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Benzopyrans : Part 40† - Alumina mediated transformations of 4-oxo-4*H*-1-benzopyran-3-carbaldehyde, -3-carboxylic acid and their 2-methylhomologues

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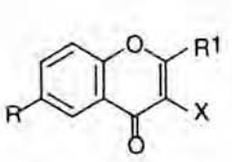
In contact with alumina, the title aldehyde **1** (R = H, Me, Cl) gives the chromones **5** and **9-12** whereas the acid **2** affords the chromones **7**, **10** and acetophenone **23**. Alumina converts the aldehyde **3** to the xanthone **14**, and the corresponding acid **4** to the chromone **8** and diketone **24**.

The surface of alumina is polar and contains immobile catalytic Bronsted and Lewis acid as well as base sites; the composition and nature of these sites can be altered by heating[2], and hydroxy groups on oxide surfaces are much weaker nucleophiles than the lattice oxide anions[3]. That is why alumina not only functions as a solid support for interacting reagents[4] but also mediates several types of reactions e.g. Cannizzaro reaction[5,6], Meerwein-Pondorf-Verley type reduction[7] including internal redox reaction of some ketols[8], epimerisation[9], Favorskii rearrangement[10], acyloin[11], oxirane[12], cyclopropylketone[13] rearrangements, skeletal rearrangement of quadricyclanone[14], shifting of ethylenic linkages[15], self-condensation of methylene aldehydes, methylene ketones[16] and 3-acetylchromone[17], deacetalisation and subsequent deformylation[18] and conversion of benzyl halide to dibenzyl ether[19]. Alumina mediated reactions of chloroacetone with 4-oxo-4*H*-1-benzopyran-3-carbaldehyde, -3-carbonitrile and -3-carboxylate give the products different from those arising from the respective reactions conducted in acetone containing anhydrous potassium carbonate[20]. The transformation of the title 4-oxo-4*H*-1-benzopyran (chromone) derivatives **1-4**, each containing three electropositive centres (namely C-2, formyl- or hydroxycarbonyl- and pyrone carbonyl-carbon) and a masked phenolic OH group, into various products by alumina is described in this paper.

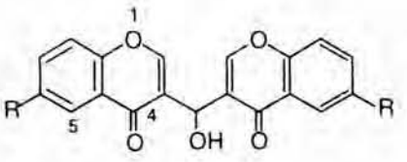
Results and Discussion

Each of the aldehydes **1** dissolved in dichloromethane was stirred with Brockman neutral alumina (previously dried at 120°C under vacuum) at room temperature for 5-7 hr. TLC of the reaction mixture indicated the presence of at least six products, a few of which could be isolated in pure state. Each member of **1** gave the chromones **5**, **9** and **10**, the former being identical with an authentic sample prepared by diborane reduction of the appropriate aldehyde **1**[21]; the aldehydes **1a** and **1c** afforded respectively **12a** and **11c** in addition to the aforesaid chromones. No trace of the acid **21**[22] could even be detected in the reacton mixture. It is relevant to mention here that the bischromone **9a** also results from the reaction of **1a** with sodium naphthalenide[23] and its *O*-methyl derivative is one of the products in the triethylamine mediated transformation of **1a** in methanol[24]. Alumina mediated conversion of **1** into **9** resembles the

† For Part 39, see ref. 1.



	R^1	X
1	H	CHO
2	H	CO_2H
3	Me	CHO
4	Me	CO_2H
5	H	CH_2OH
6	H	COMe
7	H	H
8	Me	H



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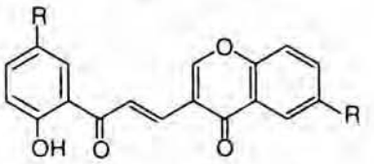

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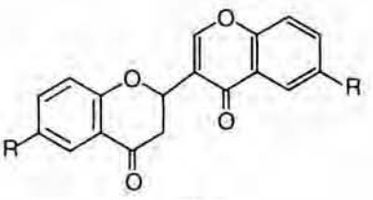

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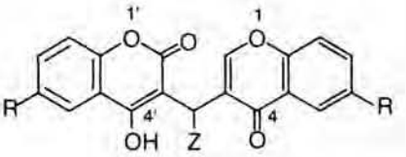
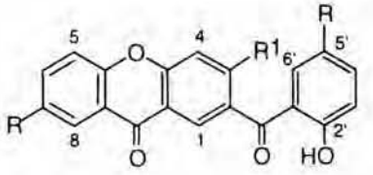


12 Z = H
13 Z = OH



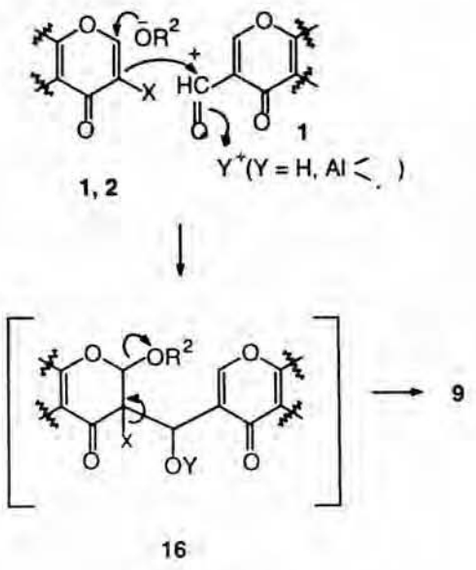
14 R^1 = H
15 R^1 = Me

1 - 15	a	b	c
R	H	Me	Cl

formation of bischromonylacetonitrile **9** (CN in place of OH) by treating **1** with potassium cyanide[25].

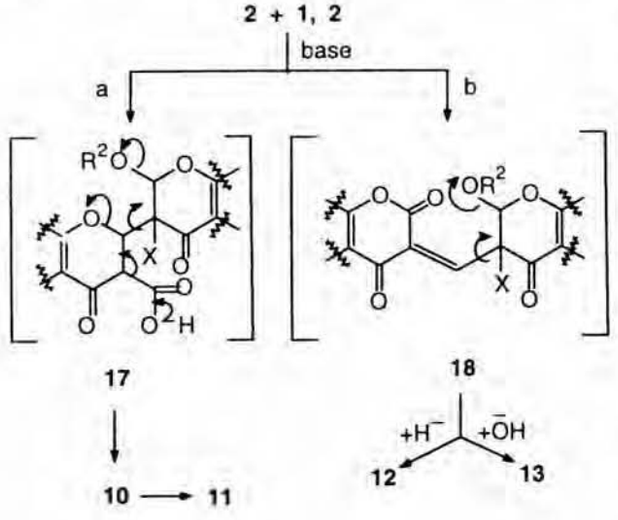
Alumina catalyses disproportionation of the aldehyde **1** to the corresponding acid **2** and alcohol **5** by a mechanism as suggested by Lamb *et al.*[6] and it plays some subtle roles to give the other products from **1** as well as **2**. Attack of either Bronsted base ($^-$OH) or Lewis base (-Al-O$^-$), generally represented by R_2O^-, at C-2 of **1** as well as **2** generates a nucleophilic centre at C-3 that attacks the aldehydic carbon[26] of **1**; the resultant intermediate **16** by decarboxylative or base catalysed deformylative expulsion of R^2O^- produces the bischromone **9** (**Scheme I**). Michael addition[27] of **1** as well as **2** through its C-3 nucleophilic centre to the acid **2** gives the intermediate **17** that by decarboxylative pyran ring opening and the operation as mentioned for the intermediate **16** gives the chromone derivative **10** which may cyclise to **11** under the reaction conditions (**Scheme II** - Path a). Similar Michael addition with concommitant pyran ring opening and subsequent cyclisation[22,28] leads to the intermediate **18** (**Scheme II** - Path b). The hydride donated by the aldehyde **1** (Cannizzaro mechanism) or the secondary alcohol **9** (Meerwein-Pondorf-Verley mechanism) in the presence of alumina undergoes 1,4-addition to the α,β-unsaturated ketone moiety of **18** giving rise to the coumarin **12**. The compound **13**, anticipated to arise from similar addition of HO$^-$ or >Al-O$^-$ to **18**, however, could not be obtained.

The mechanism as proposed for the alumina mediated transformation of **1** entails that the



Scheme I

chromones **10** and **13**, the former in particular, should arise from the acid **2**, and 3-formyl-2-methylchromone **3** is likely to give the corresponding Cannizzaro products on treatment with alumina. Stirring of a dichloromethane solution of **2** with alumina indeed produced predominantly **10** together with chromone **7** and 2-hydroxyaceto-phenone **23**. The acid **2b** afforded 6-methyl-2-hydroxychromanone **20b** in addition to the aforesaid products. Self-condensation of **20** to **10**[29] under the experimental conditions is not feasible. The intermediate **19** (R^1 = H), derived from 1,4-addition of the base to the acid **2** (**Scheme III**), gives **7** by decarboxylative expulsion of the nucleofugal base (Path a) and **20** by mere decarboxylation (Path b), the formation of the former resembling decarboxylation of **2** by refluxing alcohol[30]. Decarboxylative pyran ring opening of **19** (R^1 = H) to **21**, an equivalent of the β-ketoaldehyde **22** and subsequent alumina catalysed elimination of a formaldehyde equivalent[18] lead to **23** (Path c). The chromanone **20**, also obtainable by cyclisation of **21**, may dehydrate to **7**.

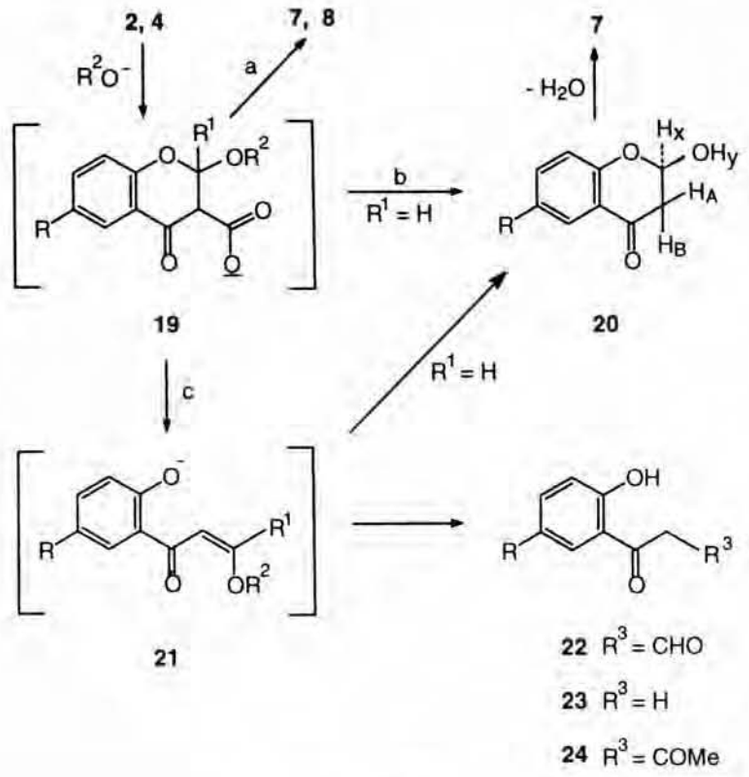


Scheme II

In the ^{1}H NMR spectrum of **20b**, protons at its 2- and 3-positions constitute an ABX system. H_X which is also coupled with hydroxy proton (H_Y) with a coupling constant of 5Hz appears at δ 5.86 as a pseudo quartet with peak intensities in the ratio of 1:3:3:1. This type of line shape for H_X is possible only when J_{XY} , J_{AX} , and J_{BX} are equal. A model of **20b** shows that the dihedral angle between H_A and H_X equals that between H_B and H_X when the hydroxy group is axially disposed in the chromanone **20b**. Interstingly, H_X appears as a singlet at δ 5.88 when a deuteriochloroform solution of **20b** is a little bit warmed with D_2O, cooled and its ^{1}H NMR spectrum recorded. This is probably due to opening of the cyclic hemiacetal **20b** on warming to its open chain isomer **22b**, exchange of the acidic diacylmethylene protons of the latter and recyclisation to **20b** (D in place of H_A , H_B and H_Y).

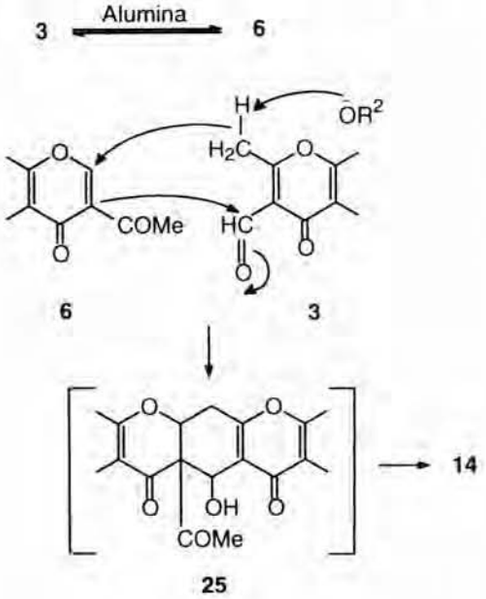
Contrary to our prior anticipation, the aldehyde **3** on treatment with alumina affords predominantly, if not exclusively, the same xanthone **14** as is obtained from 3-acetylchromone **6** and alumina[17]. Unlike alumina, pyridine-piperidine converts **3** into the xanthone **15**[31]. So the formation of **14** from **3** necessitates the alumina-catalysed isomerisation of the latter (**3**) to 3-acetylchromone **6**. Subsequent Michael initiated ring closure between **3** and **6** leads to the benzoxanthene intermediate **25** that on base catalysed deacylative hydroxy elimination and pyran ring opening (or deacetylative pyran ring opening and water elimination) gives **14** (**Scheme IV**).

Reaction of the acid **4** with alumina was very sluggish. Stirring of a solution of **4** in dichloromethane with alumina for 16 hr and usual work-up of the reaction mixture afforded the unreacted substrate (> 50%) admixed with small amounts of the chromone **8** and diketone **24**. The chromone **8**, like its corresponding lower homologue



Scheme III

7, is formed through the intermediate **19** (R^1 = Me) (**Scheme III**, Path a) and the diketone **24** through **21** (**Scheme III**, Path c), alumina being incapable of effecting its deacetylation to **23**.



Scheme IV

Conclusion

The studies on alumina mediated transformation of aldehyde **1** as well as the corresponding acid **2** reveal that alumina primarily brings about self-condensation of **1** to the bischromone **9** and its Cannizzaro reaction to the alcohol **5** and the acid **2**, the latter undergoing further conversion to chromone **7**, 2-hydroxy-chromanone **20** and 2-hydroxyaceto-phenone **23**, and condensation with itself as well as **1** to produce **10** (or its isomer **11**) and sometimes the coumarin **12**. In contrast to the base catalysed self-condensation of 3-formyl-2-methylchromone **3** to the xanthone **15**, alumina isomerises **3** to 3-acetyl-chromone **6** and subsequently brings about their condensation through a Michael initiated ring closure reaction to the xanthone **14**. Because of weak electrophilicity at its C-2, the acid **4** fails to undergo any self-condensation and its conversion, analogous to that of its lower homologue **2**, to chromone **8** and salicyloylacetone **24** is very sluggish.

Experimental Section

General. Melting points are uncorrected. Yields of the isolated pure products are not optimised. All the solid products were crystallised from $CHCl_3$ - light

petroleum. IR spectra were recorded on a Beckman IR-20A and NMR on a 200 MHz spectrometer in $CDCl_3$ with $SiMe_4$ as internal reference. Light petroleum refers to the fraction, bp 60-80 °C.

Treatment of the aldehyde 1a with alumina. A solution of **1a** (1.75 g, 10 mmoles) in dichloromethane (150 mL) was magnetically stirred at ambient temperature with Brockman neutral alumina (25 g) of activity grade 1 (previously dried at 120° under vacuum) for 7 hr. Methanol (10 mL) was added to the reaction mixture and stirring continued further for half an hour. The reaction mixture was then filtered, the filtrate concentrated and cooled. The precipitated coumarin **12a** was filtered off and the filtrate after further concentration was chromatographed over silica gel using ethyl acetate - light petroleum (1:6) as eluant when the chromones **10a**, **9a** and **5a** were eluted in this order from the chromatographic column. 3-Hydroxymethylchromone **5a** (0.53 g, 30%), mp 110 °C was identified by comparison with an authentic sample[21]. Characterisation data of the other products are given below.

Bis(4-oxo-4*H*-1-benzopyran-3-yl)methanol 9a : Colourless crystals (0.13 g, 8%), mp 200 °C. Anal. Calcd for $C_{19}H_{12}O_5$: C, 71.2; H, 3.8. Found : C, 71.5; H, 3.4%; ^{1}H NMR : δ 8.31 (2H, d, *J*= 0.6 Hz, 2-H), 8.15 (2H, dd, *J* = 8.0, 1.8 Hz, 5-H), 7.65 (2H, ddd, *J* = 7.0, 6.8, 1.4 Hz, 7-H), 7.47-7.34 (4H, m, 6- and 8-H), 5.84 (1H, td, *J* = 8.8, 0.6 Hz, C*H*OH) and 5.35 (1H, d, *J* = 8.8 Hz, D_2O exchangeable, OH); ^{13}C NMR : δ 177.8 (4-C), 156.5 (8a-C), 155.4 (2-C), 133.8 (7-C), 125.7 (5- or 6-C), 125.2 (6- or 5-C), 124.1 (4a-C), 123.0 (3-C), 118.3 (8-C), 66.0 (CHOH).

3-[2-(2-Hydroxybenzoyl)vinyl]-1-benzopyran-4-one 10a : Light yellow crystals (0.08 g, 6%), mp 178 °C (lit.,[29,32] mp 177-179 °C); IR (KBr) : 3042 (chelated OH), 1652 (pyrone CO), 1609 (benzoyl CO), 1585 (C=C) cm^{-1}; ^{1}H NMR : δ 12.76 (1H, s, D_2O exchangeable, OH), 8.84 (1H, d, *J* = 15.2 Hz, C*H*=CHCO *trans*), 8.32 (1H, dd, *J* = 8, 1.8 Hz, benzopyran 5-H), 8.22 (1H, s, pyran 2-H), 8.03 (1H, dd, *J* = 8, 1.4 Hz, PhH *ortho* to CO and *meta* to OH), 7.72 (1H, ddd, *J* = 7.8, 7, 1.8 Hz, benzopyran 7-H), 7.51 (1H, d, *J* = 15.2 Hz, CH=C*H*CO, *trans*), 7.53 - 7.44 (3H, m, benzopyran 6-H + PhH *para* to OH and *meta* to CO), 7.01 - 6.91 (2H, m, benzopyran 8-H + PhH *ortho* to OH); Mass : *m/z* 292 (M^+, 14%), 170 (M - HOC_6H_4CO - H, 100).

4-Hydroxy-3-(4-oxo-4*H*-1-benzopyran-3-yl)methylcoumarin 12a : Faintly yellow crystals (0.32 g, 20%), mp 230 °C. Anal. Calcd for $C_{19}H_{12}O_5$: C, 71.2; H, 3.8. Found : C 70.9; H 3.5%; IR (KBr) : 3074 (OH), 1689 (lactone CO), 1631 (γ-pyrone CO), 1585 (C=C) cm^{-1}; ^{1}H NMR : δ 11.81 (1H, s, D_2O exchangeable, OH), 8.44 (1H, s, 2-H), 8.26 (1H, dd, *J* = 7.8, 1.4 Hz, 5-H), 7.94 (1H, dd, *J* = 8.2, 1.6 Hz, 5′-H), 7.73 (1H, ddd, *J* = 7.2, 7, 1.8 Hz, 7-H), 7.54 - 7.41 (3H, m, 6-, 6′-, 7′-H), 7.28 - 7.19 (2H, m, 8-, 8′-H), 3.69 (2H, s, CH_2); ^{13}C NMR : δ 118.7, 164.4, 162.2, 156.6, 152.7, 122.8, 122.4, 117.1, 116.3(s), 155.8, 134.6, 131.7, 126.0, 125.9, 125.7, 124.1, 118.4, 116.3(d), 21.0(t); MS m/z 320 (M^+, 21%), 292 (M–CO, 3), 170 (292 –HOC_6H_4CO – H, 100).

Treatment of the aldehyde 1b with alumina. This aldehyde (**1b**) was treated with alumina and the reaction mixture worked-up similarly as in the case of **1a**. 3-Hydroxymethyl-6-methylchromone **5b**[21] (21%), mp 141 °C, crystallised out from the reaction mixture and the chromones **10b** (9%) and **9b** (12%) were isolated by column chromatography over silica gel. Brief characteristics of the new compounds are as follows:

Bis (6-methyl-4-oxo-4*H*-1-benzopyran-3-yl)methanol 9b : Colourless crystals, mp 150 °C. Anal. Calcd for $C_{21}H_{16}O_5$: C, 72.6; H, 4.6. Found : C, 72.8; H, 4.4%; ^{1}H NMR : δ 8.28 (2H, s, 2-H), 7.94 (2H, ill defined d, 5-H), 7.48 (2H, dd, *J* = 8, 1.5 Hz, 7-H), 7.36 (2H, d, *J* = 8 Hz, 8-H), 5.88 (1H, d, *J* = 8 Hz, C*H*OH), 5.41 (1H, d, *J* = 8 Hz, exchangeable, OH), 2.43 (6H, s, 2 x Me).

3-[2-(2-Hydroxy-5-methylbenzoyl)vinyl]-6-methyl-1-benzopyran-4-one 10b : Light yellow crystalline solid, mp 200 °C. Anal. Calcd for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0. Found : C, 74.7; H, 4.6%; ^{1}H NMR : δ 12.67 (1H, s, exchangeable, OH), 8.82 (1H, d, *J* = 15.2 Hz, C*H*=CHCO *trans*), 8.21 (1H, s, benzopyran 2-H), 8.11 (1H, ill split d, benzopyran 5-H), 7.82 (1H, ill split d, PhH *ortho* to CO and *meta* to OH), 7.53 (1H, d, *J* = 15.2 Hz, CH=C*H*CO *trans*), 7.52 - 7.34 (3H, m, benzopyran 7-, 8-H + PhH *para* to CO), 6.90 (1H, d, *J* = 8 Hz, PhH *ortho* to OH), 2.51 (3H, s, benzopyran 6-Me), 2.36 (3H, s, PhMe).

Treatment of the aldehyde 1c with alumina. This aldehyde (**1c**)was treated with alumina in the same manner as described for treatment of **1a**. The reaction mixture after removal of alumina from it by

filtration was concentrated and cooled when the bischromone **9c** precipitated out. It was filtered off and the filtrate charged on a silica gel column. Ethyl acetate (10%) in light petroleum eluted the chromones **11c**, **10c** and **5c** from the column. 6-Chloro-3-hydroxymethylchromone **5c** (32%), mp 164 °C, was identical with an authentic sample[21]. The new compounds were characterised as given below.

Bis(6- chloro -4- oxo -4*H*- 1- benzopyran -3-yl)-methanol 9c : White solid (10%), mp 262 °C (decomp.). Anal. Calcd for $C_{19}H_{10}Cl_2O_5$ C, 46.1; H, 2.0. Found : C, 46.4; H, 2.3%; ^{1}H NMR : δ 8.30 (2H, s, 2-H), 8.12 (2H, d, J = 2.4 Hz, 5-H), 7.62 (2H, dd, J = 8, 2.4 Hz, 7-H), 7.45 (2H, d, J = 8 Hz, 8-H), 5.84 (1H, d, J = 8 Hz, C*H*OH), 5.17 (1H, d, J = 8 Hz,D_2O exchangeable, OH).

3-[2-(5-Chloro-2-hydroxybenzoyl)vinyl]-6-chloro-1-benzopyran-4-one 10c : Light yellow crystals (5%), mp 212 °C. Anal. Calcd for $C_{18}H_{10}Cl_2O_4$ requires C, 59.9; H, 2.8. Found : C, 60.3; H, 2.4%; ^{1}H NMR : δ 13.08 (1H, s, D_2O exchangeable, OH), 8.76 (1H, d, J = 15.2 Hz, C*H*=CHCO *trans*), 8.30 - 6.96 (8H, m, other H).

2,3-Dihydro-6-chloro-2-(6-chloro-4-oxo-4*H*-1-benzopyran-3-yl)-1-benzopyran-4-one 11c. Greyish solid (6%), mp 220 °C (decomp). Anal. Calcd for $C_{18}H_{10}Cl_2O_4$ C, 59.9; H, 2.8.Found : C, 59.7; H, 3.2%; IR (KBr) : 1683 (pyranone CO), 1630 (pyrone CO), 1610 (C=C) cm^{-1}; ^{1}H NMR : δ 8.24 (1H, d, J = 0.8 Hz, vinyl H), 8.20 - 6.96 (6H, m, other ArH), 5.72 (1H, m, pyranone 2-H), 3.02 (2H, *AB* part of an *ABX* system, J = 16, 14, 3 Hz, pyranone 3-H).

General procedure for conversion of the aldehydes 3 into the xanthones 14. The aldehyde **3** (2 mmoles), prepared according to a literature procedure[33], was dissolved in dichloromethane (75 mL) containing alumina (7 g) and the solution stirred magnetically at room temperature for 7 hr. The reaction mixture after acidification with glacial acetic acid (2 mL) was filtered, the filtrate washed with water, dried (Na_2SO_4), concentrated and cooled. The deposited solid was collected by filtration and crystallised to give xanthone **14** as white crystals. The following compounds were prepared by this method.

2-(2-Hydroxybenzoyl)-9H-xanthen-9-one 14a : From **3a** in 48% yield, mp and mixed[17] mp 185 °C; ^{13}C NMR : δ 199.4 (benzoyl CO), 176.5 (9-C), 163.2 (2′-C), 158.1 (4a-C), 156.0 (4b-C), 136.6 (4′-C), 135.4 (3-C), 135.2 (6-C), 133.4 (2-C), 133.2 (7-C), 128.9 (6′-C), 126.8 (1-C), 124.8 (8-C), 121.8 (8a-C), 121.1 (9a-C), 119.0 (4-C), 118.9 (1′-C), 118.8 (5-C), 118.5 (5′-C), 116.1 (3′-C).

2-(2-Hydroxy-5-methylbenzoyl)-7-methyl-9H-xanthen-9-one 14b : From **3b** in 55% yield, mp 204 °C. Anal. Calcd for $C_{22}H_{18}O_4$ C, 76.7; H, 4.7. Found : C, 77.0; H, 4.9%; ^{1}H NMR : δ 11.80 (1H, s, D_2O exchangeable, OH), 8.64 (1H, d, J = 2 Hz, 1-H), 8.12 (2H, m, 8-, 6-H), 8.08 (1H, dd, J = 8, 2 Hz, 3-H), 7.68 - 6.92 (4H, m, other ArH), 2.48 (3H, s, Me), 2.28 (3H, s, Me).

7-Chloro-2-(5-chloro-2-hydroxybenzoyl)-9H-xanthen-9-one 14c : From **3c** in 52% yield, mp 228 °C. Anal. Calcd for $C_{20}H_{10}Cl_2O_4$ requires C, 62.4; H, 2.6. Found : C, 62.7; H, 2.3%; ^{1}H NMR : δ 11.76 (1H, s, D_2O exchangeable, OH), 8.68 (1H, d, J = 2 Hz, 1-H), 8.34 (1H, d, J = 2 Hz, 8-H), 8.12 (1H, dd, J = 8, 2 Hz, 3-H), 7.84-7.02 (6H, m, other ArH).

General procedure for treatment of the acids 2 with alumina. A solution of **2** (2 mmoles) in dichloromethane (75 mL) containing alumina (10 g) was magnetically stirred at room temperature for 6 hr. The reaction mixture after addition of acetic acid (3 mL) to it was further stirred for half an hour and then filtered. The filtrate was washed with water to remove of acetic acid, dried (Na_2SO_4), concentrated and cooled. In case of the reaction of **2b**, the chromanone **20b** crystallised out but in other cases no deposition of any solid material took place. The concentrated solution was charged over a silica gel column and the column eluted with ethyl acetate - light petroleum (1:10) when the products **23**, **10** and **7** came out in this order. The oily products **23** (~10%) were characterised by co-TLC with the corresponding authentic samples. Each of the chromones **7** (72-84%) was identified by comparison with an authentic sample[34].

2,3-Dihydro-2-hydroxy-6-methyl-1-benzopyran-4-one 20b : From **2b** as white crystals (25%), mp 146 °C (lit.[29] mp 132°C); IR (KBr) : 3304 (OH), 1665 (CO), 1617 (C=C) cm^{-1}; ^{13}C NMR : δ 7.68 (1H, d, J = 2 Hz, 5-H), 7.32 (1H, dd, J = 8, 2 Hz, 7-H), 6.88 (1H, d, J = 8 Hz, 8-H), 5.86 (1H, pseudo q with peak intensities in the ratio of 1:3:3:1, $J_{XY} = J_{AX} = J_{BX}$ = 5 Hz, H_X), 3.74 (1H, d, J = 5 Hz, D_2O exchangeable, H_Y), 2.98 (2H, AB part of ABX

system, J_{AB} = 16 Hz, J_{BX} = 5 Hz, exchangeable, H_AH_B), 2.28 (3H, s, Me).

General procedure for treatment of the acids 4 with alumina. Synthesis of the acids **4a** and **4b** has been described earlier[35]. The acid **4c**, similarly prepared starting from **24c**, had mp 230 °C. Each of the acids **4** was treated with alumina similarly as described for **2**, only the reaction period being prolonged to 16 hr. Usual work-up of the reaction mixture gave a mixture of the unreacted acid **4** (52-60%), ϖ-acetyl-2-hydroxyacetophenone **24** and chromone **8** which were separated by fractional crystallisation from chloroform - light petroleum. The products **24a,b,c** having mp 98°, 102° and 116 °C, respectively were identical with the authentic samples prepared by acetylation of the appropriate *o*-hydroxyacetophenones **23** with ethyl acetate[36]. The chromones **8a,b,c** having mp 72°, 102° and 121 °C respectively were characterised by comparison (mp and mixed mp) with the respective authentic samples obtained by acid catalysed cyclisation of the appropriate acetophenones **24**.

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References

1 Ghosh C K, Bhattacharyya S & Patra A, *Indian J Chem*, 37B, **1998**, 423.
2 Pagni R M, Kabalka G W, Hondrogiannis G, Bains S, Anosike P & Kurt R, *Tetrahedron*, 49, **1993**, 6743 and references therein.
3 Barteau G H, *Chem Rev*, 96, **1996**, 1413.
4 (a) Posner G H, *Angew Chem Int Ed Eng*, 17, **1978**.
(b) 487; McKillop A & Young D W, *Synthesis*, **1979**, 481.
(c) Laszlo P, *Acc Chem Res*, 19, **1986**, 121.
(d) Ranu B C, Bhar S, Chakraborty R, Das A R, Saha M, Sarkar A, Chakraborti R & Sarkar D C, *J Indian Inst Sci*, 74, **1994**, 15.
(e) Kabalka G W & Pagni R M, *Tetrahedron*, 53, **1997**, 7999.
5 Nayak U R & Dev S, *Tetrahedron*, 19, **1963**, 2293.
6 Lamb F A, Cote P N, Slutsky B & Wittimberga B B, *J Org Chem*, 39, **1974**, 2796.
7 Posner G H, Runquist A W & Chapdelaine M J, *J Org Chem*, 42, **1979**, 1202.
8 (a) Acklin W & Prelog V, *Helv Chim Acta*, 42, **1959**,1239.
(b) Ichira A & Matsumoto T, *Bull Soc Chem Jpn*, 47B, **1974**, 1030.
9 (a) Buchhi G & Loewenthal J J E, *Proc Chem Soc*, **1962**, 280.
(b) Hellyer R O & Lassak E V, *Aust J Chem*, 20, **1967**, 2297.
(c) Subba Rao H N, Damodaran N P & Dev S, *Tetrahedron Lett*, **1967**, 227.
10 Barnes R A & Lira E P, *Chem and Ind*, **1964**, 2100.
11 Matsumoto T, Fukuokes Y, Ichihara A, Mori Y, Shirahama H, Takahasi Y & Watnabel M, *Bull Soc Chem Jpn*, 37, **1964**, 1716.
12 (a) Joshi V S, Damodaran N P & Dev S, *Tetrahedron*, 24, **1968**, 5817; 27, **1971**, 459.
(b) Joshi V & Dev S, *Tetrahedron*, 33, **1977**, 2955 and references therein.
13 Alonso M E & Morales A, *J Org Chem*, 45, **1980**, 4530.
14 Story P R & Fahrenholtz S R, *J Am Chem Soc*, 87, **1963**, 1623.
15 (a) Stedman R L, Swain A P & Rusaniwsky W, *J Chromatogr*, 4, **1960**, 252.
(b) Benesova V, Hernot V & Sorm F, *Coll Czech Chem Commun*, 26, **1961**, 1832.
(c) Markovic L & Landa S, *Coll Czech Chem Commun*, 29, **1964**, 2309; 30, **1965**, 3672.
16 (a) Vittimberga B M & Herz M L, *J Org Chem*, 35, **1970**, 3974.
(b) Muzart J, *Synthesis*, **1982**, 60 and references therein.
17 Ghosh C K, Bhattacharyya A & Bandyopadhyay C, *J Chem Soc, Chem Commun*, **1984**, 1319.
18 (a) Ghosh C K, Biswas S, Bhattacharyya A & Sasmal N, *J Chem Res(S)*, **1990**, 117.
(b) Ghosh C K & Biswas S, *J Indian Chem Soc*, 67, **1990**, 568.
19 Hondrogiannis G, Tan L C, Pagni R M, Kabalka G W, Herold S, Ross E, Green J & McGinnis M, *Tetrahedron Lett*, 35, **1994**, 6211.
20 Ghosh C K, Bhattacharyya S, Ghoshal N & Achari B, *J Chem Res(S)*, **1998**, 117; *J Chem Res(M)*, **1998**, 859.
21 Ghosh C K & Bhattacharyya S, *Indian J Chem*, 36B, **1997**, 267.
22 Klutchko S, Cohen M P, Shavel J (Jr) & von Strandtmann M, *J Heterocycl Chem*, 11, **1974**, 183.
23 Bandyopadhyay C, personal communication.
24 Ghosh C K, Bandyopadhyay C & Tewari N, *J Org Chem*, 49, **1984**, 2812.
25 (a) Harnish H, *Liebigs Ann Chem*, 765, **1972**, 8.
(b) Ellis G P, Becket G J P, Shaw D, Wilson H K, Vardey C J & Skidmore I F, *J Med Chem*, 21, **1978**, 1120.
26 Taxier-Boulet F & Foucaud A, *Tetrahedron Lett*, 23, **1982**, 4927 and references therein.
27 (a) Ranu B C, Bhar S & Sarkar D C, *Tetrahedron Lett*, 32, **1991**, 2811.
(b) Ranu B C & Bhar S, *Tetrahedron*, 48, **1992**, 1327 and references therein.
28 Chantegrel B, Nadi A-I & Gelin S, *Tetrahedron Lett*, 24, **1983**, 381; *J Org Chem*, 49, **1984**, 4419.
29 Soni R R & Trevedi K N, *Indian J Chem*, 27B, **1988**, 811.
30 Cremins P J & Wallace T W, *J Chem Soc, Chem Commun*, **1986**, 1602.
31 Ghosh C K, Sahana S & Patra A, *Tetrahedron*, 49, **1993**, 4127.
32 (a) Schoenberg A & Singer E, *Chem Ber*, 96, **1963**, 1529.
(b) Nohara A, Umetani T & Sanno Y, *Tetrahedron Lett*, **1973**, 1995; *Tetrahedron*, 30, **1974**, 3553.
33 Ghosh C K, Pal C, Maiti J & Ssarkar M, *J Chem Soc, Perkin Trans 1*, **1988**, 1489.
34 Ghosh C K & Khan S, *Synthesis*, **1981**, 719.
35 Ghosh C K & Pal C, *Indian J Chem*, 24B, **1985**, 1288.
36 Baker W, *J Chem Soc*, **1933**, 1381.