Benzopyrans. Part 41.¹ Reactions of 2-(2-dimethylaminovinyl)-1benzopyran-4-ones with various dienophiles

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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.³2-(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.

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 ¹³C 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



Scheme 1 Reagents and conditions: i, $R'CO_2Et$ (R' = Me, Ph), Na, reflux (ref. 4); ii, aq. HCl, MeOH, reflux (ref. 5); iii, Ac₂O, fused NaOAc, reflux (ref. 6); iv, dimethylformamide dimethyl acetal (DMFDMA), C_6H_5N , reflux (ref. 7); v, DMFDMA, C_6H_6 , reflux (ref. 8). " The suffixes **a**, **b** and **c** associated with all other structures bear the same connotation for **R** as written here.

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.

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

Comp."		Mp/°C	$\delta_{\rm H}({\rm CDCl}_3; 300 {\rm ~MHz})^b$							
	Yield (%)		5-H	o-H of COPh (m)	$= CHNMe_2$ (d, $J \approx 13$)	Other ArH (m)	3-H/Ac (s)	2-Me (s)/ CH=CHNMe ₂ (d, $J \approx 13$)	NMe ₂ (br s)	
7b ^{<i>c</i>}	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	
^{<i>a</i>} All the co	mpounds ga	ve satisfactorv	elemental a	unalvsis. ^b All a	aromatic protons s	how normal aro	matic splitting	. ^c Protons of 6-Me gr	oup 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 ¹³C NMR data ($\delta_{\rm C}$; CDCl₃; 75 Hz) of some representative 1-benzopyran-4-ones 7, 8 and 1–3

Carbon	_	Compound										
number/nature	7c	8b	8c	1 a	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		
CHNMe.				146.5	146.5	146.7	150.9	151.5	148.5	149.1		
CH=CHNMe.				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.		2017		a	a 2010	a	40.7^{b}	45 5 ^b 37 2 ^b	a 2010	а		
3-COMe	a						201.0	200.7				
3-COMe	32.0						32.8	33.1				
3-COPh	0210	193.8	193 1				02.0	2011	196 1	195.6		
COPh: 1'-C		137.4	137.0						139.2	138.8		
2'-C		129.3	129.3						129.2	129.1		
3'-C		128.6	129.3						129.2	129.1		
4'-C		133.5	133.7						132.5	132.7		





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

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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.96 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 ¹³C 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.

	Mp/°C	Found (%) (Requires)		$\delta_{\rm H}({\rm CDCl}_3; 300 {\rm ~MHz})^a$					
Comp.		С	Н	OH/OAc (s) ^b	8-H	6-H	3-H	Other ArH	
11 a	148 °			12.63	8.26	7.74	7.53	7.45-6.78	
11b ^{<i>d,e</i>}	140	74.2	4.7	12.70	8.04	7.53	7.57	7.41-6.77	
		(74.3	4.5)						
11c	177	63.0	3.2	12.41	8.22	7.67	7.60	7.47-6.81	
		(63.3	2.9)						
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	2.0	13.45	8.29	7.83	8.06	7.66-7.46	
		(42.2	1.6)						

^{*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 4¹³C NMR data of 1-hydroxy-9H-xanthen-9-ones 11 and 13

	Compound							
Carbon	11a ^{<i>a</i>}	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*	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						
Dools assignmo	nt is confirma	d by ¹³ C H	orrelation b	Dooles assigned				

" Peak assignment is confirmed by ¹³C–H correlation. " 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 2,3olefinic 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 ¹H 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 con-



Scheme 2

sequently 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.

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 pyrano-pyridine **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

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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 $30 \longrightarrow 31$ may not be completely ruled out.^{13,14} The ring-opened intermediate 31 incorporating a pre-existing double bond at the pyran 2,3position behaves as a hexatriene system which by electrocyclisation¹⁵ (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 electronrich 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 electrondeficient 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



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Comp			Found (%)		$\delta_{\rm H}({\rm CDCl}_3; 300 {\rm MHz})^a$						
(Mol. formula)	Yield (%)	Mp/°C	C	H	1-H/1-Me (s)	8-H	4-H (s)	6-H	5-H and other ArH (m)	CO ₂ Me (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 ^{<i>d</i>}		(65.4	3.9)						3.96	
33b ^{<i>e</i>,<i>f</i>}	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 ^{<i>f</i>}	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 ^{<i>f</i>}	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*} v_{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*} v_{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. ^{*s*} Mean position of the multiplets due to four *ortho* protons of the two benzoyl groups. ^{*h*} λ_{max} (EtOH)/nm 212 (log *e* 4.32), 241 (4.37), 256 (4.45) and 357 (3.67); v_{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
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	Compound											
number	33b	33c	35b	36a	36b	36c	37b ^{<i>a</i>}					
Xanthenone C:1	129.2	129.3	132.1 ^{<i>b</i>}	131.9 ^{<i>b</i>}	132.1 ^{<i>b</i>}	132.7 ^{<i>b</i>}	129.3					
2	125.4	126.4	131.4 ^b	132.1 ^{<i>b</i>}	132.3 ^{<i>b</i>}	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					
CO ₂ Alkyl	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	,	<i>,</i>	,						
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						

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 ¹H 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 known¹⁸ 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).

 $\begin{array}{c} F_{3}\ddot{N} \\ F_{3}\ddot{N} \\ F_{3}\ddot{N} \\ F_{3}\ddot{N} \\ F_{3}\ddot{N} \\ F_{3}\dot{N} \\$

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 $\alpha,\beta,\gamma,\delta$ -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 heteroatomcontaining nucleophiles¹⁹ in giving substituted fumarate with acetylenedicarboxylic ester.



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 esters²² 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 CDCl₃ 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 Na₂SO₄ unless stated otherwise, and solid products were dried over P₂O₅ *in vacuo*.

ω-Acyl-2-hydroxyacetophenones 5a-c

2-Hydroxyacetophenone **4a** on acylation with ethyl acetate in the presence of molecularised sodium⁴ gave ω -acetyl-2hydroxyacetophenone **5a** (R¹ = Me) (68%), mp 110 °C (lit.,⁴ 90– 92 °C). The other two acetophenones **4b** and **4c** were similary converted into **5b** and **5c** (R¹ = Me), respectively, having mps 112 and 118 °C, respectively. ω -Benzoyl-2-hydroxyacetophenone **5a** (R¹ = Ph) was similarly prepared, only ethyl acetate being replaced by ethyl benzoate. The compounds **5a,b,c** (R¹ = 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** (R¹ = 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 (R¹ = Me) and 5 (R¹ = Ph) on refluxing with acetic anhydride in the presence of fused sodium acetate⁶ 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, \approx 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); $\delta_{\rm H}$ 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, CH₂CH₂); $\delta_{\rm C}$ 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·HCONMe2 was obtained from fractions 6-9 as yellow crystals (42%), mp 254 °C (Found: C, 64.4; H, 3.4; N, 6.3. C₂₁H₁₀NClO₄·HCONMe₂ requires C, 64.2; H, 3.8; N, 6.2%); $\delta_{\rm H}$ 9.26 (1H, s, *H*CONMe₂), 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-9H-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 (Na₂SO₄) 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-9Hxanthen-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. C₂₁H₁₂O₅ requires C, 73.2; H, 3.5%); v_{max} (KBr)/ cm⁻¹ 3070 (chelated OH), 2900 (CH of CHO), 1698 (CHO), 1660 (CO), 1620 (CO) and 1605 (C=C); $\delta_{\rm H}$ 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-9H-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).

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, $\approx 0.2 \text{ ml}$) 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, \approx 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 benzenetricarboxylate 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-1,3,5tricarboxylate **46** had mp 134 °C (lit., ¹⁸ 135–136 °C); $\delta_{\rm H}$ 8.84 (3H, s, ArH), 4.43 (6H, q, OCH₂Me) and 1.43 (9H, t, OCH₂-*Me*); $\delta_{\rm C}$ 165.1 (ester CO), 134.4 (phenyl C-H), 131.7 (phenyl carbon linked to CO₂Et), 61.6 (OCH₂Me) and 14.3 (Me); m/z 294 (M⁺, 18%), 266 (M - C₂H₄, 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, OCH₂Me) and 1.43 (3H, t, CH₂Me).

Ethyl 7-methyl-9-oxo-9H-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, OCH₂Me), 2.41 (3H, s, 7-Me) and 1.46 (3H, t, CH₂Me). ¹³C NMR data are given in Table 6.

Ethyl 7-chloro-9-oxo-9H-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%); v_{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, OCH₂Me) and 1.44 (3H, t, CH₂Me).

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 × CH₂*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 × OCH₂Me) and 1.46 (6H, t, 2 × CH₂Me).

Treatment of enaminone 2a with EP 29

The enamine **2a** (514 mg, 2 mmol) and EP **29** (2 mmol, \approx 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. C₂₄H₂₂O₇ requires C, 68.2; H, 5.3%); v_{max} (KBr)/cm⁻¹ 1750 (ester CO), 1705 (acetyl CO), 1665 (pyrone CO), 1635 (C=C); $\delta_{\rm H}$ 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 × OCH₂Me), 2.62 (3H, s, COMe), 2.50 (3H, s, 6-Me) and 1.44 (6H, t, 2 × CH₂Me).

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 derivatives 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-1,2dicarboxylate 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-H₂), 3.89 (3H, s, CO₂Me) and 3.73 (3H, s, CO₂Me).

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-H₂), 3.87 (3H, s, CO₂Me), 3.71 (3H, s, CO₂Me) and 2.45 (3H, s, 6'-Me); δ_C 178.1 (4'-C), 170.6 (CO₂Me), 166.7 (CO₂Me), 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 (CO₂Me), 52.4 (CO₂Me), 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-4H-1-benzopyran-2-yl)-propene-1,2-dicarboxylate49c.From 1cas colourless crystals(37%), mp 140 °C (Found: C, 56.8; H, 4.1. $C_{16}H_{13}ClO_6$ requiresC, 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-H₂), 3.88 (3H, s, CO_2Me) and 3.71 (3H, s, CO_2Me).

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