Pergamon

Tetrahedron 56 (2000) 3583–3587

TETRAHEDRON

Synthesis of Coumarin Derivatives from 4-Oxo-4*H*-1-benzopyran-3-carboxaldehyde via 3-(Arylaminomethylene)chroman-2,4-dione

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Received 4 October 1999; revised 6 March 2000; accepted 23 March 2000

Abstract—K-10 Montmorillonite mediated condensation of aldehyde **1** with arylamine **2** affords chroman-2,4-dione **5** which gives tricoumarol **8** by acid hydrolysis, 4-arylamino-3-formylcoumarin **11** and 1-benzopyrano[4,3-*b*]quinoline **12** on heating with $POCl_3$.

The diverse biological activity of coumarin derivatives[1] as anticoagulants and antithrombotics is well known. Some 3-substituted-4-hydroxycoumarins[2] and tricoumarol[3] possess some HIV inhibitory potency. Some 1-benzopyrano[4,3-*b*]-quinolines are antispasmodic and antihistaminic[4] whereas 1-benzopyrano[3,4-*f*]quinolines are nonsteroidal human progesterone receptor (HPR) agonists.[5] Heterocycles fused at 3,4-position of coumarin also draw special attention.[6] We report herein new syntheses of some coumarin derivatives from easily accessible 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde.[7]

Clay-mediated reaction of aldehyde **1** with arylamine **2** in benzene produced the enaminone **5** (stereoisomeric mixture) instead of the corresponding simple Schiff-base **3**. The *Z*:*E* ratios of **5** were determined from their ^{1}H NMR spectra. The relatively higher deshielding effect on the β-H which is *cis* to the ester function of an α,β-unsaturated ester compared to that of an α,β-unsaturated ketone[8] helps to distinguish the *E* and *Z* isomer. The additional support is from comparable δ values for NH protons in *E*-isomers of **5a–e** with that for NH proton of **6**. The high δ value (δ 11.52) for NH proton in **6** is due to intramolecular H-bonding in its *Z*-configuration. The presently reported preparation of **5** involving a short reaction time, easy working procedure and devoid of any chromatographic separation is advantageous over its earlier syntheses (a) by reaction of 4-hydroxycoumarin with triethyl orthoformate and aniline,[6] (b) by oxidation of 3-aryliminomethylchromone **3** with MnO_2[9] or (c) as a side product from the thermal rearrangement of *N*-phenylnitrones of **1**.[10]

The attack of the primary amino group at the 2-position of aldehyde **1**[11] with concomitant opening of the pyran ring and recyclisation gives the intermediate **4** which needs oxidation to form **5** (Scheme 1). This oxidation may be accomplished by clay itself or by Schiff-base **3**. Oxidation of 4-*t*-butylphenol by K-10 montmorillonite doped with Fe(III) ion,[12] that of secondary as well as benzylic alcohols by clayfen[13,14] and aromatisation of 1,4-dihydropyridine by claycop[15] are known. In all these cases of oxidation by impregnated clay, NO_3^- ion was responsible for oxidation though $NaNO_3$ impregnated clay fails to perform oxidation[14] and the role of metal ion remained unclear. The clay used in our reaction was found to contain Fe(III) ion but no NO_3^- or manganese ion was detected. So Fe(III) may be considered to be responsible for this oxidation. When the clay, made almost free from iron by leaching with 4N HCl at room temperature, was employed in the above reaction, a sharp decrease in yield of **5** (to ~5%) was noted. The residual mixture obtained after isolation of **5** could not be properly analysed but on treatment with fresh K-10 montmorillonite again produced enaminone **5** in moderate yield.

Treatment of 1 (R=H and Me) with arylamine **2** (X=Me) in the presence of K-10 montmorillonite produced respectively **6** (10%) and **7** (15%) in addition to the corresponding enaminone **5**. The formation of these two reduced Schiff-bases **6** and **7** indicates oxidation to some extent of **4** to **5** by the appropriate Schiff-base intermediates. The anil **3** when prepared by *p*-toluenesulfonic acid catalysed condensation of **1** and **2** is always associated with other compounds, presumably arising due to the oxidising property of the anil **3** itself. It should be mentioned here that the reaction of **1** with **2** in the presence of anhydrous $FeCl_3$ in benzene fails to produce **5**.

Compound **5**, a vinylogous benzanilide, survived refluxing in ethanol containing aqueous HCl but produced tricoumarol **8**[16,17] on heating with 70% H_2SO_4 at 100°C, presumably via 3-formyl-4-hydroxycoumarin **9** (Scheme 2).

Keywords: coumarin derivatives; montmorillonite; heterocycles; benzopyran.

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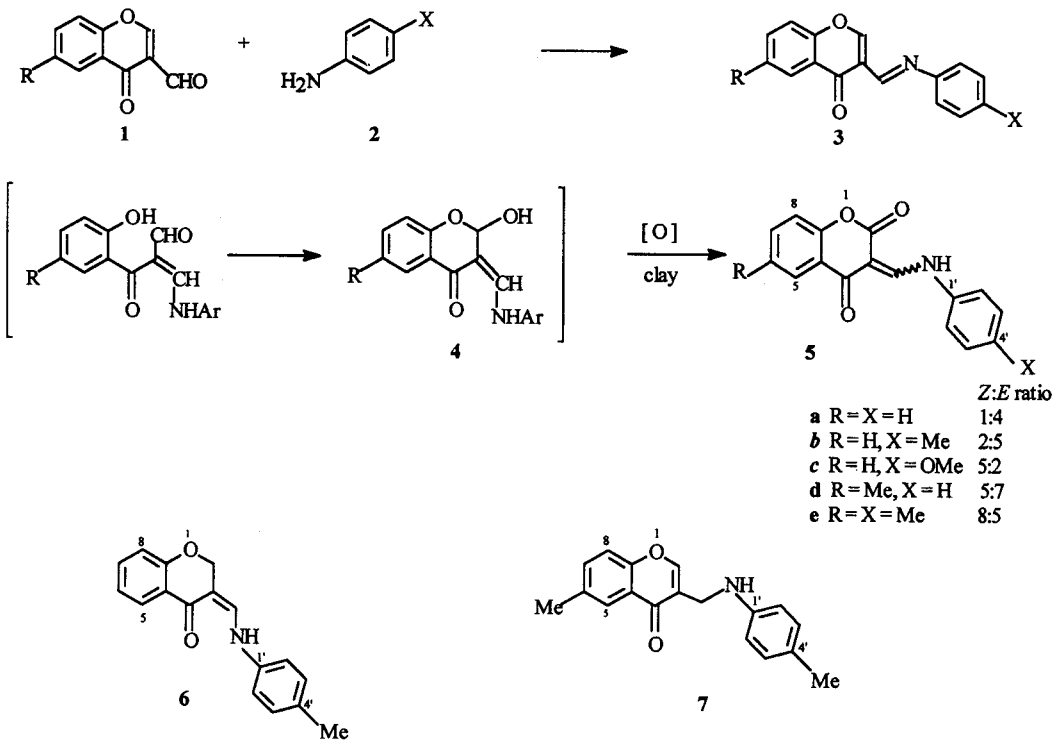
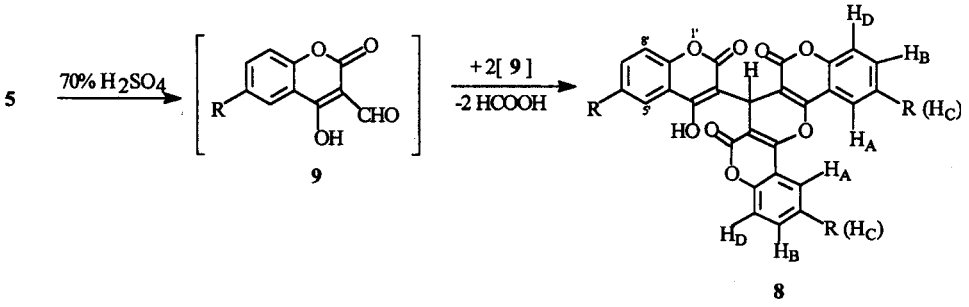
PII: S0040-4020(00)00269-6

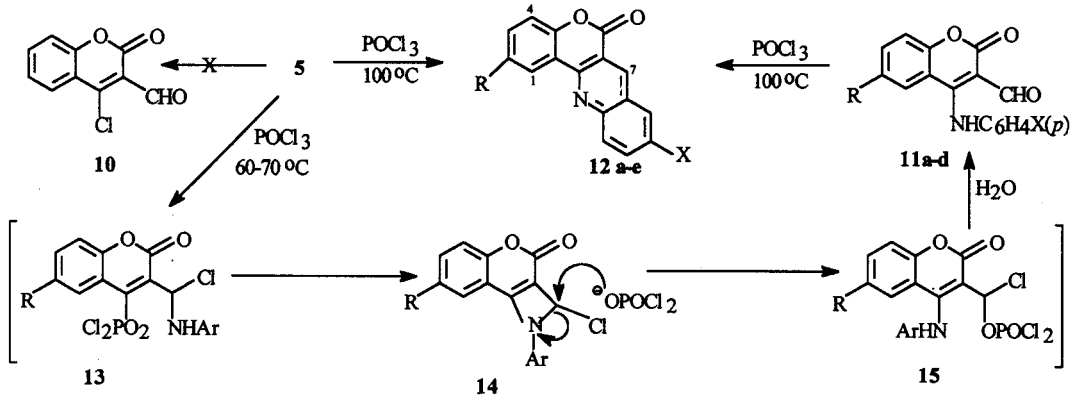


Scheme 1.



Scheme 2.

Two conflicting publications on the Vilsmeier–Haack reaction of 4-hydroxycoumarin have appeared, one reporting the formation of **8**[17] and the other 4-chloro-3-formylcoumarin **10**.[18] We found that the above reaction was dependent on reaction temperature; it gave mainly **10** at room temperature and **8** at 60–70°C; the former on prolonged (2–3 days) standing in aqueous-acetone gradually transformed into the latter.



Scheme 3.

The enaminones **5a**, **b**, **d**, **e** on treatment with $POCl_3$ at 100°C gave the 1-benzopyranoquinolines **12a**,[4] **b**,[19] **d**, **e** but not the anticipated **10**. The regioselectivity of the reaction of **2** (X=Me) with **10** leading to **12b**[19] is the same as observed in that of **2** with β-chloroacraldehyde.[20] The conversion of **5** to **12** involves the rearrangement of the former to 4-arylamino-3-formylcoumarin **11** followed by its cyclisation. When heated with $POCl_3$ at 60–70°C **5a–d** indeed formed **11a–d**, the latter on further treatment with $POCl_3$ at 100°C yielding **12**. The plausible mechanism for the transformation of **5** into **11** is depicted in Scheme 3. The compound **5** reacts with $POCl_3$ to form **13** which rearranges to **15** possibly via azetine **14**. Subsequent hydrolysis of **15** during aqueous work-up produces **11**. The conversion of **5** to **12** is analogous to thermal as well as photochemical cyclisation of 4-chloro-3-aryliminomethyl-2*H*-chromene to 1-benzopyrano[4,3-*b*]quinoline involving the rearranged intermediate 4-arylamino-3-formyl-2*H*-chromene though its isolation or independent synthesis was not achieved.[21]

Experimental

The recorded melting points are uncorrected. IR spectra were recorded in KBr on a Beckman IR-20A and NMR spectra in $CDCl_3$ with $SiMe_4$ as internal reference on a 300 MHz spectrophotometer unless otherwise stated; *J* values are given in Hz. Light petroleum refers to the fraction with bp 60–80°C.

General procedure for the preparation of 3-(arylaminomethylene)chroman-2,4-diones (5a–e)

A mixture of K-10 montmorillonite (2 g), 3-formylchromone **1** (5 mmol) and arylamine **2** (5 mmol) in dry benzene (60 ml) was heated under reflux with constant stirring for 2 h and the resulting mixture filtered hot. The solid obtained after concentration of the filtrate was crystallised from benzene to afford **5** as faint yellow fluffy solid whose IR and ^1H NMR spectral data are recorded in Table 1. The reported melting points are of the isomer mixtures shown in Scheme 1. The yields and CHN analytical data are given below.

5a:[9] Yield (600 mg, 45%); mp 204–208°C; **5b**: Yield (560 mg, 40%); mp 193–196°C (Found: C, 73.0; H, 4.5; N, 5.2. $C_{17}H_{13}NO_3$ requires C, 73.1; H, 4.7; N, 5.0%); **5c**: Yield (680 mg, 46%); mp 164–166°C (Found: C, 69.3; H, 4.2; N, 4.9 $C_{17}H_{13}NO_4$ requires C, 69.1; H, 4.4; N, 4.7%); **5d**: Yield (590 mg, 42%); mp 214–218°C (Found: C, 73.2; H, 4.5; N, 5.1. $C_{17}H_{13}NO_3$ requires C, 73.1; H, 4.7; N, 5.0%) **5e**: Yield (510 mg, 35%); mp 188–192°C (Found: C, 73.5; H, 5.2; N, 4.9. $C_{18}H_{15}NO_3$ requires C, 73.7; H, 5.1; N, 4.8%).

In the reaction of **1a** (R=H) and **1b** (R=Me) with **2** (X=Me), the filtrate after recovery of the corresponding enaminone **5** was chromatographed over silica gel (100–200) using 50% benzene-light petroleum mixture as eluent to produce **6** and **7**, respectively.

3-(*p*-Tolylaminomethylene)2*H*-chromen-4-one (6). The *title compound* **6** (130 mg, 10%) was obtained as a yellow amorphous solid, mp 158°C (Found: C, 77.1; H, 5.8; N, 5.5. $C_{17}H_{15}NO_2$ requires C, 77.0; H, 5.7; N, 5.3%); IR: 3220, 1650, 1590, 1470 cm^{-1}; ^1H NMR: δ 2.32 (3H, s, ArMe), 4.93 (2H, s, OCH_2), 6.94 (1H, dd, *J*=7.8 Hz, 1.9, 8-H), 6.98 (2H, d, *J*=8.2 Hz, 2′-H and 6′-H), 7.05 (1H, m, 6-H), 7.14 (2H, d, *J*=8.2 Hz, 3′-H and 5′-H), 7.31 (1H, d, *J*= 12 Hz, =CH), 7.41 (1H, m, 7-H), 7.94 (1H, dd, *J*= 7.7 Hz, 1.5, 5-H) and 11.52 (1H, exchangeable, d, *J*= 12 Hz, NH).

6-Methyl-3(*p*-tolylaminomethyl)chromen-4-one (7). The *title compound* **7** (200 mg, 15%) was obtained as a yellow crystalline solid, mp 166°C (Found: C, 77.3; H, 6.0; N, 5.1. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); IR: 3200, 1700, 1660, 1620 cm^{-1}; ^1H NMR: δ 1.9 (1H, exchangeable, bs, NH), 2.21 (3H, s, ArMe), 2.48 (3H, s, ArMe), 4.28 (2H, s, CH_2), 6.57 (2H, d, *J*=8.2 Hz, 2′-H and 6′-H), 6.97 (2H, d, *J*=8.2 Hz, 3′-H and 5′-H), 7.32 (1H, d, *J*=8.5 Hz, 8-H), 7.46 (1H, dd, *J*=8.5 Hz, 2.0, 7-H), 7.89 (1H, s, 2-H) and 8.00 (1H, d, *J*=2.0 Hz, 5-H); ^{13}C NMR (75 MHz): δ 20.3 (CH_3), 20.8 (CH_3), 40.8 (CH_2), 113.7 (2′-C and 6′-C), 117.9 (8-C), 121.4 (4′-C), 123.6 (3-C), 125.0 (7-C), 127.3 (4a-C), 129.8 (3′-C and 5′-C), 134.8 (5-C), 135.0 (6-C), 145.3 (1′-C), 153.0 (2-C), 154.9 (8a-C) and 177.9 (CO).

Table 1. 3-(Arylaminomethylene)chroman-2,4-dione (**5a–e**)

Product	IR (cm^{-1})			δ values ($CDCl_3$) (*J* values in Hz)								
	N–H	OC=O	C=O	*NH*[a]		*=CH*		*H-5*		*H-7*	*ArH*	*Me*[b]
				Z	*E*	*E*	*Z*	*E*	*Z*	*Z+E*	*Z+E*	*Z+E*
5a	3250	1690	1660	13.80 (13.6)	11.95 (14.5)	9.05 (14.5)	8.90 (13.6)	8.12 (7.8, 1.6)	8.06 (7.8, 1.6)	7.60–7.58 (m)	7.50–7.27 (m)	–
5b	3220	1700	1670	13.68 (13.7)	11.93 (14.6)	9.00 (14.6)	8.86 (13.7)	8.13 (8,1.5)	8.06 (8,1.5)	7.63–7.56 (m)	7.32–7.25 (m)	2.38 (s)
5c	3240	1720	1640	13.73 (13.6)	11.95 (14.5)	8.90 (14.5)	8.76 (13.6)	8.10 (7.7, 1.5)	8.03 (7.7, 1.5)	7.61–7.54 (m)	7.33–6.93 (m)	3.83 (s)
5d	3250	1700	1660	13.71 (13.5)	11.96 (14.5)	9.03 (14.5)	8.89 (13.5)	7.91 (1.3)	7.84 (1.2)	7.50–7.46 (m)	7.45–7.14 (m)	2.42 (s)
5e	3230	1700	1670	13.62 (13.7)	11.92 (14.5)	8.93 (14.5)	8.79 (13.7)	7.85 (1.3)	7.77 (1.3)	7.35–7.31 (m)	7.29–7.14 (m)	2.31, 2.29 (s) (s)

[a] High δ values of NH protons are due to intramolecular H-bonding in both isomers.
[b] Me groups of the isomers appear as a singlet.

General procedure for the synthesis of tricoumarol (8a–b) from 5

An enaminone **5** (1 mmol) was heated in 70% H_2SO_4 (20 ml) at 100°C for 3 h. The reaction mixture was cooled and poured into crushed ice (150 g). The separated white solid was filtered off, washed with water, dried in air, and crystallised from $CHCl_3$–MeOH to afford the corresponding tricoumarol **8** as a white solid.

8a (R=H): Yield (150 mg, 95%); mp >300°C (lit.[16] >300°C); IR: 2960–3200 (br), 1725, 1670, 1610 cm^{-1}; ^1H NMR: δ (DMSO-d_6) 5.41 (1H, s, methine H), 7.16 (1H, dd, J=8.2 Hz, 1.9, 8′-H), 7.22 (1H, m, 6′-H), 7.36 (2H, dd, J=8.3 Hz, 2.0, 2×H_D), 7.40 (2H, m, 2×H_C), 7.46 (1H, m, 7′-H), 7.62 (2H, m, 2×H_B), 7.88 (1H, dd, J=7.7 Hz, 1.8, 5′-H), 8.25 (2H, dd, J=7.8 Hz, 1.9, 2×H_A) and 12.18 (1H, exchangeable, bs, OH). Compound **8a** (R=H) had superimposable IR with the authentic sample.[16] **8b** (R=Me): Yield (160 mg, 95%); mp >300°C (Found: C, 71.6; H, 3.8. $C_{31}H_{20}O_8$ requires C, 71.5; H, 3.9%); IR: 3000–3240 (br), 1725, 1660, 1615 cm^{-1}; ^1H NMR: δ (DMSO-d_6) 2.39 (3H, s, 6′-Me), 2.49 (6H, s, 2×Me), 5.53 (1H, s, methine H), 7.19 (1H, d, J=8.5 Hz, 8′-H), 7.37 (2H, d, J=8.5 Hz, 2×H_D), 7.41 (1H, dd, J=8.5 Hz, 1.9, 7′-H), 7.53 (2H, dd, J=8.5 Hz, 1.8, 2×H_B), 7.82 (1H, d, J=1.9 Hz, 5′-H), 8.13 (2H, d, J=1.8 Hz, 2×H_A) and 12.15 (1H, exchangeable, bs, OH).

Reaction of 4-hydroxycoumarin with DMF-$POCl_3$

To a clear solution of 4-hydroxycoumarin (810 mg, 5 mmol) in DMF (4 ml, 50 mmol), $POCl_3$ (0.5 ml, 5 mmol) was added at room temperature, producing a semi-solid mass. A clear solution appeared after stirring for 4 h at room temperature. It was further stirred for 6 h. The reaction mixture was poured into crushed ice (200 g) with stirring. The separated solid was filtered off and washed thoroughly with water. A portion of this solid went into solution in boiling acetone, the insoluble portion was filtered off and recrystallised from $CHCl_3$–MeOH to give tricoumarol **8a** (R=H) (200 mg, 25%). It is identical in all respects to that produced from **5a** by acid hydrolysis. The acetone solution on concentration and subsequent dilution with water produced 4-chloro-3-formylcoumarin **10** (400 mg, 40%), mp 122°C (lit.[18] 120–22°C). When the above reaction was performed at 60–70°C for 6 h instead of 10 h at room temperature, tricoumarol (400 mg, 50%) and **10** (50 mg, 5%) were obtained.

General procedure for the synthesis of 6-oxo-6*H*-1-benzopyrano[4,3-*b*]quinolines 12 from 5

An enaminone **5** (1 mmol) was heated with $POCl_3$ (15 ml) at 100°C with stirring for 10 h. The reaction mixture was cooled, poured in crushed ice (150 g) and kept overnight at room temperature. The separated solid was filtered off, washed with water and dried. The crude product was eluted through a small column of silica-gel (60–120) using 50% benzene-light petroleum mixture to afford the corresponding quinoline **12** as a white fluffy solid. The compounds **12a** (R=X=H) and **12b** (R=H; X=Me) were identical (mp, mixed mp and IR) with the respective authentic samples.[4,19] **12a** (R=X=H): Yield (200 mg, 80%); mp 175°C (lit.[4] 167°C). **12b** (R=H; X=Me): Yield (220 mg, 85%); mp 234°C (lit.[19] 240°C); ^1H NMR: δ 2.57 (3H, s, Me), 7.35–7.44 (2H, m, ArH), 7.57 (1H, m, ArH), 7.70–7.73 (2H, m, ArH), 8.08 (1H, d, J=9.3 Hz, 11-H), 8.73 (1H, dd, J=7.8 Hz, 1.5, 1-H) and 9.06 (1H, s, 7-H). **12d** (R=Me; X=H): Yield (235 mg, 90%); mp 224°C (Found: C, 78.3; H, 4.0; N, 5.2. $C_{17}H_{11}NO_2$ requires C, 78.1; H, 4.2; N, 5.4%); IR: 2920, 1710, 1500 1190 cm^{-1}; ^1H NMR: δ 2.52 (3H, s, Me), 7.28 (1H, d, J=8.4 Hz, 4-H), 7.39 (1H, dd, J=8.4 Hz, 1.7, 3-H), 7.63 (1H, m, 10-H), 7.92 (1H, m, 9-H), 8.01 (1H, dd, J=8.2 Hz, 1.2, 8-H), 8.23 (1H, dd, J=8.6 Hz, 1.2, 11-H), 8.56 (1H, d, J=1.7 Hz, 1-H) and 9.21 (1H, s, 7-H). **12e** (R=Me; X=Me): Yield (205 mg, 75%); mp 214°C (Found: C, 78.3; H, 4.7; N, 5.0. $C_{18}H_{13}NO_2$ requires C, 78.5; H, 4.8; N, 5.1%); IR: 2920, 1720, 1585. 1180 cm^{-1}; ^1H NMR: δ 2.52 (3H, s, 2-Me), 2.60 (3H, s, 9-Me), 7.29 (1H, d, J=8.3 Hz, 4-H), 7.38 (1H, dd, J=8.3 Hz, 2.1, 3-H), 7.74-7.78 (2H, m, 8-H and 10-H), 8.14 (1H, d, J=8.2 Hz, 11-H), 8.56 (1H, d, J=2.1 Hz, 1-H) and 9.14 (1H, s, 7-H).

General procedure for the preparation of 4-arylamino-3-formylcoumarines 11 from 5

An enaminone **5** (1 mmol) was heated with $POCl_3$ (15 ml) at 60–70°C for 10 h. The reaction mixture was cooled, poured in ice water, kept overnight, deposited solid filtered off, washed with water, dried and recrystallised from benzene-light petroleum to afford the corresponding coumarin **11** as a faint yellow fine crystalline solid.

11a (R=X=H): Yield (225 mg, 85%); mp 185°C (Found: C, 72.6; H, 4.3; N, 5.1. $C_{16}H_{11}NO_3$ requires C, 72.4; H, 4.2; N, 5.3%); IR ($CHCl_3$): 3220, 3000, 2880, 2850, 1720, 1690, 1615 cm^{-1}; ^1H NMR: δ 6.87 (IH, m, 6-H), 7.13 (1H, dd, J=8.6 Hz, 1.8, 8-H), 7.29–7.50 (7H, m, other ArH), 10.27 (1H, s, CHO) and 13.21 (1H, exchangeable, s, NH). **11b** (R=H; X=Me): Yield (225 mg, 80%); mp 175°C; (Found: C, 73.3; H, 4.9; N, 5.1. $C_{17}H_{13}NO_3$ requires C, 73.1; H, 4.7; N, 5.0%); IR ($CHCl_3$): 3200, 3010, 2880, 2860, 1720, 1700, 1620, 1610 cm^{-1}; ^1H NMR: δ 2.43 (3H, s, Me), 6.88 (1H, m, 6-H), 7.14–7.18 (3H, m, ArH), 7.24–7.27 (2H, m, ArH), 7.29 (1H, dd, J=8.4 Hz, 2.0, 5-H), 7.50 (1H, m, 7-H), 10.25 (1H, s, CHO) and 13.16 (1H, exchangeable, s, NH). **11c** (R=H; X=OMe): Yield (265 mg, 90%); mp 165°C (Found: C, 69.0; H, 4.4; N, 4.5. $C_{17}H_{13}NO_4$ requires C, 69.1; H, 4.4; N, 4.7%); IR (CHCl3): 3200, 3000, 2925, 2880, 1720, 1700, 1620, 1610 cm^{-1}; ^1H NMR: δ 3.86 (3H, s, OMe), 6.87–7.63 (8H, m, ArH), 10.30 (1H, s, CHO) and 13.20 (1H, exchangeable, s, NH). **11d** (R=Me; X=H): Yield (230 mg, 82%); mp 226–228°C (Found: C, 73.0; H, 4.6; N, 4.9. $C_{17}H_{13}NO_3$ requires C, 73.1; H, 4.7; N, 5.0%); IR ($CHCl_3$): 3220, 3000, 2870, 1710, 1620 cm^{-1}; ^1H NMR: δ 2.01 (3H, s, ArMe), 6.83 (1H, d, J=1.8 Hz, 5-H), 7.19 (1H, d, J=8.4 Hz, 8-H), 7.29–7.50 (6 H, m, other ArH), 10.26 (1H, s, CHO) and 13.20 (1H, exchangeable, s, NH).

Conversion of 11 into 12

Aminoaldehydes **11a**, **b**, **d** (50 mg) were heated with $POCl_3$ (5 ml) at 100°C for 4 h. Each reaction mixture after usual

work up as in the previous cases produced a solid. Crude compounds were eluted through a very small column of silica gel (60–120) using 50% benzene-light petroleum mixture to afford white compounds **12a**, **b**, **d**, identical in all respects to those produced directly from **5a**, **b**, **d**, respectively.

Acknowledgements

Thanks are due to UGC, New Delhi for financial assistance. We are grateful to the learned referee and the editor for their valuable comments, to Prof. C. K. Ghosh, Department of Biochemistry, Calcutta University, Calcutta 700019, for his valuable advice and to Dr S. B. Maiti, Department of Chemistry, Bangabasi College, Calcutta, for his help in drawing the structures.

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