Benzopyrans. Part 41.[1] Reactions of 2-(2-dimethylaminovinyl)-1-benzopyran-4-ones with various dienophiles

Chandra Kanta Ghosh,*[,a] Samita Bhattacharyya,[a] Chandreyi Ghosh[a] and Amarendra Patra[b]

[a] *Organic Chemistry Laboratory, Department of Biochemistry, Calcutta University, Calcutta-700 019, India*
[b] *Department of Pure Chemistry, Calcutta University, Calcutta-700 009, India*

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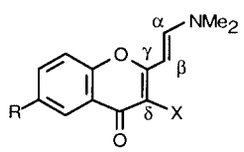
Dienamine **1** with *N*-phenylmaleimide and chromenone **14** as well as **15** produces, through initial [4 + 2]cycloaddition, xanthenones **10** and **18**, respectively. Initial Michael addition of **1** to chromenones **14** and **16**, and dimethyl acetylenedicarboxylate (DMAD), triggers the formation of xanthenone **19**, 4-azaxanthenone **26** and substituted fumarate **49**, respectively. Initial [2 + 2]cycloadducts of dienamines **1**–**3** with electrophilic acetylenes always undergo further transformations. Thus, **1** with DMAD, dibenzoylacetylene and ethyl propiolate (EP) ultimately gives xanthenones **33**, **34** and **37**, respectively, the latter being admixed with flavone **43**. Enamine **2**, cyclisable to xanthenone **11**, gives **33** and **35** with DMAD, and **37** and **44** with EP. Reaction of **3** with DMAD affords **36** exclusively.

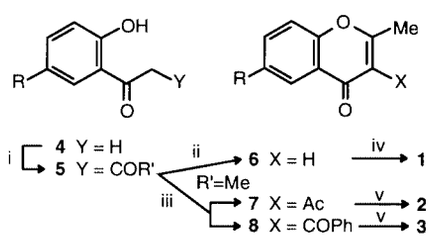
Introduction

[4 + 2]Cycloaddition reactions of 2- and 3-vinyl-1-benzopyran-4-one derivatives in which the 2,3-olefinic bond of the pyran moiety constitutes a part of the diene system have been described in a recent review article.[2] Diels–Alder reaction of (*E*)-2-styrylchromenone with maleic anhydride and *N*-phenylmaleimide (NPMI) is always followed by a 1,3-hydrogen shift giving 1,2,3,4-tetrahydroxanthenone derivatives.[3] 2-(2-Dimethylaminovinyl)-1-benzopyran-4-ones **1**, because of their strong electron-releasing dimethylamino group, are evidently more reactive dienes than the analogous 2-styrylchromenones and are likely to undergo [4 + 2]cycloaddition even with moderately active dienophiles. Alternatively, **1** may function as enamines to undergo either [2 + 2]cycloaddition with or Michael addition to dienophiles containing an α,β-unsaturated carbonyl or allied functionality. Furthermore, in the Michael addition reaction, the dienamines **1** may add through either their β- or δ-carbon depending on the nature of the Michael acceptors and the reaction conditions. The diene as well as Michael donor activity of the 3-acylchromenones **2** and **3** is less than that of their 3-unsubstituted analogues **1**. Whatever may be the mode of addition, the initial adduct having the nucleofugal dimethylamino group is likely to undergo further transformation. We report here the behaviour of the title dienaminones **1**–**3** towards various alkenic as well as alkynic dienophiles under different reaction conditions.



1 X = H
2 X = Ac
3 X = COPh

1 - 3	a	b	c[a]
R	H	Me	Cl



Scheme 1 *Reagents and conditions*: i, $R'CO_2Et$ (R′ = Me, Ph), Na, reflux (ref. 4); ii, aq. HCl, MeOH, reflux (ref. 5); iii, Ac_2O, fused NaOAc, reflux (ref. 6); iv, dimethylformamide dimethyl acetal (DMFDMA), C_6H_5N, reflux (ref. 7); v, DMFDMA, C_6H_6, reflux (ref. 8). [a] The suffixes **a**, **b** and **c** associated with all other structures bear the same connotation for R as written here.

Results and discussion

All the dienamine substrates **1**–**3** were prepared starting from the appropriate 2-hydroxyacetophenones **4** by the known reaction sequences as shown in Scheme 1. 3-Acyl-2-methylchromenones **7b**,**c** and **8b**,**c**, prepared from the appropriate ω-acyl-2-hydroxyacetophenones **5** in 75–87% yield, are new compounds (Tables 1 and 2). *E*-Geometry around the exocyclic olefinic bond of the enamines **1**–**3** is established from their ^1H NMR spectra (Table 1); in their ^{13}C NMR spectra (Table 2), the peaks due to carbons of the dimethylamino group, because of their long relaxation time, are rarely observed.

None of the dienamines **1**–**3** reacted with NPMI in refluxing toluene. The dienes **1** with NPMI in refluxing dimethylformamide (DMF), however, produced the xanthenone derivatives **10** evidently through the initially formed [4 + 2]cycloadducts **9** which readily eliminated dimethylamine and were dehydrogenated under the reaction conditions.[7] By treating **1c** with two mole equivalents of NPMI we could isolate from the reaction mixture *N*-phenylsuccinimide in addition to the xanthenone **10c**. Therefore it is highly likely that NPMI is at least partly responsible for dehydrogenation of intermediates **9** or the corresponding deaminated compounds and itself is reduced to *N*-phenylsuccinimide. A molecule of DMF remains associated with **10c** as solvent of crystallisation. Even drying of the sample in a drying pistol under vacuum with refluxing DMF could not remove this solvent of crystallisation. Failure of [4 + 2]cycloaddition between **1** and NPMI (to **9**) in refluxing toluene and success of the same in refluxing DMF may suggest that the diene system in **1**, and for that matter in **2** and **3**, remains in the *s-trans* conformation in non-polar toluene but assumes the *s-cis* one in a refluxing polar medium like DMF.

Table 1 3-Acyl-2-methyl- and 2-(2-dimethylaminovinyl)-1-benzopyran-4-ones **7**, **8** and **1**–**3**

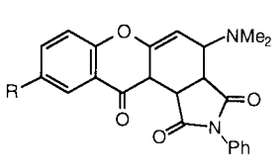
			δ_H($CDCl_3$; 300 MHz)[b]							
Comp.[a]	Yield (%)	Mp/°C	5-H	*o*-H of COPh (m)	=C*H*NMe_2 (d, $J \approx 13$)	Other ArH (m)	3-H/Ac (s)	2-Me (s)/ C*H*=CHNMe_2 (d, $J \approx 13$)	NMe_2 (br s)
7b[c]	85	126	7.98			7.60–7.30	2.64	2.52	
7c	75	130	8.13			7.62–7.36	2.56	2.54	
8b[c]	87	112	7.96	7.93		7.61–7.26		2.42	
8c	78	118	8.10	7.88		7.62–7.26		2.35	
1a	55	130	8.13		7.33	7.33–7.25	5.66	4.77	2.93
1b[c]	48	152	7.93		7.36	7.35–7.22	5.87	4.88	2.97
1c	45	180	8.07		7.32	7.45–7.25	5.82	4.76	2.98
2a	66	150	8.20		7.80	7.68–7.24	2.69	6.20	3.30, 3.20
2b[c]	72	192	7.89		7.67	7.32–7.10	2.64	6.08	3.00, 2.92
2c	68	178	7.98		7.60	7.37–7.07	2.62	6.04	3.14, 2.87
3a	57	238	7.96	7.90	7.64	7.60–7.20		5.12	3.04, 2.87
3b[c]	67	200	7.91	7.89	7.58	7.55–7.36		5.12	2.94
3c	63	244	8.04	7.89	7.60	7.56–7.26		5.13	3.12, 2.85

[a] All the compounds gave satisfactory elemental analysis. [b] All aromatic protons show normal aromatic splitting. [c] Protons of 6-Me group of **7b**, **8b**, **1b**, **2b** and **3b** appear as singlets at δ 2.44, 2.32, 2.47, 2.42 and 2.40 ppm, respectively.

Table 2 ^{13}C NMR data (δ_C; $CDCl_3$; 75 Hz) of some representative 1-benzopyran-4-ones **7**, **8** and **1**–**3**

Carbon number/nature	Compound									
	7c	**8b**	**8c**	**1a**	**1b**	**1c**	**2b**	**2c**	**3b**	**3c**
4	174.7	175.7	174.4	176.7	177.3	175.5	175.9	174.3	175.0	173.4
2	168.8	165.0	165.5	166.2	166.2	166.4	167.6	167.8	165.3	165.6
8a	153.8	154.4	154.3	155.4	153.4	153.7	152.7	152.4	153.5	153.4
7	134.2	135.1	134.1	132.1	133.3	132.1	133.9	132.7	133.8	132.7
6	131.9	135.4	131.3	125.1	133.9	129.6	134.0	129.7	134.2	130.1
5	125.5	125.4	125.4	123.8	124.9	124.7	125.5	125.1	125.7	125.3
4a	123.7	123.1	123.2	124.0	123.7	125.1	123.8	124.8	123.7	125.0
8	119.8	117.6	119.6	116.6	116.6	116.5	116.2	118.0	116.5	116.8
3	125.0	123.3	124.5	102.2	102.5	102.1	113.6	112.3	114.0	113.4
*C*HNMe_2				146.5	146.5	146.7	150.9	151.5	148.5	149.1
*C*H=CHNMe_2				87.8	88.1	87.6	87.8	87.3	86.7	86.3
2-Me	19.7	18.9	18.9							
6-Me		20.7			20.8		20.7		20.8	
NMe_2				[a]	[a]	[a]	40.7[b]	45.5,[b] 37.2[b]	[a]	[a]
3-*C*OMe	[a]						201.0	200.7		
3-CO*Me*	32.0						32.8	33.1		
3-*C*OPh		193.8	193.1						196.1	195.6
CO*Ph*: 1′-C		137.4	137.0						139.2	138.8
2′-C		129.3	129.3						129.2	129.1
3′-C		128.6	128.7						128.3	128.4
4′-C		133.5	133.7						132.5	132.7

[a] No peak appeared. [b] Very weak and broad peak.



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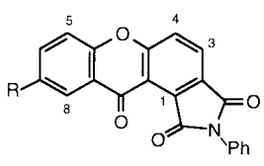

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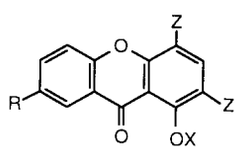
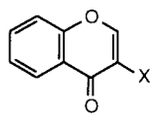


11 X = Z = H
12 X = Ac, Z = H
13 X = H, Z = Br



14 X = CHO
15 X = CO_2H
16 X = CN

On heating under reflux in DMF, the enamines **3** remained inert towards NPMI whereas **2** cyclised through electrocyclisation of their enol form followed by elimination of dimethylamine to afford 1-hydroxy-9*H*-xanthen-9-ones **11**, NPMI having no participation in this conversion. The enaminones **2** in refluxing sodium methoxide–methanol also gave compounds **11**. The yields of **11** in both these processes were in the range of 37–47%. Enamines **2** survived refluxing in pyridine but gave intractable polymeric compounds in refluxing acetic acid containing a catalytic amount of conc. sulfuric acid. The present reported synthesis of **11** from **2** compares well to the known preparation starting from either γ-resorcylic acid[9a] or *o*-hydroxyphenacyl methyl sulfoxide.[9b] A chloroform solution of **2a** on treatment with excess of bromine gave, evidently through non-isolable 3-bromoacetyl-2-(1-bromo-2-dimethylaminovinyl)chromenone, the dibromoxanthenone **13a**, which was also obtained by similar treatment of **11a** with bromine. The characterisation data of the xanthenones **11**, corresponding acetates **12** and dibromoxanthenone **13a** are given in Tables 3 and 4. In their ^{13}C NMR spectra, C-9 of 1-unsubstituted, 1-alkyl- and 1-phenylxanthenone appears at $\delta \approx 175$ ppm (*vide infra*) whereas that of 1-hydroxyxanthenones **11** appears at a relatively lower field ($\delta \approx 182$ ppm) evidently due to chelation between hydroxy hydrogen and xanthenone carbonyl oxygen.

Table 3 9*H*-Xanthen-9-ones **11**–**13**

Comp.	Mp/°C	Found (%) (Requires) C	H	δ_H($CDCl_3$; 300 MHz)[a] OH/OAc (s)[b]	8-H	6-H	3-H	Other ArH
11a	148[c]			12.63	8.26	7.74	7.53	7.45–6.78
11b[d,e]	140	74.2 (74.3	4.7 4.5)	12.70	8.04	7.53	7.57	7.41–6.77
11c	177	63.0 (63.3	3.2 2.9)	12.41	8.22	7.67	7.60	7.47–6.81
12a	173			2.50	8.25	7.71	7.70	7.48–7.00
12b[e]	148			2.50	8.04	7.51	7.68	7.41–6.97
12c	199			2.49	8.21	7.64	7.71	7.43–7.00
13a	226	41.8 (42.2	2.0 1.6)	13.45	8.29	7.83	8.06	7.66–7.46

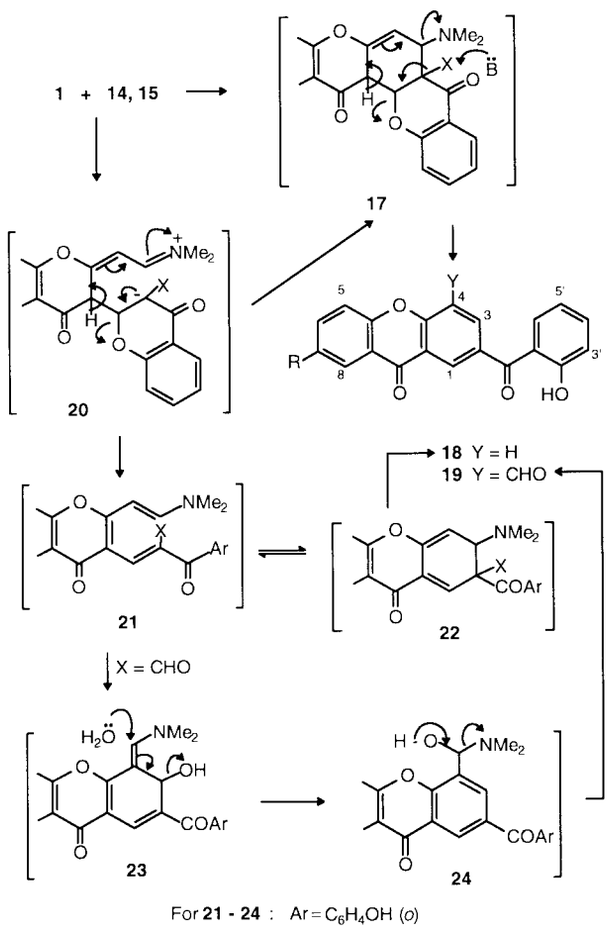
[a] Normal aromatic splitting. [b] Hydroxy proton is exchangeable. [c] Lit.,[9] 148–149 °C. [d] λ_{max}(EtOH)/nm 231 (log ε 4.80), 255 (4.65), 267 (4.46), 303 (3.96), 3.72 (3.83) and 415 (3.80); ν_{max}(KBr)/cm^{-1} 3070 (chelated OH), 1650 (CO) and 1625 (C=C). [e] 6-Me protons of **11b** and **12b** appear as singlets at δ 2.49 and 2.43, respectively.

Table 4 ^{13}C NMR data of 1-hydroxy-9*H*-xanthen-9-ones **11** and **13**

Carbon	Compound **11a**[a]	**11b**	**11c**	**13a**
1	162.1	162.2	162.1	151.8
2	110.5	110.2	110.9	103.4
3	136.8	136.4	135.6	142.0
4	107.0	106.9	107.0	98.9
4a[b]	156.4	156.4	156.3	158.1
4b[b]	156.3	154.5	154.6	156.2
5	117.9	117.5	119.6	118.3
6	135.5	136.6	137.1	136.3
7	124.1	133.9	130.7	125.1
8	126.1	125.3	125.4	126.3
8a	120.7	120.4	121.6	120.2
9	182.3	182.2	181.2	181.7
9a	109.0	109.1	109.1	110.1
7-Me		20.6		

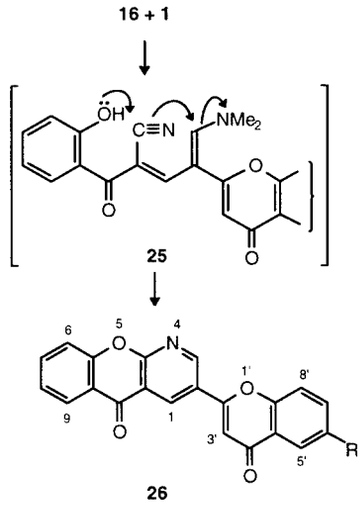
[a] Peak assignment is confirmed by ^{13}C–H correlation. [b] Peaks assigned to C-4a and C-4b may be interchanged.

The 3-substituted chromenones **14**–**16**, because of two electron-withdrawing groups at one end of the pyran 2,3-olefinic bond, are likely to function as dienophiles. [4 + 2]Cycloaddition of **14**–**16** with 2,3-dimethylbuta-1,3-diene catalysed by titanium tetrachloride and that of **14** and **16** with highly electron-rich dienes without the assistance of any Lewis acid catalyst are known, the stability of the resultant cycloadducts depending on the nature of the X group.[10] The dienes **1** in refluxing DMF gave the xanthenones **18** exclusively with the acid **15** but a mixture of **18** and **19** with the aldehyde **14**. The adduct **17** (X = CO_2H), derived from **1** and **15** through either a straightforward [4 + 2]cycloaddition reaction or a two-step process involving the ionic intermediate **20**, transforms into **18** by base-catalysed dehydroamination and decarboxylative pyran-ring opening, the adduct **17** itself functioning as the base (Scheme 2). The xanthenones **18** may also arise by sequential Michael addition of the dienamines **1** through their δ-carbon to **15** with concomitant decarboxylative pyran-ring opening of the latter moiety (to **21**, X = H), electrocyclisation (to **22**, X = H), and elimination of dimethylamine. The reaction of **1** with **14** may similarly lead to the intermediates **17** and **22** (X = CHO) which undergo base-catalysed conversion into **18**. The formation of **19** from **1** and **14** necessitates the cyclisation (intramolecular addition of the enamine to the aldehyde functionality) of **21** to **23** followed by addition–elimination of water (to **24**) and elimination of dimethylamine (Scheme 2). In the ^{1}H NMR spectra of **19**, the two low-field singlets at $\delta \approx 11.7$ and 10.9 are attributed to hydroxy and aldehydic protons, respectively. Both 1-H and 3-H of **19** are flanked by two carbonyl groups and consequently are highly deshielded. Two low-field singlets at δ 8.9 and 8.6 do indeed appear but it is difficult to pinpoint which one of the above mentioned two protons appears at a relatively lower field.



Scheme 2

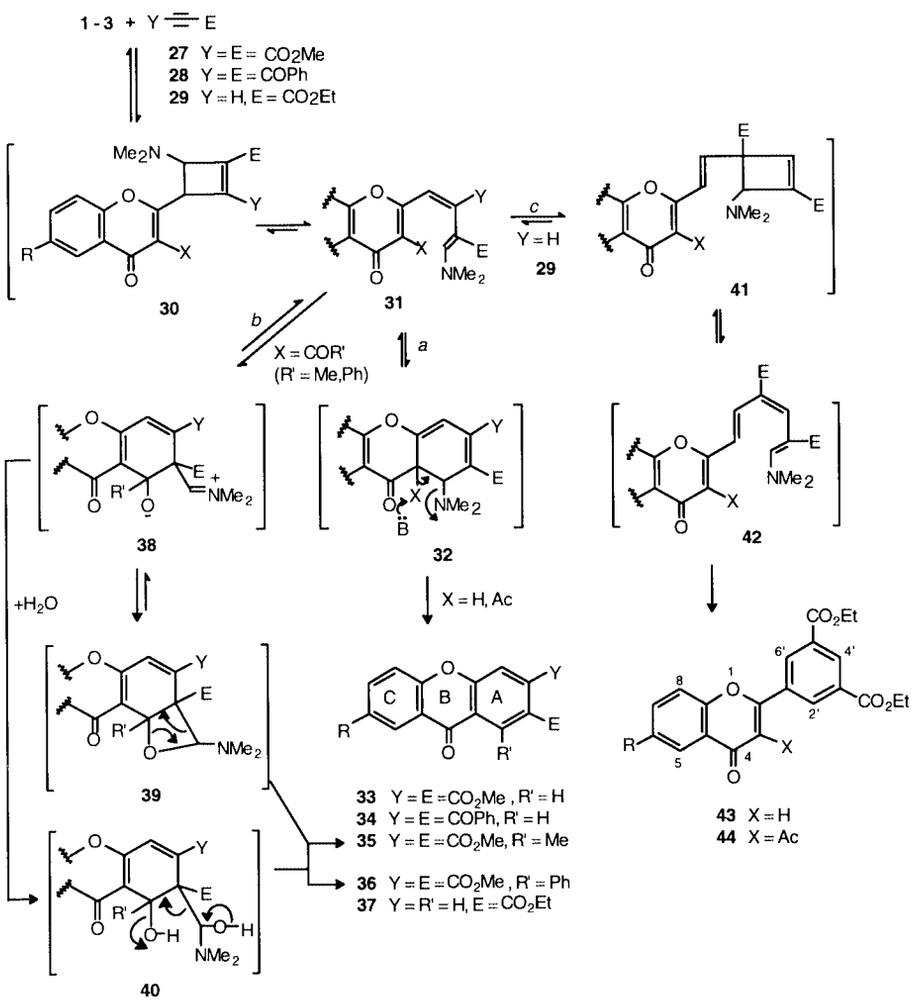
The nitrile **16** behaved differently from its analogues **14** and **15** towards the enamine **1**. From the reaction mixture of **1** and **16** in refluxing DMF we could isolate only the 1-benzopyrano-[2,3-*b*]pyridine **26** albeit in low yield. Here the dienamine **1** attacks through its β-carbon at the 2-position of **16** with concomitant opening of the latter's pyran ring to give the intermediate **25** which by double cyclisation affords the pyranopyridine **26** (Scheme 3). The proposed mechanism for the formation of **26** resembles that for the base-catalysed condensation of **16** with several active methylene compounds, leading to 2,3-disubstituted 1-benzopyrano[2,3-*b*]pyridine derivatives.[11]



Scheme 3

The dienamines **1** with dimethyl acetylenedicarboxylate (DMAD) **27** in refluxing DMF did not afford any [4 + 2]cycloadduct or the corresponding dehydroaminated product; instead, they gave exclusively the xanthenones **33**.[7] Here compounds **1** behave like an unconjugated enamine in undergoing [2 + 2]cycloaddition with **27** to give the adducts **30** (X = H) which isomerise to **31** (Scheme 4).[12] The ring opening of the cyclobutene **30** having both an acceptor and a donor substituent in an appropriate disposition most probably occurs in a symmetry-allowed fashion,[13] though involvement of an ionic mechanism with participation of the nitrogen lone pair of the dimethylamino group in the rearrangement **30** ⟶ **31** may not be completely ruled out.[13,14] The ring-opened intermediate **31** incorporating a pre-existing double bond at the pyran 2,3-position behaves as a hexatriene system which by electrocyclisation[15] (to **32**) and subsequent elimination of dimethylamine affords the xanthenone **33** (Scheme 4, path *a*). Dibenzoylacetylene **28**, like **27**, with **1** produced the xanthenones **34**.

The enamines **2** on treatment with **27** in refluxing DMF produced the xanthenones **33** and **35** admixed with a little (4–7%) of the hydroxyxanthenones **11**. The formation of the former two products indicates that the acetyl group at the 3-position of **2** does not prevent its initial [2 + 2]cycloaddition with **27** to **30** (X = Ac) and the 1,9a-dihydroxanthenone intermediate **32** (X = Ac) obtained from **30** (X = Ac) *via* the intermediate **31** (X = Ac) (path a, Scheme 4) undergoes base-catalysed deacylative deamination to **33**, **32** itself functioning as the base. The formation of products **35** may be rationalised as follows: the enamine intermediate **31** (X = Ac) by intramolecular addition (to **38**) and subsequent cyclisation gives the fused oxetane **39**, which eliminates DMF to afford **35** (Scheme 4, path *b*). Oxetane formation by thermal [2 + 2]cycloaddition between an electron-rich alkene and an electron-poor carbonyl compound is well known.[16] So the envisaged conversion of **31** into **39** involving intramolecular [2 + 2]cycloaddition between an appreciably electron-rich enamine moiety and an appreciably electron-deficient carbonyl group is plausible. Formation of **35** by elimination of DMF from **39** is analogous to thermal cycloreversion of oxetanes to olefinic and carbonyl compounds.[17] An alternative pathway for the formation of **35** involving addition of water to the zwitterion **38** and subsequent elimination of DMF and water from the resultant intermediate **40** may not be ruled out, formation of the resonance-stabilised xanthenone system



Scheme 4

Table 5 Substituted 9*H*-xanthen-9-ones **33**–**36**

Comp. (Mol. formula)	Yield (%)	Mp/°C	Found (%) (Requires) C	H	δ_H($CDCl_3$; 300 MHz)[a] 1-H/1-Me (s)	8-H	4-H (s)	6-H	5-H and other ArH (m)	CO_2Me (s)
33a[b]	40,[c]	138	65.2	3.7	8.82	8.33	7.71	7.78	7.55–7.42	3.98,
($C_{17}H_{12}O_6$)	9[d]		(65.4	3.9)						3.96
33b[e,f]	37,[c]	166	66.0	4.2	8.83	8.11	7.70	7.58	7.43	3.98,
($C_{18}H_{14}O_6$)	10[d]		(66.3	4.3)						3.96
33c	38,[c]	182	59.2	3.4	8.82	8.31	7.73	7.73	7.51	3.99,
($C_{17}H_{11}ClO_6$)	15[d]		(58.9	3.2)						3.96
34a	38	262	80.5	3.8	8.62	8.36	7.70		7.64–7.39,	
($C_{27}H_{16}O_4$)			(80.2	4.0)					7.82[g]	
34b[f]	32	228	80.3	4.7	8.61	8.13	7.67		7.62–7.40,	
($C_{28}H_{18}O_4$)			(80.4	4.3)					7.80[g]	
34c	26	278	73.6	3.5	8.60	8.32	7.72		7.63–7.41,	
($C_{27}H_{15}ClO_4$)			(73.9	3.4)					7.80[g]	
35a	38	167	66.6	4.0	2.92	8.30	8.02	7.76	7.76–7.32	4.00,
($C_{18}H_{14}O_6$)			(66.3	4.3)						3.98
35b[f,h]	36	192	66.8	4.7	2.81	7.88	7.83	7.42	7.25	3.95,
($C_{19}H_{16}O_6$)			(67.1	4.8)						3.91
35c	42	214	60.2	3.4	2.82	8.21	7.98	7.66	7.42	3.98,
($C_{18}H_{13}ClO_6$)			(59.9	3.6)						3.96
36a	42	180	71.5	4.4		8.13	8.20	7.73	7.51–7.23	3.97,
($C_{23}H_{16}O_6$)			(71.1	4.2)						3.52
36b[f]	45	214	71.4	4.7		7.87	8.14		7.50–7.24	3.96,
($C_{24}H_{18}O_6$)			(71.6	4.5)						3.52
36c	46	240	65.0	3.2		8.07	8.18	7.66	7.43–7.21	3.97,
($C_{23}H_{15}ClO_6$)			(65.3	3.6)						3.52

[a] Aromatic protons show normal aromatic splitting. [b] ν_{max}(KBr)/cm^{-1} 1745 (ester CO), 1735 (ester CO), 1670 (keto CO) and 1620 (C=C). [c] Yield from **1**. [d] Yield from **2**. [e] ν_{max}(KBr)/cm^{-1} 1740 (ester CO), 1730 (ester CO), 1675 (keto CO) and 1625 (C=C); *m*/*z* 326 (M^+, 47%), 295 (M − OMe, 100), 236 (295 − OMe − CO, 7) and 208 (236 − CO, 11). [f] 7-Me protons of **33b**, **34b**, **35b** and **36b** appear as singlets at δ 2.48, 2.49, 2.37 and 2.37 ppm, respectively. [g] Mean position of the multiplets due to four *ortho* protons of the two benzoyl groups. [h] λ_{max} (EtOH)/nm 212 (log ε 4.32), 241 (4.37), 256 (4.45) and 357 (3.67); ν_{max} (KBr)/cm^{-1} 1760 (ester CO), 1730 (ester CO), 1660 (xanthenone CO) and 1625 (C=C).

Table 6 ^{13}C NMR data of the xanthenone derivatives **33**, **35**–**37**

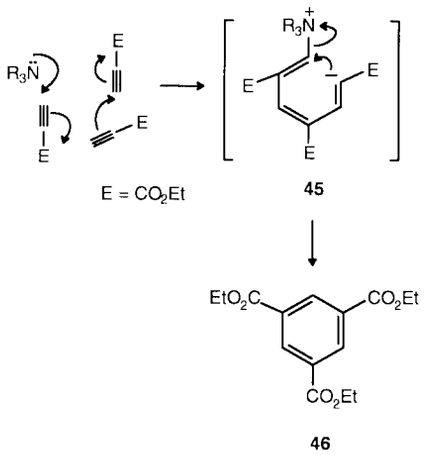
Carbon type/ number	Compound **33b**	**33c**	**35b**	**36a**	**36b**	**36c**	**37b**[a]
Xanthenone C:1	129.2	129.3	132.1[b]	131.9[b]	132.1[b]	132.7[b]	129.3
2	125.4	126.4	131.4[b]	132.1[b]	132.3[b]	132.8[b]	126.4
3	138.6	139.2	140.2	142.3	142.5	142.7	136.4
4	118.6	119.9	118.3	120.2	120.0	120.1	118.3
4a	157.0	157.1	156.8	156.4	156.6	156.5	158.8
4b	154.1	154.4	153.3	155.3	153.7	153.9	154.4
5	117.7	118.9	117.2	117.6	117.3	119.3	117.8
6	136.6	135.6	136.1	135.2	136.2	135.2	135.2
7	134.7	130.8	134.2	124.5	134.4	130.6	134.5
8	126.0	126.2	126.1	127.0	126.4	126.5	126.3
8a	122.0	122.7	122.5	122.7	122.8	123.9	121.6[b]
9	175.6	174.6	177.9	176.0	175.8	174.8	176.6
9a	121.2	122.0	122.4	121.7	121.9	121.6	121.5[b]
CO_2Alkyl	167.2, 165.8	166.9, 165.7	168.8, 164.8	167.7, 164.6	167.4, 164.7	167.3, 164.6	165.4
CO_2*Me*	53.0, 52.6	53.0, 52.7	52.8, 52.5	53.1, 52.2	52.8, 51.9	53.0, 52.0	
1-Me			18.8				
7-Me	27.0		20.7		20.8		20.8
1-Ph: 1′				137.4	137.7	137.3	
2′				128.3	128.6	128.6	
3′				127.5	127.4	127.5	
4′				127.7	127.5	127.8	

[a] Methylene carbon and methyl carbon of the CO_2Et group appear at δ 61.3 and 14.3 ppm, respectively. [b] Assignments may be interchanged.

being the driving force for the envisaged elimination process. The dienamines **3** on similar treatment with **27** gave the xanthenones **36** in complete absence of their 1-unsubstituted analogues **33**. Here the base-catalysed debenzoylation of **32** (X = COPh) is not possible, so the intermediate **31** (X = COPh) follows the reaction course as depicted in Scheme 4, path *b* to afford **36**. The characterisation data of the xanthenones **33**–**36** are given in Tables 5 and 6. In the ^{1}H NMR spectra, the protons of two methoxycarbonyl groups in **33** and **35** appear as two singlets around $\delta \approx 3.97$ whereas those in the 1-phenyl analogues **36** appear as two singlets at δ 3.97 and 3.52. In the latter case, presumably the restricted rotation of the single bond connecting C-1 of the xanthenone moiety to the phenyl substituent prevents coplanarity between the phenyl ring and ring A of **36**, and consequently methyl protons of the methoxycarbonyl at its 2-position falling in the phenyl ring current zone are shielded to some extent.

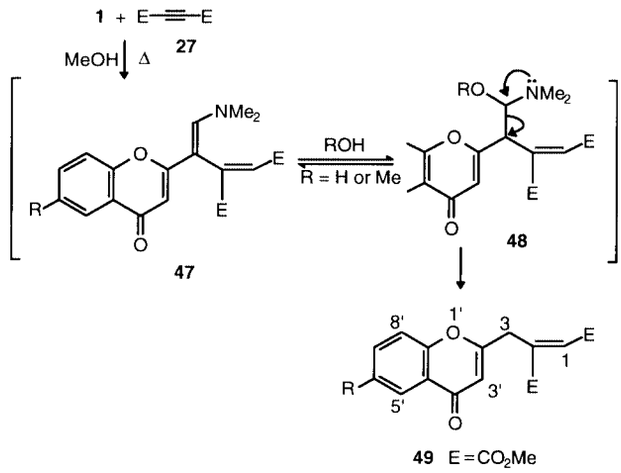
The dienamines **1** on reaction with three equivalents of ethyl propiolate (EP) **29** gave a mixture of xanthenones **37**, flavones **43** and benzene-1,3,5-tricarboxylate **46**. The mixture of these three

products was also obtained by using two mole equivalents of **29**, a portion of **1** being recovered unchanged. The formation of **37** from **1** and EP, analogous to that of **33** from **1** and DMAD, follows the reaction course involving the intermediates **30**–**32** (X = Y = H, E = CO_2Et) as depicted in Scheme 4, path *a*. [2 + 2]Cycloaddition of a second molecule of EP with the enamine moiety of **31** (X = Y = H, E = CO_2Et) (path *c*) competes with electrocyclisation of the latter (path *a*); the cyclobutene **41** thus formed isomerises to **42** which ultimately gives **43** by electrocyclisation and elimination of dimethylamine. On reaction of the dienaminone **2a** as well as **2b** with an excess of EP we could isolate from the reaction mixture, respectively, **37a** and **44b**, a substantial amount of **46** being obtained in both cases. The xanthenone **37a** from **2a** and EP arises through the intermediates **30**–**32** (X = Ac, R = Y = H, E = CO_2Et) (path *a*) whereas **44b** results from **2b** and EP by the mechanism involving the reaction intermediates **30**, **31**, **41** and **42** (X = Ac, Y = H, E = CO_2Et) (path *c*). Trimerisation of **29** to **46** catalysed by dicarbonylbis(triphenylphosphine)-nickel is known[18] but the same reaction either uncatalysed or catalysed by an enamine remains hitherto unreported. Prolonged heating of EP in DMF under reflux gave a mixture of at least two products, none of which was identical with **46** (TLC). The reaction mixture of EP in refluxing DMF containing triethylamine, however, showed the presence of **46** (TLC) among several other products. So it is likely that the enamines **1** and **2** behave like a trialkylamine in triggering head-to-tail joining of three molecules of **29** to give the zwitterionic intermediate **45** that ultimately cyclises to **46** (Scheme 5).



Scheme 5

Refluxing a methanolic solution of **1** and DMAD **27** produced the chromenone derivatives **49** admixed with a small amount of **33**. Under these reaction conditions, enamines **1** undergo through their β-carbon a Michael addition to DMAD giving the intermediate **47** (Scheme 6). 1,6-Addition of methanol (or water available during aqueous work-up) to the α,β,γ,δ-unsaturated carbonyl functionality of **47** gives **48** that ultimately result in products **49**, the envisaged bond cleavage being facilitated by the presence of two electron-withdrawing moieties (1-benzopyran-4-one and ethylene-1,2-dicarboxylate) at the same end of this bond. The olefinic protons of methyl maleate and fumarate resonate at δ 6.28 and 6.89 respectively. The appearance of the exocyclic olefinic proton of products **49** at δ 7.40 indicates *E*-stereochemistry around this olefinic bond. This contention is further corroborated by the non-observance of an NOE between this olefinic proton and allylic methylene protons. It is worth mentioning here that the enamines **1**, carbon-nucleophiles, behave similarly to several heteroatom-containing nucleophiles[19] in giving substituted fumarate with acetylenedicarboxylic ester.



Scheme 6

Conclusions

Unlike several chromenone-derived dienes giving exclusively [4 + 2]cycloadducts with various dienophiles,[2,20] the dienaminone **1** undergoes either Diels–Alder reaction with the alkenic dienophiles or Michael addition (through its β- or δ-carbon) to them; the nature of the electron-withdrawing group(s) in the dienophile favouring one over the other type of the above mentioned reactions is yet to be ascertained. So far as [4 + 2]-*vis-à-vis* [2 + 2]-cycloaddition of dienamines with electrophilic acetylenes is concerned, the latter is predominant, if not exclusive, as revealed in the present and many earlier reports.[21] So, the initial [4 + 2]cycloaddition as postulated for the formation of aromatic carboxylic esters from 1-dialkylaminobuta-1,3-diene and acetylenecarboxylic esters[22] deserves further scrutiny.

Experimental

Yields and uncorrected mps (determined in open capillaries in a H_2SO_4 bath) of the products crystallised from chloroform–light petroleum (defined below) are reported and no attempts were made to optimise the yield. NMR spectra of the compounds dissolved in $CDCl_3$ were recorded mostly at 300 MHz and occasionally at 200 MHz on Bruker AM 300L and DRX 200 supercon spectrometers, respectively; *J*-values are given in Hz. IR spectra were obtained on a Perkin-Elmer 782 and UV on a Hitachi U-2000 spectrometer. Mass spectra were recorded on a JEOL DX 303 spectrometer. Light petroleum refers to the fraction with distillation range 60–80 °C. Extracts were dried over anhydrous Na_2SO_4 unless stated otherwise, and solid products were dried over P_2O_5 *in vacuo*.

ω-Acyl-2-hydroxyacetophenones 5a–c

2-Hydroxyacetophenone **4a** on acylation with ethyl acetate in the presence of molecularised sodium[4] gave ω-acetyl-2-hydroxyacetophenone **5a** (R^1 = Me) (68%), mp 110 °C (lit.,[4] 90–92 °C). The other two acetophenones **4b** and **4c** were similary converted into **5b** and **5c** (R^1 = Me), respectively, having mps 112 and 118 °C, respectively. ω-Benzoyl-2-hydroxyacetophenone **5a** (R^1 = Ph) was similarly prepared, only ethyl acetate being replaced by ethyl benzoate. The compounds **5a**,**b**,**c** (R^1 = Ph) thus prepared had mps of 120, 126 and 112 °C, respectively and these products without further purification were utilised for the preparation of chromenones **8**.

2-Methyl-1-benzopyran-4-ones 6a–c

A solution of an ω-acylacetophenone **5** (R^1 = Me) (0.5 mol) in aq. methanol (1 : 9; 100 ml) containing a few drops of conc. HCl was warmed for 30 min. Usual work-up of this reaction mixture

afforded the corresponding 2-methylchromenone **6** in 80–90% yield. The chromenones **6a**,**b**,**c** melted at 72, 98 and 121 °C, respectively.

3-Acyl-2-methyl-1-benzopyran-4-ones 7 and 8

ω-Acyl-2-hydroxyacetophenones **5** (R^1 = Me) and **5** (R^1 = Ph) on refluxing with acetic anhydride in the presence of fused sodium acetate[6] gave in 70–90% yield the corresponding 3-acyl-2-methylchromenones **7** and **8**, respectively. The characterisation data of the new compounds **7b**,**c** and **8b**,**c** are given in Tables 1 and 2.

2-(2-Dimethylaminovinyl)-1-benzopyran-4-ones 1–3

A reflux apparatus containing a solution of a 2-methylchromenone **6** (25 mmol) in pyridine (40 ml) containing dimethylformamide dimethyl acetal (DMFDMA, 3 ml, ≈25 mmol) was heated for 8 h on a water-bath with circulation of cold water in the condenser. The reaction mixture was concentrated, cooled, and diluted with water. The precipitated solid was filtered off, dried, and crystallised from benzene to afford the corresponding enamine **1** as yellow crystals. The enamines **2** and **3** were prepared by treating the appropriate 2-methylchromenones **7** and **8**, respectively, with DMFDMA in refluxing benzene as described in an earlier publication.[8] The characterisation data of **1**–**3** are given in Tables 1 and 2.

Treatment of enamine 1 with *N*-phenylmaleimide

Treatment of **1a**,**b** with one equivalent of NPMI in refluxing DMF leading to the corresponding xanthenone **10a**,**b** is described in an earlier communication.[7] Similar treatment of **1c** with 2 equivalents of NPMI, followed by usual work-up of the reaction mixture did not give any solid compound so the reaction mixture was extracted with chloroform and the concentrated organic extract was chromatographed over silica using ethyl acetate–light petroleum (1:8) as eluent. Fractions 5–8 (each fraction measuring ≈10 ml) contained *N*-phenylsuccinimide (5%), mp 154 °C (lit.,[23] 153–154 °C); δ_H 7.48 (2H, m, Ph *meta* to imide), 7.40 (1H, m, Ph *para* to imide), 7.32 (2H, m, Ph *ortho* to imide) and 2.88 (4H, s, CH_2CH_2); δ_C 176.0, 132.0 (s), 129.1, 128.5, 126.4 (d) and 28.4 (t). After elution of *N*-phenylsuccinimide the chromatographic column was further eluted with ethyl acetate–light petroleum (1:4), when *7-chloro-9-oxo-N-phenyl-9H-xanthene-1,2-dicarboximide* **10c**·$HCONMe_2$ was obtained from fractions 6–9 as yellow crystals (42%), mp 254 °C (Found: C, 64.4; H, 3.4; N, 6.3. $C_{21}H_{10}NClO_4$·$HCONMe_2$ requires C, 64.2; H, 3.8; N, 6.2%); δ_H 9.26 (1H, s, *H*$CONMe_2$), 8.28 (1H, d, *J* 8.5, 3-H), 8.26 (1H, d, *J* 2.2, 8-H), 7.66 (1H, dd, *J* 8.8 and 2.6, 6-H), 7.61 (1H, d, *J* 8.5, 4-H), 7.50–7.12 (6H, m, 5-H + Ph), 3.21 (3H, s, NMe) and 2.75 (3H, s, NMe).

General procedure for the conversion of dienaminones 2 to 1-hydroxy-9*H*-xanthen-9-ones 11

Method A. An enaminone **2** (1 mmol) was heated under reflux in DMF (8–10 ml) for 8 h. The reaction mixture was then concentrated, cooled, diluted with water and extracted with chloroform. The organic extract was dried (Na_2SO_4), concentrated, and charged over a silica gel column. Elution of the column with ethyl acetate–light petroleum (1:10) afforded in the first few fractions the corresponding xanthenone **11** as bright yellow crystals (Tables 3 and 4) in 37–45% yield.

Method B. To a solution of sodium methoxide (prepared from ≈200 mg of sodium) in methanol (30 ml) was added an enamine **2** (1 mmol). The reaction mixture was refluxed for 6 h, concentrated, diluted with water and acidified with hydrochloric acid. The precipitated yellow solid was collected by filtration, dried, and crystallised from ethyl acetate–light petroleum to afford the corresponding **11** in 40–47% yield.

The compounds **11** on usual treatment with pyridine–acetic anhydride at room temperature yielded the corresponding acetates **12** as white crystals (Table 3).

2,4-Dibromo-1-hydroxy-9*H*-xanthen-9-one 13a

Bromine (1 mmol, ≈0.55 ml) in chloroform (10 ml) was gradually added to a solution of enamine **2a** (128 mg, 0.5 mmol) in chloroform (20 ml) at room temperature. After complete addition of the bromine solution, the reaction mixture was warmed on a hot water-bath for 15 min, cooled, and washed with aq. sodium bicarbonate. The chloroform solution was dried (Na_2SO_4) and concentrated. The deposited solid was filtered off, and crystallised from chloroform–light petroleum to afford **13a** (74 mg, 40%) as yellow crystals (Tables 3 and 4). The xanthenone **13a** (55 mg, 60%) precipitated out when bromine (≈ 0.30 ml) was added to a solution of **11a** (53 mg, 0.25 mmol) in chloroform (20 ml) and the reaction mixture subsequently concentrated.

Treatment of enamines 1 with aldehyde 14

Enamine **1a** (230 mg, 1 mmol) and the aldehyde **14** (174 mg, 1 mmol) were refluxed together in DMF (15 ml) for 8 h. The reaction mixture was diluted with water (80 ml) and extracted with chloroform. The organic extract was dried, concentrated, and chromatographed over silica gel, ethyl acetate–light petroleum (1:10) being the eluent. Fractions 3–6 (each fraction measuring ≈ 25 ml) together contained 2-salicyloyl-9*H*-xanthen-9-one **18a** (16 mg, 5%), mp 184 °C (lit.,[24] 184 °C; lit.,[25] 185–187 °C), and fractions 10–12 gave *4-formyl-2-salicyloyl-9H-xanthen-9-one* **19a** (68 mg, 20%), mp 208 °C (Found: C, 73.4; H, 3.4. $C_{21}H_{12}O_5$ requires C, 73.2; H, 3.5%); ν_{max} (KBr)/cm^{-1} 3070 (chelated OH), 2900 (CH of CHO), 1698 (CHO), 1660 (CO), 1620 (CO) and 1605 (C=C); δ_H 11.76 (1H, s, exchangeable, OH), 10.85 (1H, s, CHO), 8.89 (1H, d, *J* 2.2, 1- or 3-H), 8.62 (1H, d, *J* 2.2, 3- or 1-H), 8.37 (1H, dd, *J* 8.0 and 1.5, 8-H), 7.86 (1H, ddd, *J* 8.5, 8.5 and 1.5, 6-H), 7.66 (1H, dd, *J* 8.5 and 0.8, 5-H), 7.59 (1H, dd, *J* 8.5 and 1.5, 6′-H), 7.53 (2H, m, 7- and 4′-H), 7.12 (1H, dd, *J* 8.0 and 0.8, 5′-H) and 6.93 (1H, m, 3′-H). Further elution of the column gave an oily mass from which no pure compound could be obtained.

The two other 6-substituted chromenones **1b**,**c** on similar treatment with **14** gave also a mixture of respective products **18b**,**c** and **19b**,**c**, which were separated by column chromatography over silica gel.

7-Methyl-2-salicyloyl-9*H*-xanthen-9-one 18b. From **1b**, yield 4%; mp 184 °C (Found: C, 76.2; H, 4.2. $C_{21}H_{14}O_4$ requires C, 76.4; H, 4.3%); δ_H 11.8 (1H, s, exchangeable, OH), 8.68 (1H, d, *J* 2.0, 1-H), 8.14 (1H, d, *J* 1.5, 8-H), 8.11 (1H, dd, *J* 8.7 and 2.0, 3-H), 7.64 (1H, d, *J* 8.7, 4-H), 7.63–6.93 (6H, m, other ArH) and 2.50 (3H, s, Me).

7-Chloro-2-salicyloyl-9*H*-xanthen-9-one 18c. From **1c**, yield 6%; mp 222 °C (Found: C, 68.8; H, 2.9. $C_{20}H_{11}ClO_4$ requires C, 68.5; H, 3.2%); δ_H 11.85 (1H, s, exchangeable, OH), 8.66 (1H, d, *J* 2.3, 1-H), 8.31 (1H, d, *J* 2.6, 8-H), 8.13 (1H, dd, *J* 8.8 and 2.3, 3-H), 7.73 (1H, dd, *J* 8.7 and 2.6, 6-H), 7.66 (1H, d, *J* 8.7, 5-H), 7.61 (1H, dd, *J* 8.0 and 1.6, 6′-H), 7.56 (1H, m, 4′-H), 7.53 (1H, d, *J* 8.8, 4-H), 7.12 (1H, m, 3′-H) and 6.93 (1H, m, 5′-H).

4-Formyl-7-methyl-2-salicyloyl-9*H*-xanthen-9-one 19b. From **1b** in 15% yield; mp 228 °C (Found: C, 74.1; H, 4.3. $C_{22}H_{14}O_5$ requires C, 73.7; H, 3.9%); δ_H 11.79 (1H, s, exchangeable, OH), 10.85 (1H, s, CHO), 8.90 (1H, d, *J* 2.1, 1- or 3-H), 8.69 (1H, *J* 2.1, 3- or 1-H), 8.16 (1H, poorly split d, 8-H), 7.67 (1H, dd, *J* 8.6 and 1.8, 6′-H), 7.60–7.54 (3H, m, 6-, 4′-, 3′-H), 7.13 (1H, d, *J* 8.2, 5-H), 6.94 (1H, m, 5′-H) and 2.53 (3H, s, Me).

7-Chloro-4-formyl-2-salicyloyl-9*H*-xanthen-9-one 19c. From **1c** in 18% yield; mp 240 °C (Found: C, 66.2; H, 2.7. $C_{21}H_{11}ClO_5$ requires C, 66.6; H, 2.9%); δ_H 11.74 (1H, s, exchangeable, OH), 10.83 (1H, s, CHO), 8.89 (1H, d, *J* 2.4, 1- or 3-H), 8.64 (1H, d, *J* 2.4, 3- or 1-H), 8.34 (1H, d, *J* 2.6, 8-H), 7.80 (1H, dd, *J* 8.8 and 2.6, 6-H), 7.64 (1H, d, *J* 8.8, 5-H), 7.59 (1H, ddd, *J* 8.5, 7.8 and 1.6, 4′-H), 7.52 (1H, dd, *J* 8.0 and 1.6, 6′-H), 7.13 (1H, dd, *J* 8.5 and 0.9, 3′-H) and 6.94 (1H, m, 5′-H).

Treatment of enamines 1 with acid 15

An enamine **1** was treated with the acid **15** similarly as described for treatment of **1** with the aldehyde **14**. The solid that precipitated after cooling of the reaction mixture and subsequent dilution with water was filtered off, dried, and crystallised from chloroform (charcoal)–light petroleum to afford the corresponding xanthenone **18**. The xanthenones **18a**,**b**,**c** were obtained in 40, 35 and 37% yield from the enamines **1a**,**b**,**c**, respectively.

Treatment of enamines 1a,b with nitrile 16: synthesis of 3-(4-oxo-4*H*-1-benzopyran-2-yl)[1]benzopyrano[2,3-*b*]pyridines 26. General procedure

An enamine **1** (0.5 mmol) and the nitrile **16** (85.5 mg, 0.5 mmol) were refluxed together in DMF (20 ml) for 7 h. The reaction mixture was concentrated, cooled, diluted with water and the deposited solid was filtered off. This was dried, and crystallised from chloroform–light petroleum. By this procedure the following compounds were prepared.

26a. Yellow solid (16%) from **1a**; mp >282 °C (Found: C, 74.2; H, 2.9; N, 4.4. $C_{21}H_{11}NO_4$ requires C, 73.9; H, 3.2; N, 4.1%); δ_H 9.28 (1H, d, *J* 2.6, 1-H), 9.24 (1H, d, *J* 2.6, 3-H), 8.38 (1H, dd, *J* 8.0 and 1.7, 5′-H), 8.26 (1H, dd, *J* 8.0 and 1.5, 9-H), 7.86 (1H, ddd, *J* 8.0, 7.2 and 1.6, 7′-H), 7.76 (1H, ddd, *J* 8.0, 7.2 and 1.5, 7-H), 7.73–7.38 (4H, m, other ArH) and 6.97 (1H, s, 3′-H).

26b. Yellow solid (18%) from **1b**; mp >282 °C (Found: C, 74.0; H, 3.3; N, 4.2. $C_{22}H_{13}NO_4$ requires C, 74.4; H, 3.7; N, 3.9%); δ_H 9.26 (1H, d, *J* 2.5, 1-H), 9.22 (1H, d, *J* 2.5, 3-H), 8.37 (1H, dd, *J* 7.6 and 1.7, 9-H), 8.04 (1H, d, *J* 1.8, 5′-H), 7.85 (1H, ddd, *J* 7.6, 7.2 and 1.6, 7-H), 7.78 (1H, dd, *J* 8.0 and 1.5, 7′-H), 7.56–7.47 (3H, other ArH), 6.94 (1H, s, 3′-H) and 2.50 (3H, s, 6′-Me).

General procedure for treatment of dienamines 1 with DMAD 27 and with dibenzoylacetylene 28

A solution of a dienamine **1** (2 mmol) and DMAD **27** (2 mmol, ≈0.4 ml) in DMF (15 ml) was heated under reflux for 5 h. Usual work-up of the reaction mixture gave a brown solid, which on crystallisation from chloroform (charcoal)–light petroleum afforded the corresponding 2,3-bis(methoxycarbonyl)-9*H*-xanthen-9-one **33**. Similar treatment of a dienamine **1** with an equimolar amount of dibenzoylacetylene **28** yielded the corresponding 2,3-dibenzoyl-9*H*-xanthen-9-one **34**. Tables 5 and 6 contain the characterisation data of xanthenones **33** and **34**.

Treatment of dienamines 2 with DMAD 27

A solution of a dienamine **2** (1 mmol) and DMAD **27** (1 mmol, ≈0.2 ml) in DMF (20 ml) was refluxed for 4 h, the solution becoming progressively darker in colour on refluxing. The solution was concentrated, cooled, and diluted with water, when an oily mass separated out. This was extracted with chloroform and the solid obtained therefrom was subjected to fractional crystallisation from chloroform–light petroleum, when the corresponding xanthenone **35** (Tables 5 and 6) first crystallised out, followed by the corresponding lesser homologue **33** (9–15%). The mother liquor left after obtention of the aforesaid two xanthenones was further concentrated and subsequently diluted with light petroleum to afford the corresponding 1-hydroxyxanthenone **11** (4–7%).

2,3-Bis(methoxycarbonyl)-1-phenyl-9*H*-xanthen-9-ones 36. General procedure

A benzoylenaminone **3** was allowed to react with an equimolar amount of DMAD **27** in refluxing DMF similarly as described for the treatment of **1** with DMAD. The brown solid mass obtained after usual work-up of the reaction mixture was crystallised twice from chloroform–light petroleum to afford the corresponding title xanthenone **36** (Tables 5 and 6).

Treatment of enamines 1 with ethyl propiolate (EP) 29

A mixture of an enamine **1** (1 mmol) and EP (0.3 ml, ≈3 mmol) in DMF (15 ml) was heated under reflux for 8 h. The reaction mixture was then concentrated, cooled, diluted with water and extracted with chloroform. The chloroform extract was concentrated, and chromatographed over silica using a 1 : 10 mixture of ethyl acetate and light petroleum as eluent, when the benzene-tricarboxylate **46** (2–4%), the corresponding xanthenone **37** (26–35%) and the corresponding flavone **43** (5–7%) were eluted in that order. The expected flavone **43a** could not be obtained from the reaction mixture of **1a** and EP. Triethyl benzene-1,3,5-tricarboxylate **46** had mp 134 °C (lit.,[18] 135–136 °C); δ_H 8.84 (3H, s, ArH), 4.43 (6H, q, OC*H*$_2$Me) and 1.43 (9H, t, OCH$_2$-*Me*); δ_C 165.1 (ester CO), 134.4 (phenyl C-H), 131.7 (phenyl carbon linked to CO_2Et), 61.6 (O*C*H$_2$Me) and 14.3 (Me); *m*/*z* 294 (M^+, 18%), 266 (M − C_2H_4, 34), 249 (M − OEt, 100), 238 (266 − C_2H_4, 34), 221 (249 − CO, 68), 210 (238 − C_2H_4, 32), 193 (221 − C_2H_4, 38), 176 (193 − OH, 12), 165 (193 − C_2H_4, 16) and 148 (193 − OEt, 18). The following xanthenones **37** and flavones **43** were obtained by this procedure.

Ethyl 9-oxo-9*H*-xanthene-2-carboxylate 37a. From **1a** in 35% yield; mp 152 °C (Found: C, 71.4, H, 4.2. $C_{16}H_{12}O_4$ requires C, 71.6; H, 4.5%); δ_H 9.01 (1H, d, *J* 2.2, 1-H), 8.38 (1H, dd, *J* 8.8 and 2.2, 3-H), 8.35 (1H, dd, *J* 9.1 and 1.7, 8-H), 7.75 (1H, ddd, *J* 7.3, 7.2 and 1.7, 6-H), 7.55–7.39 (3H, m, other ArH), 4.43 (2H, q, OC*H*$_2$Me) and 1.43 (3H, t, CH$_2$*Me*).

Ethyl 7-methyl-9-oxo-9*H*-xanthene-2-carboxylate 37b. From **1b** in 28% yield; mp 148 °C (Found: C, 71.9; H, 5.2. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0%); δ_H 9.00 (1H, d, *J* 2.1, 1-H), 8.35 (1H, dd, *J* 8.8 and 2.1, 3-H), 8.11 (1H, poorly split d, 8-H), 7.55 (1H, dd, *J* 8.6 and 2.0, 6-H), 7.51 (1H, d, *J* 8.8, 4-H), 7.40 (1H, d, *J* 8.6, 5-H), 4.42 (2H, q, OC*H*$_2$Me), 2.41 (3H, s, 7-Me) and 1.46 (3H, t, CH$_2$*Me*). ^{13}C NMR data are given in Table 6.

Ethyl 7-chloro-9-oxo-9*H*-xanthene-2-carboxylate 37c. From **1c** in 26% yield; mp 146 °C (Found: C, 63.6; H, 3.9. $C_{16}H_{11}ClO_4$ requires C, 63.5; H, 3.7%); ν_{max} (KBr)/cm^{-1} 1730 (ester CO), 1675 (keto CO); δ_H 9.05 (1H, d, *J* 2.1, 1-H), 8.40 (1H, dd, *J* 8.8 and 2.1, 3-H), 8.31 (1H, d, *J* 2.6, 8-H), 7.70 (1H, dd, *J* 8.9 and 2.6, 6-H), 7.55 (1H, d, *J* 8.8, 4-H), 7.49 (1H, d, *J* 8.9, 5-H), 4.43 (2H, q, OC*H*$_2$Me) and 1.44 (3H, t, CH$_2$*Me*).

3′,5′-Bis(ethoxycarbonyl)-6-methylflavone 43b. Colourless crystals (5%) from **1b**, mp 171 °C (Found: C, 69.7; H, 5.5. $C_{22}H_{20}O_6$ requires C, 69.5; H, 5.3%); δ_H 8.81 (1H, t, *J* 1.5, 4′-H), 8.75 (2H, d, *J* 1.5, 2′-, 6′-H), 8.03 (1H, poorly split d, 5-H), 7.55 (2H, m, 7-, 8-H), 6.94 (1H, s, 3-H), 4.48 (4H, q, *J* 7.2, 2 × OC*H*$_2$Me), 2.49 (3H, s, 6-Me) and 1.46 (6H, t, *J* 7.2, 2 × CH$_2$*Me*).

6-Chloro-3′,5′-bis(ethoxycarbonyl)flavone 43c. Colourless crystals (7%) from **1c**, mp 160 °C (Found: C, 63.1; H, 4.2. $C_{21}H_{17}ClO_6$ requires C, 62.9; H, 4.3%); δ_H 8.83 (1H, t, *J* 1.4, 4′-H), 8.74 (2H, d, *J* 1.4, 2′-, 6′-H), 8.21 (1H, d, *J* 2.5, 5-H), 7.70 (1H, dd, *J* 9.0 and 2.5, 7-H), 7.63 (1H, d, *J* 9.0, 8-H), 6.96 (1H, s, 3-H), 4.41 (4H, q, 2 × OC*H*$_2$Me) and 1.46 (6H, t, 2 × CH$_2$*Me*).

Treatment of enaminone 2a with EP 29

The enamine **2a** (514 mg, 2 mmol) and EP **29** (2 mmol, ≈0.3 ml) were refluxed together in DMF (25 ml) for 7 h. Concentration of the reaction mixture, subsequent dilution with water, extraction with chloroform and chromatography of the concentrated chloroform extract over silica gel with light petroleum yielded the xanthenone **11a** (82 mg, 19%). Further elution of the column with 1 : 10 ethyl acetate–light petroleum yielded the xanthenone **37a** (49 mg, 10%).

Treatment of enaminone 2b with EP 29

Enamine **2b** (271 mg, 1 mmol), like **2a**, was treated with EP **29** (≈0.2 ml). The reaction mixture after usual work-up was charged over a silica gel column, and elution of the column with ethyl acetate–light petroleum (1 : 10) gave the xanthenone **11b** (23 mg, 10%), benzene derivative **46** (8%), xanthenone **37b** (20 mg, 7%) and flavone **44b** (93 mg, 22%), mp 159 °C (Found: C, 67.9; H, 4.9. $C_{24}H_{22}O_7$ requires C, 68.2; H, 5.3%); ν_{max} (KBr)/cm^{-1} 1750 (ester CO), 1705 (acetyl CO), 1665 (pyrone CO), 1635 (C=C); δ_H 8.81 (1H, t, *J* 1.5, 4′-H), 8.45 (2H, d, *J* 1.5, 2′-, 6′-H), 8.04 (1H, poorly split d, 5-H), 7.56 (1H, dd, *J* 8.5 and 2.1, 7-H), 7.45 (1H, d, *J* 8.5, 8-H), 4.45 (4H, q, 2 × OC*H*$_2$Me), 2.62 (3H, s, COMe), 2.50 (3H, s, 6-Me) and 1.44 (6H, t, 2 × CH$_2$*Me*).

Treatment of the enamines 1 with DMAD 27 in refluxing methanol. General procedure

A mixture of an enamine **1** (1 mmol) and DMAD **27** (1 mmol, ≈0.15 ml) was heated under reflux in dry methanol (30 ml) for 8 h. The reaction mixture was concentrated, cooled, diluted with water and extracted with chloroform. The chloroform extract on concentration was subjected to column chromatography over silica gel. Elution of the column with ethyl acetate–light petroleum (1 : 5) gave the corresponding xanthenone **33** (9–15%) in the first few fractions and the corresponding chromenone derivative **49** (32–37%) in the later fractions. The following chromenone derivatives **49** were prepared by this method.

Dimethyl (*E*)-3-(4-oxo-4*H*-1-benzopyran-2-yl)propene-1,2-dicarboxylate 49a. From **1a** as colourless crystals (35%), mp 152 °C (Found: C, 63.2; H, 4.4. $C_{16}H_{14}O_6$ requires C, 63.6; H, 4.7%); δ_H 8.19 (1H, dd, *J* 7.9 and 1.5, 5′-H), 7.70 (1H, m, 7′-H), 7.46 (2H, m, 6′-, 8′-H), 7.41 (1H, s, 1-H), 6.46 (1H, s, 3′-H), 4.01 (2H, s, 3-H$_2$), 3.89 (3H, s, CO$_2$Me) and 3.73 (3H, s, CO$_2$Me).

Dimethyl (*E*)-3-(6-methyl-4-oxo-4*H*-1-benzopyran-2-yl)-propene-1,2-dicarboxylate 49b. From **1b** as white solid (32%), mp 140 °C (Found: C, 64.8; H, 4.7. $C_{17}H_{16}O_6$ requires C, 64.5; H, 5.1%); δ_H 7.98 (1H, d, *J* 1.5, 5′-H), 7.50 (1H, dd, *J* 8.5 and 1.5, 7′-H), 7.42 (1H, s, 1-H), 7.35 (1H, d, *J* 8.5, 8′-H), 6.42 (1H, s, 3′-H), 3.99 (2H, s, 3-H$_2$), 3.87 (3H, s, CO$_2$Me), 3.71 (3H, s, CO$_2$Me) and 2.45 (3H, s, 6′-Me); δ_C 178.1 (4′-C), 170.6 (*C*O$_2$Me), 166.7 (*C*O$_2$Me), 159.1 (2′-C), 154.1 (8′a-C), 135.8 (6′-C), 135.6 (7′-C), 132.3 (1-C), 132.0 (2-C), 125.1 (5′-C), 123.6 (4′a-C), 117.7 (8′-C), 115.8 (3′-C), 53.0 (CO$_2$*Me*), 52.4 (CO$_2$*Me*), 34.0 (3-C) and 20.9 (6′-Me); *m*/*z* 316 (M$^+$, 100%), 285 (M − OMe, 56), 257 (285 − CO, 99), 226 (257 − OMe, 53), 198 (226 − CO, 83), 170 (198 − CO, 78).

Dimethyl (*E*)-3-(6-chloro-4-oxo-4*H*-1-benzopyran-2-yl)-propene-1,2-dicarboxylate 49c. From **1c** as colourless crystals (37%), mp 140 °C (Found: C, 56.8; H, 4.1. $C_{16}H_{13}ClO_6$ requires C, 57.1; H, 3.9%); δ_H 8.13 (1H, d, *J* 2.6, 5′-H), 7.64 (1H, d, *J* 8.9, 2.6, 7′-H), 7.43 (1H, d, *J* 8.9, 8′-H), 7.38 (1H, s, 1-H), 6.45 (1H, s, 3′-H), 3.98 (2H, s, 3-H$_2$), 3.88 (3H, s, CO$_2$Me) and 3.71 (3H, s, CO$_2$Me).

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