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The synthesis of the 7-dimethylamino-1,4-benzoxazin-2-ones (5), fluorescent dyes, by condensing α-keto-acids with 2-amino-5-dimethylaminophenol is described. When the 3-substituent is a methyl group, these compounds can be further condensed with aromatic aldehydes to provide the styryl dyes (6). These products are easily opened by hydrochloric acid in ethanolic solution to afford the corresponding benzalketoacid ethyl esters (7).

The 7-amino-1,4-benzoxazin-2-ones, a new class of fluorescent dyes, have been recently described [1]. In these molecules, as in the 7-aminocoumarins, for instance, the chromophore is not symmetrical, and the dipole moment in the excited state is much larger than in the ground state.

In these molecules, the first singlet state offers an internal charge transfer character [2], owing to conjugation between the electron-donor amino substituent in the 7-position, and the electron withdrawing carbonyl group of the heterocycle. Consequently, a large Stokes shift between absorbance and fluorescence maxima is expected. We found, indeed, for dyes 1, that these shifts are often greater than 100 nm. If the donor character of the 7-substituent were increased, by replacement of H atoms by alkyl groups, for example, the shift should be even larger [3,4], because the polar excited state 5B in this dyes would be even more stabilized.

With this in mind, we have carried out the synthesis of several 7-dimethylamino-1,4-benzoxazin-2-ones 5, by cyclising 2-amino-5-dimethylaminophenol 3 with α-ketoacids or α-ketoesters. The diaminophenol was previously obtained by Möhlbau [5], by reducing 5-dimethylamino-2-nitrosophenol 2 in hydrochloric acid with a stannous salt. In neutral or basic solution this product is very quickly oxydized producing 8-amino-3-dimethylaminophenoxazine-7-one 4 [5], a blue dye. We prefer to perform a catalytic hydrogenation of nitrosophenol 2 to diamine 3, which is either immediately cyclized under inert gas or is converted into the dihydrochloride which may be isolated. The cyclisation is easy, but less fast than for 2,5-diaminophenol in the synthesis of dyes 1.

The dyes 5 exhibit an intense fluorescence, not only in organic solutions, but also in the crystalline state. The solutions are stable, provided that the dyes are carefully purified; otherwise, impurities catalyze a fast deterioration in solution.
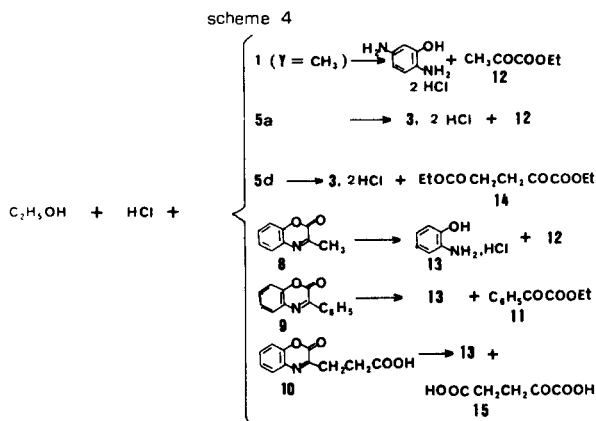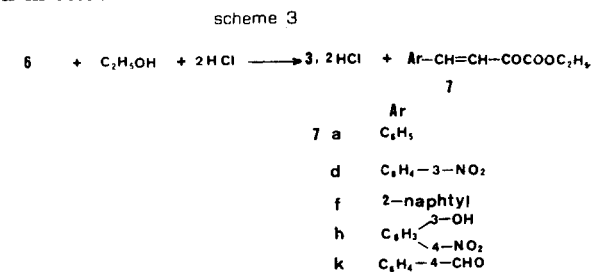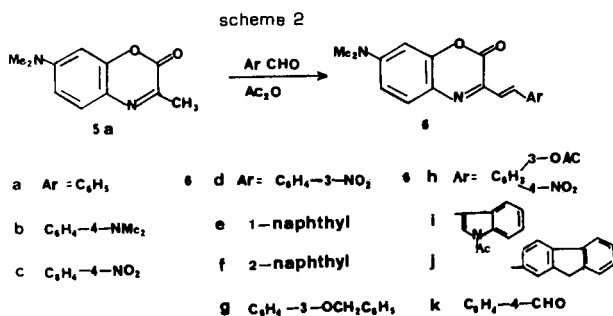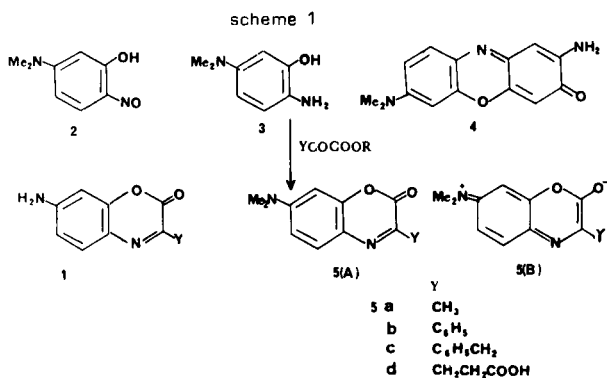
scheme 1

scheme 2

scheme 3

scheme 4

Table 1

Melting Points, Yields and Analytical Data for Dyes 5 and 6

Compound No.	Yield (%)	Mp °C	Recrystallization Solvent	Molecular Formula	Analysis % Calcd./Found		
					C	H	N
5a	74-80 [a]	124	ethanol or diluted pyridine	$C_{11}H_{12}N_2O_2$	64.70 / 64.76	5.88 / 6.11	13.72 / 13.65
5b	82 [a]	177	ethanol or diluted pyridine	$C_{16}H_{14}N_2O_2$	72.18 / 72.02	5.26 / 5.40	10.53 / 10.49
5c	55 [a]	136	ethanol or diluted pyridine	$C_{17}H_{16}N_2O_3$	72.86 / 72.84	5.71 / 5.86	10.00 / 9.99
5d	41 [a]	217	acetone	$C_{13}H_{14}N_2O_4$	59.54 / 59.97	5.34 / 5.48	10.69 / 10.41
6a	96	176	pyridine-water (70-30)	$C_{18}H_{16}N_2O_2$	73.97 / 73.67	5.48 / 5.64	9.59 / 9.65
6b	21	254	pyridine	$C_{20}H_{21}N_3O_2$	71.64 / 71.80	6.27 / 6.09	12.54 / 12.55
6c	77	253	pyridine	$C_{18}H_{15}N_3O_4$	64.09 / 64.00	4.45 / 4.33	12.46 / 12.57
6d	68	217	pyridine	$C_{18}H_{15}N_3O_4$	64.09 / 63.97	4.45 / 4.53	12.46 / 12.28
6e	83	192	pyridine-water (50-50)	$C_{22}H_{18}N_2O_2$	77.19 / 76.99	5.26 / 5.18	8.19 / 8.02
6f	78	209	pyridine-water (50-50)	$C_{22}H_{18}N_2O_2$	77.19 / 76.79	5.26 / 5.20	8.19 / 8.04
6g	78	174	pyridine-water (40-60)	$C_{25}H_{22}N_2O_3$	75.38 / 75.18	5.53 / 5.59	7.03 / 6.89
6h	65	267 dec	pyridine	$C_{20}H_{17}N_3O_6$	60.76 / 60.32	4.30 / 4.35	10.63 / 10.48
6i	64	234	pyridine-water (65-35)	$C_{22}H_{19}N_3O_3$	70.78 / 70.81	5.09 / 5.16	11.26 / 11.26
6j	32	270 dec	pyridine	$C_{25}H_{20}N_2O_2$	78.95 / 78.73	5.26 / 5.36	7.37 / 7.52
6k	84	235	pyridine	$C_{19}H_{16}N_2O_3$	71.25 / 71.36	5.00 / 5.09	8.75 / 8.92

[a] From 5-dimethylamino-2-nitrosophenol.

The benzoxazinone 5a (Y = CH$_3$) easily reacts on heating with various aromatic aldehydes. The styryl derivatives 6 are obtained with good yields. this reaction has been utilized previously with other heterocycles having a methyl group on the carbon atom α to the heterocyclic nitrogen, for example 2-methylquinoxaline [6] or benzoxazinone [7]. If the reaction is conducted in the absence of solvent, the final products are less pure and the yields lower than they are when the reaction is performed in acetic anhydride. In all cases the vinyl group is *trans*.

In contrast to the behaviour of benzoxazinones unsubstituted in 7-position, the 7-dimethylamino compounds do not undergo opening of the heterocyclic ring upon reaction with aromatic primary amines. On the other hand, these molecules are cleaved by reaction with alcoholic hydrochloric acid to give 2-amino-5-dimethylaminophenol dihydrochloride and the corresponding ethyl benzalpyruvate 7. These esters can be easily identified, either just as they are or by conversion into the dinitrophenylhydrazones. The cleavage of the heterocyclic ring likely proceeds by acid-catalyzed alcoholysis, followed or preceded

by acid hydrolysis of the azomethine C=N bond. The exact nature of the products appears to depend on the starting materials, thus, dyes 1 and 5a regenerate their initial constituents, the diaminophenyl (alkylated or not) and ethyl pyruvate 12, but the carboxylic acid 5d leads to the diethyl ester of α-ketoglutaric acid (14). In the same way, 3-methylbenzoxazinone (8) and 3-phenylbenzoxazinone (9) give 2-aminophenol hydrochloride (13), and ethyl pyruvate (12) and ethyl benzoylformate (11) respectively; but, surprisingly, under the same conditions, 3-carboxyethylbenzoxazinone (10) yields free α-ketoglutaric acid (15) and not its ester.

Fluorescent Properties.

For all dyes 6, an important bathochromic effect was observed in the absorption and emission spectra. The Stokes shift is always large and, consequently, the overlap between the absorption spectrum and the emission spectrum is very small.

Except for the nitro compounds, the dyes 1, 5 and 6 have an interesting laser action. Their lasing properties

Table 2

Spectral Data of Dyes **5** and **6**

Compound No.	UV-Visible Ethanol [a] λ max, nm (ε.10⁻⁴)	Fluorescence λ max, nm	IR ν cm⁻¹ C=O lactone	C=N	C=C (conjugate) CH=CH (trans) or others	N(CH₃)₂ (s)	H₈ (d)	H₆ (q)	H₅ (d) [b]	CH=CH [c]	Others
5a	255 (2.26) 403 (2.49)	551	1715	1620	—	2.81	6.42	6.61	7.57		2.47 (s, CH₃)
5b	270 (1.38) 443 (2.47)	549	1720	1605	—	2.78	6.37	6.59	7.63		7.25-7.63 (m, 3H), 8.35-8.57 (m, 2H)
5c	257 (1.73) 411 (2.02)	544	1732	1615	—	2.79	6.45	6.65	7.67		4.27 (s, CH₂), 7.28-7.70 (m, 5H)
5d	255 (2.34) 400 (2.64)	546	1720 1700 (acid)	1615	2200-3280 (OH bonded)	2.86	6.54	6.72	7.75		3.21, 3.44 (A′₂B′₂ CH₂-CH₂, J = 6.5 Hz)
6a	257 (1.14) 271 (1.60) 468 (3.20)	584	1720	1620	1590 3050	2.76	6.25	6.45	7.42	7.40 (d) 7.92 (d)	
6b	501 (7.70) (pyridine)	632 (pyridine)	1720	1625	1590 3040	2.78 2.82	6.51	6.70	6.72	7.73 (d) 8.32 (d)	7.65-7.75 (A₂B₂, 4H, J = 9 Hz)
6c	257 (1.58) 312 (2.46) 494 (3.64)	no fluorescence	1725	1625	1580 3060						
6d	290 (2.19) 477 (3.42)	no fluorescence	1715	1625	1600 3070						
6e	249 (1.53) 328 (0.9) 474 (3.83)	600	1718	1650	1600 3030						
6f	277 (1.70) 324 (1.90) 476 (3.97)	587	1720	1620	1590 3030						
6g	303 (1.26) 471 (2.94)	584	1725	1630	1590 3020	2.83	6.50	6.68	7.74	7.85 (d) 8.25 (d)	5.13 (s, CH₂), 7.10 (m, 1H), 7.32-7.50 (m, 6H), 7.57 (d, 2H)
6h	254 (1.58) 318 (1.63) 496 (4.59)	no fluorescence	1720 1772 (ester)	1615	1590 3100	2.86 [d] (+ CH₃)	6.52	6.70	7.74	7.86 (d)	7.24 (q, H′₃), 7.55 (d, H′₂), 8.10 (d, 8.12 (d) H′₅), J₂′,₆′ = 1.3, Hz, J₅′,₆′ = 8 Hz
6i	270 (1.36) 324 (1.09) 477 (3.40)	599	1720 1700 (amide)	1655	1590 3040						
6j	250 (1.2) 339 (2.30) 481 (2.65)	597	1720	1615	1595 3050						
6k	488 (3.95)	590	1720 1687 (conjugated aldehyde)	1625	1592 3050	2.86 [d]	6.53	6.61	7.76 (+ H₂′ + H₆′)	7.88 (d) 8.20 (d) = 8 Hz	7.94 (d, H₃′ + H₅′), J₂′,₃′, or J₅′,₆′ = 8 Hz, 10.10 (s, CHO)

[a] Except for **6b**. [b] For all benzoxazinones, the coupling constants of the aromatic protons are identical: $J_{6,8} = 3$ Hz, $J_{5,6} = 9$ Hz. [c] For vinyl group, CH=CH *trans*, in dyes **6**, J = 16 Hz. [d] At 350 MHz.

are comparable to those of commercial dyes, the coumarin family for instance. For dyes **1** (Y = CH₂C₆H₅) and **5a**, the laser yields are larger than that of coumarin 480. In particular, the tuning range of dye **5a** is remarkably wide, since two commercial dyes (rhodamine 6G and coumarin 495) are necessary to overlap the whole tuning range of this dye [8,9].

As regards spectral properties, the most interesting compound is the dye **6k**, obtained by condensation of the diaminophenol **3** with terephthalaldehyde. Owing to its terminal aldehydic group being in conjugation with the dimethylamino group, this dye exhibits a large red shift, as compared to the other dyes. It shows also the best quantum yield and the best photochemical stability. These spectral properties have already been reported [10].

EXPERIMENTAL

Melting points were determined on a Kofler hot plate and are uncorrected. Above 260° a Mettler FP 2 apparatus was used. The uv and visible spectra were recorded on a UVIKON 820 spectrophotometer. The ir spectra were obtained on a Perkin-Elmer 197 spectrophotometer as potassium bromide discs. The ¹H nmr spectra were obtained on a Perkin-Elmer R 32 spectrometer, except for less soluble substances which were studied with a CAMECA 350 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane (δ units). The mass spectra were determined on an AEI MS 902 or a VG 70-70 F spectrometer.

Table 3

Benzal Ketoesters from Dyes 6

Ar-CH=CH-CO-COOC$_2$H$_5$
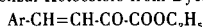
Product No.	Ar	Yield %	Mp, °C (Solvent)	Molecular Formula	Analysis % Calcd./Found			UV (ethanol) λ max (ε.10^{-4})	IR ν cm^{-1}				CH$_3$ (t)	CH$_2$ (q)	^{1}H NMR (ppm) [b] (pyridine d5)	
					C	H	N		CH=CH	C=O (ester)	C=O (ketone)	others			CH=CH (d,d)	others
7a [a]	C$_6$H$_5$	82	184 [a] (ethanol)	C$_{18}$H$_{16}$N$_4$O$_6$ [a]	56.25 56.39	4.16 3.96	14.58 14.67	424 (4.87), 308 (1.44), 251 (2.9)	3100	1688 (chelate)		3160 (NH)	1.36	4.48	lost in C$_6$H$_5$ signal (m, 7.23, 7.94)	6.78 (broad signal NH), 8.3 (d, H$_6$), 8.53 (q, H$_5$), 9.18 (d, H$_3$), J$_{3,5}$ = 2, J$_{5,6}$ = 10
7d	C$_6$H$_4$-3-NO$_2$	74	110 (ethanol-water 60-40)	C$_{12}$H$_{11}$NO$_5$	57.83 57.75	4.42 4.41	5.62 5.57	272 (2.46)	3080	1715	1685		1.23	4.35	7.68, 8.10	8.56 (s, H$_2$), 7.40-8.35 (m, 3H)
7f	2-naphtyl	59	105 (heptane)	C$_{16}$H$_{14}$O$_3$	75.59 75.71	5.51 5.56		326 (2.11), 277 (1.64)	3042	1722	1680		1.27	4.43	7.96, 8.28	5.56-8.13 (m, 6H), 8.18 (s, H$_1$)
7h	C$_6$H$_3$-3-OH-4-NO$_2$	58	145 (heptane)	C$_{12}$H$_{11}$NO$_6$	54.33 54.92	4.15 4.07	5.28 5.28	316 (2.13)	3100	1720	1690	3300 (OH)	1.36	4.45	8.0 (d, J = 12)	7.45 (q, H$_6$), 7.78 (d, H$_2$), 8.3 (d, H$_5$), 9.2 (s, OH)
7k	C$_6$H$_4$-4-CHO	64	100 (ethanol-water 50-50)	C$_{13}$H$_{12}$O$_4$	67.24 67.10	5.17 5.16		315 (2.38)	3060	1715	1685	1695 (CHO)	1.21	4.32	lost in aromatic signals	7.48-8.06 (m, 6H), 10.42 (CHO)

[a] Identified by its 2,4-dinitrophenylhydrazone. [b] For all vinylic ketoesters: J$_{CH=CH}$ $_{trans}$ = 16 Hz (except for 7h), J$_{CH_2-CH_3}$ = 7 Hz.

The physical, analytical and spectral data (except for mass spectra) for compounds 5, 6 and 7 are reported in Tables 1, 2 and 3.

5-Dimethylamino-2-nitrosophenol (2).

Nitrosation of 3-dimethylaminophenol 1 was performed in the same way as for N,N-dimethylaniline [11]. The stirred aqueous suspension of the hydrochloride thus obtained was treated with sodium acetate and the base 2 was recrystallized from acetone as red needles, mp 171° (lit [5] (169°), yield 82%; uv (ethanol): λ max, nm (ε) 403 (7500), 333 (7900); ir: ν cm^{-1} 3660-3160 (OH, intramolecular association), 1625 (C-N=O), 1520-1470 (N=O); nmr (DMSO-d$_6$): 5.7 (d, H$_6$), 6.84 (q, H$_4$), 7.26 (d, H$_3$), J$_{4,6}$ = 2 Hz, J$_{3,4}$ = 10 Hz, 18.24 (s, OH with intramolecular bonding). The N(CH$_3$)$_2$ signal is merged into the water band of dimethylsulfoxide; ms: m/e (relative intensity) 166 (M$^+$ 100), 152 (86), 149 (59), 136 (50), 44 (95).

2-Amino-5-dimethylaminophenol (3).

The crystalline nitroso compound 2 (4.15 g, 0.025 mole) in absolute alcohol (300 ml) was subjected to catalytic hydrogenation in the presence of Raney Nickel at room temperature and under ordinary pressure. After complete reduction a colorless solution was obtained.

For the preparation of benzoxazinones, this reaction mixture, kept under an inert atmosphere, was handled in one of two ways: either the α-ketoacid was added, and the solution was treated as shown below. Or, nickel was filtered off, hydrogen chloride gas was bubbled through the mixture, and the very hygroscopic, bluish, sternutatory hydrochloride was filtered off, washed with ether and kept protected from oxygen. The yield was quantitative; ir: (cm^{-1}) 3300-2100 (OH bonded and NH$^+$), 1940 (NH$_3$$^+$).

Anal. Calcd. for C$_8$H$_{14}$Cl$_2$N$_2$O: C, 42.67; H, 6.22; N, 12.44; Cl, 31.55. Found: C, 42.41; H, 6.20; N, 12.32; Cl, 31.11.

In order to obtain benzoxazinones, a mixture of this salt with a stoechiometric quantity of a α-ketoacid was treated by diluted pyridine (50/50).

8-Amino-3-dimethylaminophenoxazin-7-one (4).

This compound was described previously [4] but of course, in 1892, no spectral data were provided. If the reduction mixture above was submitted to oxygen action, it became very quickly purplish-blue and a crystal-

line dark green dye, with bronze reflects, was filtered off; it showed a pink fluorescence in various solvents, except in alcohols. This compound had mp 265° (diluted pyridine, yield 63%) (lit [5] 223°); visible spectra (acetone): λ max abs nm (ε) 523 (4300); λ max emission (acetone): 626 nm; ir: ν (cm^{-1}) 3410, 3300 (NH$_2$), 1635 (conjugated C=O); nmr (pyridine-d$_5$, 350 MHz): 2.86 (s, N(CH$_3$)$_2$), 6.56 (d, H$_4$), 6.66 (s, H$_9$), 6.71 (d, H$_2$), 6.89 (s, H$_6$), 7.01 (s, large NH$_2$), 7.73 (d, H$_1$, J$_{1,2}$ = 9 Hz, J$_{2,4}$ = 2.6 Hz); ms: m/e (relative intensity) 255 (M$^+$ 100), 254 (15), 240 (10), 239 (7), 228 (5), 212 (6), 79 (5).

Anal. Calcd. for C$_{14}$H$_{13}$N$_3$O$_2$: C, 65.88; H, 5.09; N, 16.47. Found: C, 65.87; H, 5.12; N, 16.51.

7-Dimethylamino-1,4-benzoxazin-2-ones 5. General Procedure.

In the following experiments, we described the cyclisation of diaminophenol 3 by α-ketoacids, directly in the reduction mixture of nitroso compound 2 (4.15 g, 0.025 mole) kept under inert gas cover, before filtration of dyes.

7-Dimethylamino-3-methyl-1,4-benzoxazin-2-one (5a).

After addition of ethyl pyruvate (4.7 g, 0.04 mole) the solution was kept for two hours on the boiling water bath. Appearance of fluorescence was almost instantaneous, the catalyst was filtered off and the alcohol evaporated to dryness. The yellow crystals were washed with acetone, filtered and crystallized; ms: m/e (relative intensity), 204 (M$^+$ 94), 176 (48), 175 (100), 160 (15), 92 (12).

7-Dimethylamino-3-phenyl-1,4-benzoxazin-2-one (5b).

Benzoylformic acid (4.5 g, 0.03 mole) was added to ethanolic solution of 3. The fluorescent mixture was kept for two hours on the boiling water bath, the catalyst was filtered hot and the filtrate evaporated almost to dryness. Orange-yellow crystals, with gilt reflects and bright-red fluorescence were obtained; ms: m/e (relative intensity) 266 (M$^+$ 45), 238 (95), 237 (100), 222 (40), 176 (30), 148 (60).

3-Benzyl-7-dimethylamino-1,4-benzoxazin-2-one (5c).

In this preparation, it should be emphasized that phenylpyruvic acid has to be very pure, as a matter of fact, this ketoacid is slowly decayed by the oxygen of air [12] and commercial product is often unsuitable. The

acid prepared by us [13], led to better yields. Phenylpyruvic acid (6.5 g, 0.04 mole) was dissolved in 50 ml of ethanol and added to the reduction solution and the mixture was heated for 3 hours on a boiling water bath, then nickel was separated and 75% of the amount of ethanol was removed. Pale yellow needles of the dye were filtered off; ms: m/e (relative intensity) 280 (M$^{+\cdot}$ 100), 252 (98), 251 (55), 12 (23), 105 (26), 91 (74).

7-Dimethylamino-3-(2-carboxyethyl)-1,4-benzoxazin-2-one (5d).

α-Keto glutaric acid (4.4 g, 0.03 mole) was added to diaminophenol, the mixture was heated on the water bath for 3 hours and left standing overnight. Nickel and the dye were filtered together, the dye dissolved in hot acetone and nickel filtered off. After evaporation of acetone, the green-yellow needles were recrystallized. They showed a beautiful pale-yellow fluorescence without solvent and yellow in organic solutions.

Styryl Derivatives 6. General Procedure.

Unless otherwise stated, a mixture of dye 5a (1 g, 0.005 mole) and 0.0075 mole of selected araldehyde were suspended in 4 ml of acetic anhydride and heated for 4 hours at 140° in an oil-bath. In most cases, after cooling, the styryl dye led to a heavy precipitate, which suspended in 10 ml of acetone and magnetically stirred for 2 hours, thus in this way the dyes were very pure.

7-Dimethylamino-3-styryl-1,4-benzoxazin-2-one (6a).

The dye 5a reacted with benzaldehyde (0.8 g). The brick-coloured styryl dye showed a bright yellow fluorescence in organic solvents and a bright red fluorescence in the crystalline state.

7-Dimethylamino-3-(4-dimethylaminostyryl)-1,4-benzoxazin-2-one (6b).

The dye 5a was heated for 5 hours with p-dimethylaminobenzaldehyde (1.2 g). After cooling the mixture was magnetically stirred with 10 ml of ethanol. We obtained dark red crystals with metallic reflects and with yellow to pink fluorescence in aprotic solvents. This fluorescence was immediately quenched by water or alcohols; ms: m/e (relative intensity) 335 (M$^{+\cdot}$ 100), 307 (25), 306 (58), 290 (13), 153 (10).

7-Dimethylamino-3-(4-nitrostyryl)-1,4-benzoxazin-2-one (6c).

After reaction of 5a with 4-nitrobenzaldehyde (1.2 g) dark red needles of the styryl dye were isolated and crystallized from pyridine. In this product the nitro group was very difficult to reduce. It was not fluorescent because of the quenching by the nitro group.

7-Dimethylamino-3-(3-nitrostyryl)-1,4-benzoxazin-2-one (6d).

This dye, prepared from 3-nitrobenzaldehyde, crystallized in dark red rod-like from pyridine. It was catalytically reduced, then its solution became fluorescent, but this fluorescence disappeared and, after evaporation of solvent, only a very impure powder was obtained.

7-Dimethylamino-3-(1-naphthylvinylene)-1,4-benzoxazin-2-one (6e).

After reaction of the dye 5a with 1.2 g of 1-naphthaldehyde, dark red needles with steel reflects and orange-yellow fluorescence were isolated.

7-Dimethylamino-3-(2-naphthylvinylene)-1,4-benzoxazin-2-one (6f).

From 2-naphthaldehyde, in the same way as that above, we isolated orange crystals which showed bright orange-yellow fluorescence in various solvents. It crystallized as brick-coloured tablets.

7-Dimethylamino-3-(3-benzyloxystyryl)-1,4-benzoxazin-2-one (6g).

When 3-hydroxybenzaldehyde reacted with the dye 5a in the presence of acetic anhydride, the phenolic group was acylated. Without anhydride both reactants led only to a resinous product. In order to avoid this disadvantage, the phenolic group should be protected before reaction. A convenient method consisted in the preparation of the benzyl ether (prepared according to ref [10]). Under the previously described conditions, 1.6 g of this ether reacted with 5a. The styryl dye 6g was orange needles with a bright yellow fluorescence in the solvents and bright red in the

crystalline state. All the attempts to reduce this ether in order to regenerate the phenolic group failed under a variety of conditions, eg. catalysts (Raney nickel, palladium chloride, palladium-charcoal); solvents (ethanol, pyridine, benzene); hydrogen pressure (1 to 15 bars), and temperature (25 to 70°), only a very impure dye was isolated. In the mass spectrum, the molecular ion had m/e = 400 (i.e. the vinyl double bond of the initial dye had been saturated).

7-Dimethylamino-3-(3-acetoxy-4-nitrostyryl)-1,4-benzoxazin-2-one (6h).

From 3-hydroxy-4-nitrobenzaldehyde (1.3 g) dark green crystals with steel reflects were obtained. Of course, by this reaction, the phenolic group had been acetylated; ms: m/e (relative abundance) 395 (M$^{+\cdot}$ 16), 352 (45), 332 (11), 322 (8), 291 (11), 263 (15), 60 (49), 45 (70), 44 (97), 43 (100).

7-Dimethylamino-3-[3-(1-acetyl)indolylvinylene]-1,4-benzoxazin-2-one (6i).

By reaction of the dye 5a with indole-3-carboxaldehyde (1.1 g) in acetic anhydride, the NH heterocyclic group of indole was acetylated. The vinyl dye showed dark red needles with metallic reflects and orange-yellow fluorescence; ms: m/e (relative intensity) 373 (M$^{+\cdot}$ 100), 358 (45), 331 (33), 330 (55), 303 (18), 302 (37), 286 (18), 43 (15).

7-Dimethylamino-3-(2-fluorenylvinylene)-1,4-benzoxazin-2-one (6j).

This dye was obtained on heating the dye 5a with 2-fluorenecarbaldehyde (1.5 g) for 6 hours. It was obtained as dark red needles with bright yellow fluorescence in organic solutions; ms: m/e (relative intensity) 380 (M$^{+\cdot}$ 100), 352 (20), 351 (44), 335 (12), 190 (18), 175 (13), 79 (18).

7-Dimethylamino-3-(4-formylstyryl)-1,4-benzoxazin-2-one (6k).

Phthalaldehyde (1.2 g) underwent a monocondensation with 5a. The styryl dye was obtained as pink-red needles and had an intense pink fluorescence in organic solvents; ms: m/e (relative intensity) 320 (M$^{+\cdot}$ 59), 292 (28), 291 (76), 275 (14), 131 (14), 92 (11), 44 (100).

Vinylic α-Ketoesters from Benzoxazinones 6. General Procedure.

The styryl dyes 6 were treated on a boiling water bath with 40 parts of a mixture of ethanol and concentrated hydrochloric acid in equal quantities. The cleavage of the heterocycle was generally very fast and was observed by bleaching of the initial solution. If the final mixture was made alkaline, the characteristic blue color of phenoxazinone 4 was immediately observed. This vinylic ketoesters can be normally prepared from araldehyde and ethyl pyruvate [13], but, most of the products described in this paper were previously unknown.

Ethyl 2-Oxo-4-phenyl-3-butenoate (7a).

The styryl dye 6a was heated on a boiling bath for 20 minutes. The ester 7a was a yellow oil [11]. In order to identify it, we obtained a 2,4-dinitrophenylhydrazone, as long bright orange needles, after heating the reaction mixture with 2,4-dinitrophenylhydrazine for 15 minutes on the water bath; ms: m/e (relative intensity) 384 (M$^{+\cdot}$ 22), 367 (10), 349 (100), 321 (40), 290 (56), 261 (24), 131 (74), 129 (52), 115 (37), 103 (35).

Ethyl 2-Oxo-4-(3-nitrophenyl)-3-butenoate (7d).

The bleaching of the solution of dye 6d is very rapid (5 minutes). On cooling, the crystalline ketoester, as silky colourless needles, partially precipitated. Upon dilution of filtrate, a second crop was isolated.

Ethyl 2-Oxo-4-(2-naphthyl)-3-butenoate (7f).

After heating dye 6f for 15 minutes on a boiling water bath, we obtained a pale yellow crystalline precipitate, which showed straw-yellow tablets after recrystallization.

Ethyl 2-Oxo-4-(3-hydroxy-4-nitrophenyl)-3-butenoate (7h).

The bleaching of dye 6h was complete after heating 20 minutes. After cooling, lemon crystals were isolated. After recrystallization, the product formed pale orange tablets. Of course, in this reaction the ester function was also hydrolysed giving a free phenolic group; ms: m/e (relative abundance) 265 (M$^{+\cdot}$ 5), 192 (100).

Ethyl 2-Oxo-4-(4-formylphenyl)-3-butenoate (**7k**).

The bleaching of the solution of dye **6k** was almost instantaneous. The pale yellow solution was evaporated to dryness and the putty-coloured ester was recrystallized and formed silky light beige platelets; ms: m/e (relative intensity) 232 (M$^{+\cdot}$ 9), 159 (100), 131 (21), 103 (41), 77 (23), 45 (13).

Acid Ethanolyse of Benzoxazinones. Generalization of the Reaction.

The reaction described above, has been applied to some other benzoxazinones besides styryl derivatives. Compound **1** (Y = CH$_3$), **5a**, **5d**, 3-methyl-1,4-benzoxazin-2-one (**8**), 3-phenyl-1,4-benzoxazin-2-one (**9**); 0.5 g of each compound was suspended in 30 ml of the ethanol-hydrochloric acid mixture and heated for 15 minutes on a boiling water bath. After cooling, the 2,4-dinitrophenylhydrazones of the ketoesters were isolated from reaction mixture. Their melting points were compared to those reported in the literature.

The 2,4-Dinitrophenylhydrazone of ethyl pyruvate (**12**) had mp 154-155° (*cf.* [14]).

The 2,4-Dinitrophenylhydrazone of ethyl benzoylfromate (**13**) had mp 162° (*cf.* [15]).

The 2,4-Dinitrophenylhydrazone of 2-ketoglutaric acid, 1,5-diethyl ester (**14**) had mp 86° (*cf.* [16]); uv (ethanol): λ max, nm (ε) 358 (55700); ir (potassium bromide): ν cm^{-1} 3180 (NH), 1720, 1690 (C=O), 1612 (NH); nmr (pyridine-d$_5$): 1.25 (t, CH$_3$), 2.90, 3.10 (q, AB, CH$_2$-CH$_2$, J = 6), 4.37 (q, CH$_2$), 8.13 (d, H$_6$), 8.54 (q, H$_5$), 9.17 (d, H$_3$), 14.20 (NH, chelate).

Anal. Calcd. for C$_{15}$H$_{18}$N$_4$O$_8$: C, 47.12; H, 4.71; N, 14.66. Found: C, 46.93; H, 4.52; N, 14.36.

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