0.45 ppm. This *peri*-proximity effect, in which the *peri*-substituent forms part of a fused aromatic ring, is much larger, and hence of greater diagnostic value, than those experienced for *peri* methyl/methyl couples as reported by Bergmann *et al.*[14] and by Claret and Osborne.[16] Further additional deshielding effects also affect the bay region aromatic protons of **6**, viz H-1, H-8, H-9 and H-12, which absorbed far downfield in the 8.7–8.9 δ region.[15]

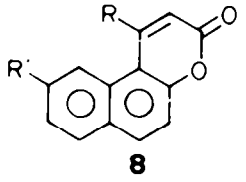
In order to establish that these effects functioned satisfactorily in the condensed pyrone series, and to obtain certain model chemical shift data, the spectra of the methylnaphthopyrones **7a** and **8a** were examined. These compounds were obtained from EAA and 1- and 2- naphthol respectively. Although their 60 MHz ^{1}H NMR spectra have been reported by Jain *et al.*,[17] the analyses of the aromatic region were very superficial and, in one instance, deficient. Accordingly, the spectra have been re-determined at higher magnetic fields, 220 MHz for **8a**, and 400 MHz for the more closely coupled **7a**. The methyl protons absorbed at 2.47 δ for **7a** and at 2.88 δ for the *peri*-substituted **8a**. The deshielding effect was similar to that experienced in the benzo(e)pyrene series.[15] The pyrone ring protons (H-3 in **7a**, H-2 in **8a**) were unremarkable and absorbed at 6.36 δ and 6.38 δ respectively, consistent with the earlier work.[17] The AB systems for H-5 and H-6 were clearly evident at the higher magnetic fields. The signals were readily distinguished since in each case the H-6 doublet was broadened by long range ^{5}J "zig-zag" coupling,[18] which collapsed upon irradiation of H-10. The remaining aromatic protons formed a complex ABCD spin system, which has been partially analysed by a simple first order treatment in the present work. For each compound the bay proton H-10 was strongly deshielded and absorbed at *ca* 8.5 δ. In their earlier studies of the NMR spectra of **7a** and **8a** Jain *et al.*[17] reported the aromatic region signals as multiplets extending from 7.27–8.43 δ and 7.40–7.91 δ respectively. The low field bay proton signal for **8a** was obviously overlooked. Narasimhan and Mali,[9] have measured the NMR spectra of **7b** and **8b**, the aromatic regions featured multiplets which extended far downfield to include the bay protons. In contrast, the *lin*-naphthopyrone **9b** did not exhibit any such low yield signals.

The *peri*-proximity effect is therefore most appropriate for differentiation between *lin*/*ang* isomers. The characteristic chemical shifts of the Me protons are of particular value which may be further supported by the absorption of the bay region aromatic protons.

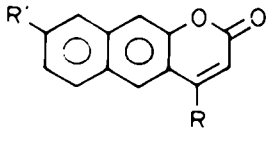
The constitution of Hantzsch and Zürchers[1] "dimethyldicoumarin" was then examined. Reactions of resorcinol with two moles of EAA, or of **5** with one



7



8



9

a R = CH_3, R′ = H

b R = R′ = H

c R = CH_3, R′ = OH

mole of EAA, followed by a basic (ammoniacal) work-up afforded a low yield of a single dimethylbenzodipyrone which after recrystallisation from ethyl acetate gave a sharp and reproducible m.p. (333–4°) either alone, or in admixture, hence both reactions lead to the same product. Earlier Merchant *et al.*[7] suggested that two different products (m.p. 319–20° and 320–2°) were obtained, although their evidence for this heterogeneity was not presented. It may be surmised that this came from a mixed m.p. depression. It would appear that these workers obtained two impure samples of the same material, which upon admixture then produced the misconstrued depression.

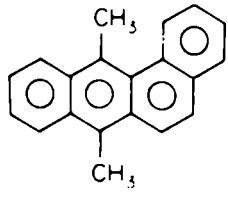
The "dimethyldicoumarin" proved to be only sparingly soluble in chloroform, as previously intimated,[7] nevertheless it was possible to obtain a satisfactory ^{1}H NMR spectrum on a saturated solution. Improved results were secured by measurement at elevated temperature and also after a short accumulation. Four singlet peaks only were present in the spectrum. The Me signal at 2.50 δ was characteristic of a non *peri*-substituted environment (*cf* 2.47 δ for **7a**) and accordingly Hantzsch and Zürchers "dimethyldicoumarin" must be the *lin* isomer *viz* 4, 6-dimethyl-2H, 8H-benzo [1, 2-b: 5, 4-b'] dipyran-2, 8-dione **1**. This structure is consistent with the three aromatic region signals for H-3/H-7, H-5 and H-10. Unfortunately, since one signal overlapped the residual $CHCl_3$ peak, the integration was not wholly conclusive. The alternative structure, **2a**, however, should exhibit a *peri*-deshielded Me as well as two singlets and two doublets in the aromatic region which was clearly not the case. In order to obtain a stronger spectrum an alternative solvent was sought. Worden *et al.*[6] had previously employed trifluoroacetic acid (TFA) for the spectrum of **4**, and accordingly this was tried, **1** proved to be readily soluble. The Me signal was a fine doublet (J = 1.1 Hz), as a result of allylic coupling to H-3/H-7 which appeared as a 2H fine quartet at 6.73 δ. Worden *et al.*[6] reported 6.78 δ for H-3/H-7 of **4**. The two remaining signals, each 1H singlets, at 7.61 δ and 8.11 δ were assigned to H-10 and H-5 respectively, consistent with the corresponding signals in **4** at 7.59 δ and 8.04 δ.[6]

Since the compound was very soluble in TFA the opportunity was taken to determine the ^{13}C NMR spectrum. Although TFA is a valuable solvent for ^{1}H NMR, it has inherent difficulties for ^{13}C NMR since the trifluoromethyl and carboxyl carbons each appear as quartets due to coupling with the ^{19}F nuclei[19] and hence obscure a large portion of the spectrum, as well as presenting certain dynamic range problems.[20] In the event these difficulties proved of no consequence since the expected eight signals were all discernible; the proton coupled spectrum was also determined and the results are shown in Table 2. The assignments were made by comparison with the reported spectrum[21] of **5** determined in DMSO-d_6, and with a spectrum measured in TFA solution in the present study, no particular problems were encountered. The Me signals for both **1** and **5** appeared at 19.4 δ indicative of the absence of any *peri*-proximity effect. In the proton coupled spectrum of **1** both C-5 and C-10 appeared as clear doublets, in accordance with the absence of *ortho* and *meta* protons. The C-9a signal was a doublet of doublets which featured couplings to H-10 and H-5, the enhanced ^{2}J coupling (5 Hz) is consistent with the presence of an *ortho* oxygenated substituent as previously noted by Chang *et al.*[22]

Differentiation between *lin* and *ang* isomers may also be accomplished by proton decoupled ^{13}C NMR spectroscopy since in this case the alternative product **2a**, which has no symmetry, would give rise to a total of fourteen peaks including two methyl resonances.

The ^{13}C NMR spectra of the methylnaphthopyrones **7a** and **8a** have also been examined in $CDCl_3$ solution. The methyl signals appeared at 19.2 δ and 26.4 δ respectively, the *peri*-proximity effect in the latter compound being immediately evident. The value of $\Delta\delta$, the downfield shift from the model compound 4-methylcoumarin,[23] was 7.9 ppm, considerably larger than previously experienced for simple *peri*-Me/Me couples such as 1, 8-dimethylnaphthalene (6.7 ppm)[24] and 4, 5, 7-trimethylcoumarin (6.5 ppm) studied in the present work. It may be recalled that the proximity effect for the C-C couple was similarly enhanced in the ^{1}H NMR when one carbon formed part of a fused aromatic ring. Such enhancement renders this effect of even greater diagnostic value.

The 12-Me group in 7, 12-dimethylbenz(a)-



10

Table 2. ^{13}C NMR spectrum of **1**

Carbon	*Chemical shift* (a)	*Multiplicity* (b)	*Couplings* (Hz)
C-2	168.0	d	$^2J_{2,3}$ 4
C-3	116.0	dq	$^1J_{3,3}$ 173 $^3J_{3,CH_3}$ 6
C-4	159.6	dq	$^2J_{4,CH_3}$ 6 $^3J_{4,5}$ (c)
C-5	124.7	d	$^1J_{5,5}$ 164
C-10	108.0	d	$^1J_{10,10}$ 171
C-4a	120.7	m	
C-9a	157.2	dd	$^2J_{9a,10}$ 5 $^3J_{9a,5}$ 11
CH_3	19.4	qd	$^1J_{CH_3}$ 130 $^3J_{CH_3,3}$ 6

(a) In TFA solution, δ ppm. from TMS.
(b) In proton coupled spectrum.
(c) Obscured by TFA peak.

anthracene **10** is deshielded by only 6.3 ppm compared with 9-methylanthracene.[25] This proximity effect operates in the reverse manner to that in **8a**, and also occurs in a larger polycyclic system with an additional buttressing effect from the H-11 proton, which would be expected to result in less molecular distortion and a smaller deshielding effect.

Following the correction of the structure of Hantzsch and Zürchers[1] "dimethyldicoumarin", the pattern of the formation of *lin*/*ang* isomers in the Pechmann reaction may now be considered. Reaction of **5** with malic acid gave the *ang* isomer,[5] whilst the reaction with EAA produced the *lin* isomer. The formation of the *lin* isomer in the latter reaction may be attributed to steric hindrance by the additional 4-Me substituent, which is considerably more prominent in the formation of the *ang* isomer than the *lin* isomer. These results parallel those found recently[26] for the Pechmann reaction of *m*-cresol with malic acid which produced a mixture of 5- and 7-methylcoumarin (12:88). In the reaction with EAA, the additional 4-Me substituent similarly rendered the hindered pathway completely ineffective, to produce 4, 7-dimethylcoumarin only.

1-Naphthol reacts readily with EAA,[27] whilst 2-naphthol reacts only with difficulty to give the more hindered *ang* isomer only,[11] in contradistinction to the reaction with **5**. Why should this be the case? The Pechmann reaction proceeds through the attack of a carbonium ion upon the aromatic ring *ortho* to the OH group.[27] If the likelihood of electrophilic substitution at either *ortho* position was similar then attack at the least hindered site would be favoured to counteract the steric effect. Hence the steric effect outweighs the electronic effects to govern the orientation. This is the situation operative for **5**, nitration of which is reported to occur at both the 6- and 8-positions.[28]

2-Naphthol is attacked by electrophilic reagents at position 1 as exemplified by the nitration with amylnitrite in ether to give the 1-nitro- and then the 1, 8-dinitro- derivative.[29] The complete lack of nitration at the 3-position may be emphasised by the fact that 3-nitro-2-naphthol may only be obtained by an indirect multi-stage sequence,[30] and that 1, 3-dinitro-2-naphthol still remains unknown. In the Pechmann reaction with 2-naphthol, since the formation of the *lin* isomer is extremely unfavourable the *ang* isomer therefore results, but as this is produced by a hindered pathway the yield is accordingly diminished. Thus in this case, the electronic effects outweigh the steric effect.

The following rules to govern the formation of *lin* and *ang* isomers in the Pechmann reaction may therefore be formulated:

(i) in the reaction with malic acid, the *ang* isomer predominates, with the *lin* isomer being formed to a small extent only. (as previously proposed by Rangaswami and Seshadri[5])

(ii) in the reaction with EAA, in cases where electrophilic attack is exclusively favoured at one *ortho* position of the phenol reactant only, then the *ang* isomer will result.

(iii) in the reaction with EAA, in cases where electrophilic attack is favoured at both *ortho* positions of the phenol reactant, then the *lin* isomer will result.

Application of these rules to predict the products from reported reactions is hampered by a lack of suitable examples, two cases have been selected for discussion. 7-Hydroxychromanone has been reported[31] to yield the *ang* isomer with malic acid, and the *lin* isomer with EAA. No nitration study of this particular compound is available, however, Mujumdar and Usgaonkar[32] have investigated the bromination of the related 7-hydroxy-2-methylchromanone, which gave the 6-bromo- or 6, 8-dibromo- derivative depending upon the particular reagent employed. Formation of the *lin* isomer in the Pechmann reaction is therefore consistent with case (iii).

The course of the orientation in the dihydroxynaphthalene series is thwart with difficulty, since the reaction of 1-naphthol with EAA is so much more facile than that of 2-naphthol. Accordingly with the 1, 3-, 1, 6- and 1, 7- dihydroxynaphthalenes the cyclisations occur exclusively at the 1 positions[33] which leaves the question of the orientation of cyclisation at the β-positions of these compounds unanswered. Furthermore, 2, 6-dihydroxynaphthalene does not react at all,[33] whilst the 2, 7- isomer has been reported to produce the *ang* isomer **8c** exclusively[33,34] or a mixture[35] of **8c** and the *lin* isomer **9c**. In the latest report[35] the compounds were identified by reference to the aromatic region of their ^{1}H NMR spectra only. A preliminary re-investigation of this reaction has been undertaken, examination of the reaction product by ^{1}H NMR in TFA solution showed that two products were formed since two methyl peaks at 2.64 δ and 2.96 δ were observed indicative of the non *peri*-substituted methyl of **9c** and the *peri*-substituted methyl of **8c** respectively. The alkyl region of the ^{13}C NMR showed two Me signals at 19.5 δ and 27.5 δ again characteristic of the aforementioned environments. The two products (lit.[35] m.p. 278° (**8c**) and m.p. 267° (**9c**)) were present in approximately equal amounts. The precise identity of the compound (m.p. 321–4°) synthesised by Wolfbeis[36] and also allocated structure **8c** therefore remains obscure. Further work on this reaction is in progress, and full details will be communicated at a later date.

EXPERIMENTAL

M.p's were determined on a Kofler hot stage apparatus. The spectrometers used for ^{1}H NMR spectroscopy were a Jeol JNM-MH-100 for measurements at 100 MHz, a Perkin Elmer R34 (at P.C.M.U., Harwell) for 220 MHz, and a Bruker WH-400 at University of Sheffield) for 400 MHz. Chemical shifts are reported as ppm (δ) downfield from TMS. ^{13}C NMR spectra were obtained with a Jeol JNM-FX-60 spectrometer operating in the pulsed Fourier transform mode at 15 MHz, with broad band noise decoupling: pulse width 7 μs (45° pulse angle), pulse repetition rate 4 sec, spectral width 2500 Hz with 8K data points. Proton coupled spectra were obtained by the Gated-1 alternatively pulsed sequence. For the measurements in TFA soln, external D_2O, contained in an insert tube, provided the lock signal. In the spectral analyses given * represents a tentative assignment only.

Synthesis of Hantzsch and Zürchers "dimethyldicoumarin"

(i) Resorcinol (33.03 g, 0.3 mole) was dissolved in ethylacetoacetate (78.09 g, 0.6 mole) and the soln added slowly to conc H_2SO_4 (150 ml) keeping the temp below 10°. The mixture was allowed to stand for 1 hr and then poured on to crushed ice. The precipitated **5** was dissolved in dil NH_4OH

and the insoluble "dimethyldicoumarin" filtered off and washed with water. Recrystallisation from EtOAc afforded **1** (54 mg, 0.07%) as colourless needles, m.p. 333–4° (lit.[5] m.p. 333–5°) (Found: C, 69.53; H, 4.19. Calc for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16%) MS *m/e* (relative intensity): 243 (11), 242.0508 (M^+, $C_{14}H_{10}O_4$, 72), 214 (M − CO, 55), 187(13), 186 (M — 2CO, 100), 185(57), 157(13), 137(10), 131(10), 129(11), 128(24), 127(13), 117(11), 115(37), 99(48), 93(12), 89(15), 77(18), 75(19), 74(15), 69(26), 65(12), 64(10).

^{1}H NMR ($CDCl_3$), saturated soln, 60°): 2.50 (3H, s, CH_3), 6.34 (2H, s, H-3,H-7), 7.31 (1H, s, H-10), 7.80 (1H, s, H-5). ^{1}H NMR (TFA): 2.76 (3H, d, J = 1.1 Hz, CH_3), 6.73 (2H, q, J = 1.1 Hz, H-3,H-7), 7.61 (1H, s, H-10), 8.11 (1H, s, H-5). ^{13}C NMR (TFA): see Table 2.

(ii) A sample of **5** was prepared by the method of Mann and Saunders.[37] The once recrystallised product (50 g) was dissolved in NaOH aq. (10%) and extracted with $CHCl_3$ (5 × 200 ml). The $CHCl_3$ extracts were washed with dil NaOH aq. and with water and then dried ($MgSO_4$). Removal of the solvent, and recrystallisation of the residue from EtOAc afforded **1** (63 mg, 0.13% recovery) as colourless microscopic needles, m.p. 333–4°.

(iii) A mixture of **5** (17.6 g, 0.1 mole), ethylacetoacetate (13.0 g., 0.1 mole) and conc H_2SO_4 (50 ml.) was allowed to stand for 24 hr. The product was isolated as described in (i) above to give **1** (21 mg, 0.009%), m.p. 333–4°.

(iv) A mixture of **5** (17.6 g, 0.1 mole), ethylacetoacetate (13.0 g., 0.1 mole) and conc H_2SO_4 (50 ml.) was heated on the water bath for 4 hr. The product was isolated as described in (i) to give **1** (1.42 g, 5.9%), m.p. 333–4°.

The spectral properties of the samples of **1** isolated in (i) to (iv) were identical.

4-Methyl-2H-naphtho[1, 2-b]*pyran-2-one* **7a** was synthesised by the procedure of Robertson *et al.*,[38] m.p. 170–1° (lit.[38] m.p. 170°) ^{1}H NMR ($CDCl_3$): 2.47 (3H, d, J = 1.2 Hz, CH_3), 6.36 (1H, q, J = 1.2 Hz, H-3), 7.56 (1H, d, J_{56} = 8.8 Hz, H-5), 7.62 (1H, m, H-9), 7.64 (1H, m, H-8), 7.67 (1H, broadened d, J_{56} = 8.8 Hz, H-6), 7.85 (1H, m, H-7), 8.53 (1H, m, H-10). ^{13}C NMR ($CDCl_3$): 19.2 (CH_3), 114.5 (C-3), 115.4 (C-4a), 120.5 (C-5), 122.8 (C-10), 123.4 (C-10a), 124.3 (C-6), 127.3 (C-9)*, 127.9 (C-7)*, 128.8 (C-8)*, 135.0 (C-6a), 150.9 (C-10b), 153.6 (C-4), 161.1 (C-2).

1-Methyl-3H-naphtho[2, 1-b]*pyran-3-one* **8a** was synthesised by the procedure of Murty *et al.*,[11] m.p. 181–2° (lit.[13] m.p. 183°) ^{1}H NMR ($CDCl_3$): 2.88 (3H, d, J = 1.2 Hz, CH_3), 6.38 (1H, q, J = 1.2 Hz, H-2), 7.45 (1H, d, J_{45} = 8.8 Hz, H-5), 7.59 (1H, m, H-8), 7.64 (1H, m, H-9), 7.93 (1H, m, H-7), 7.97 (1H, broadened d, J_{45} = 8.8 Hz, H-6), 8.59 (1H, m, H-10). ^{13}C NMR ($CDCl_3$): 26.4 (CH_3), 114.6 (C-10b), 116.7 (C-2), 117.9 (C-5), 125.2 (C-10)*, 125.6 (C-9)*, 128.0 (C-8)*, 129.9 (C-7)*, 130.4 (C-10a)*, 131.5 (C-6a)*, 133.8 (C-6), 154.3 (C-1), 154.9 (C-4a), 160.5 (C-3).

7-Hydroxy-4-methylcoumarin **5** was synthesised by the procedure of Mann and Saunders.[37] ^{13}C NMR (TFA): 19.4 (CH_3), 105.3 (C-8), 111.2(C-3), 116.3 (C-10), 116.9 (C-6), 128.6 (C-5), 156.3 (C-9), 161.9 (C-4), 162.1 (C-7), 170.0 (C-2).

4, 5, 7-*Trimethylcoumarin* was synthesised by the procedure of Clayton,[39] m.p. 181–2° (lit.[39] m.p. 175–6°, lit.[27] m.p. 183-4.5°) ^{13}C NMR ($CDCl_3$): 21.2 (CH_3-7), 24.3 (CH_3-5), 25.1 (CH_3-4), 115.6 (C-3), 116.3 (C-8), 117.0 (C-10), 129.8 (C-6), 136.7 (C-5), 142.1 (C-7), 154.5 (C-4), 155.4 (C-9), 160.9 (C-2).

Acknowledgements—We thank the S.R.C. (now S.E.R.C.) for providing funds to purchase the NMR instrumentation, and for access to facilities at Harwell and Sheffield. We are also indebted to Mr. Maurice Cooper and Dr. Brian Mann and the staff of these establishments for their assistance.

REFERENCES

[1]A. Hantzsch and H. Zürcher, *Ber Dtsch. Chem. Ges* **20**, 1328 (1887).
[2]H. von Pechmann, *Ibid.* **17**, 929 (1884).
[3]R. N. Sen and D. Chakravarti, *J. Indian Chem. Soc.* **6**, 793 (1929).
[4]7-hydroxy-4-methylcoumarin may be obtained from resorcinol and one mole of EAA in high yield, H. von Pechmann and C. Duisberg, *Ber. Dtsch. Chem. Ges* **16**, 2119 (1883).
[5]S. Rangaswami and T. R. Seshadri, *Proc. Indian Acad. Sci.* **6A**, 112 (1937).
[6]L. R. Worden, K. D. Kaufman, P. J. Smith and G. N. Widiger, *J. Chem. Soc.* (C), 227 (1970).
[7]J. R. Merchant, J. R. Patell and S. M. Thakkar, *Indian J. Chem.* **12**, 657 (1974).
[8]J. N. Marx, P.-S. Song and P. K. Chui, *J. Heterocyclic Chem.* **12**, 417 (1975).
[9]N. S. Narasimhan and R. S. Mali, *Tetrahedron* **31**, 1005 (1975).
[10]E. Späth, B. L. Manjunath, M. Pailer and H. S. Jois, *Ber. Dtsch. Chem. Ges* **69**, 1087 (1936).
[11]E. Späth and M. Pailer, *Ibid.* **68**, 940 (1935).
[12]T. Nakabayashi, *Yakugaku Zasshi* **77**, 536 (1957).
[13]K. S. Murty, P. S. Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.* **6A**, 316 (1937).
[14]F. Bergmann, I. Tamir, A. Frank and W. Pfleiderer, *J. Chem. Soc.* Perkin Trans. II, 35 (1979).
[15]H. Lee, N. Shyamasundar and R. G. Harvey, *Tetrahedron* **37**, 2563 (1981).
[16]P. A. Claret and A. G. Osborne, *Spectroscopy Letters* **11**, 345 (1978).
[17]S. K. Jain, O. P. Aggarwal, U. S. Mahnot and R. L. Mital, *Monatsh. Chem.* **101**, 1052 (1970).
[18]L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, pp. 333–334, 2nd Edn, Pergamon Press, Oxford (1969).
[19]L. F. Johnson and W. C. Janowski, *Carbon-13 NMR Spectra*, Spectrum no. 1. Wiley, New York (1973).
[20]K. Müllen and P. S. Pregosin, *Fourier Transform NMR Techniques: A Practical Approach*, p. 15. Academic Press, London (1976).
[21]N. J. Cussans and T. N. Huckerby, *Tetrahedron* **31**, 2719 (1975).
[22]C.-j. Chang, H. G. Floss and W. Steck, *J. Org. Chem.* **42**, 1337 (1977).
[23]L. Ernst, *J. Magn. Reson.* **21**, 241 (1976).
[24]N. K. Wilson and J. B. Stothers, *Ibid.* **15**, 31 (1974).
[25]D. K. Dalling, K. H. Ladner, D. M. Grant and W. R. Woolfenden, *J. Am. Chem. Soc.* **99**, 7142 (1977).
[26]A. G. Osborne, *Tetrahedron* **37**, 2021 (1981).
[27]R. N. Lacey, *J. Chem. Soc.* 854 (1954).
[28]N. M. Shah and D. H. Mehta, *J. Indian Chem. Soc.* **31**, 784 (1954).
[29]T. Ajello and G. Sigillo, *Gazz. Chim. Ital.* **69**, 55 (1939).
[30]D. Woodcock and D. R. Clifford, *J. Chem. Soc.* 4139 (1957).
[31]J. R. Merchant and J. R. Patell, *Tetrahedron Letters* 555 (1970).
[32]A. S. Majumdar and R. N. Usgaonkar, *J. Chem. Soc.* Perkin Trans 1, 2236 (1974).
[33]N. P. Buu-Hoï and D. Lavit, *Ibid.* 1743 (1956).
[34]V. V. Perekalin and G. D. Padva, *Zh. Obshchei Khim.* **27**, 2578 (1957).
[35]J. H. Pardanani and S. Sethna, *J. Indian Chem. Soc.* **55**, 806 (1978).
[36]O. S. Wolfbeis, *Monatsh. Chem.* **109**, 1421 (1978).
[37]F. G. Mann and B. C. Saunders, *Practical Organic Chemistry*, p. 305. Longmans, London, 4th Edn (1960).
[38]A. Robertson, W. F. Sandrock and C. B. Hendry, *J. Chem. Soc.* 2426 (1931).
[39]A. Clayton, *J. Chem. Soc.* **93**, 2016 (1908).