Interaction of aminals of conjugated ω-dimethylaminoaldehydes with cyclic β-dicarbonyl compounds

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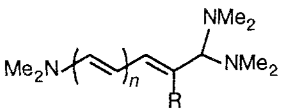
Reactions of aminals of conjugated ω-dimethylaminoaldehydes with Meldrum's acid, *N,N'*-(*o*-phenylene)malonamides, and 2,3-dihydrophenalene-1,3-dione afford δ-dimethylaminodienones, substituted 2-dimethylamino-2*H*-pyrans, or oxanine salts. Cation-anionic polymethine dyes have been obtained from the latter.

Key words: aminals of conjugated ω-dimethylaminoaldehydes, cyclic β-dicarbonyl compounds, δ-dimethylaminodienones, 2*H*-pyrans, oxanine salts, cation-anionic polymethine dyes.

Previously we showed that the condensation of aminals of β-dimethylaminoacrolein with acyclic β-dicarbonyl compounds affords a single product (δ-aminodienone, 2-dimethylaminopyrane, or their equilibrium mixture), whereas the reaction with indandione, dimedone, or 1,3-cyclohexanedione, along with δ-dimethylaminodienones, yields salts of trimethineoxanines, which are anionic dyes that can be used as the anionic constituents in the preparation of a new type of cationic-anionic polymethine dyes.[1—4]

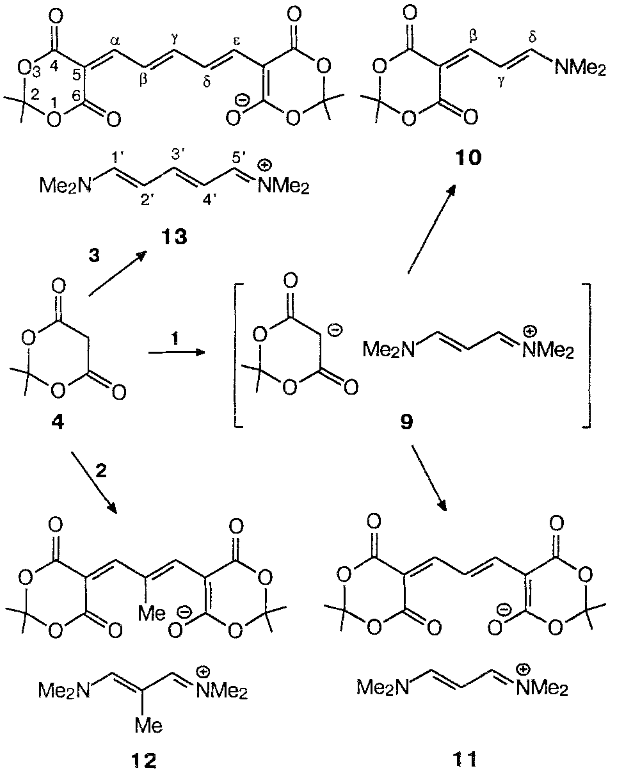
In this work, in order to elucidate the possibility of synthesizing oxanine salts from other cyclic β-dicarbonyl compounds we studied the condensation of aminals of conjugated ω-dimethylaminoaldehydes **1—3** with Meldrum's acid (**4**), *N,N'*-(*o*-phenylenemalonamide) (**5**) (see Ref. 5), *N,N'*-dimethyl-*N,N'*-(*o*-phenylene)malonamide (**6**) (see Ref. 5), 2,3-dihydrophenalene-1,3-dione (**7**) (see Ref. 6), and 1,3-cyclopentanedione (**8**).



1: R = H, $n = 0$
2: R = Me, $n = 0$
3: R = H, $n = 1$

The reaction of compound **1** with **4** initially affords salt (**9**) (λ_{max} 312 nm), which is converted upon heating into δ-dimethylaminodienodione (**10**) isolated in 45 % yield (Tables 1 and 2). The formation of a minor amount of oxanine salt **11** was indicated by a long-wave maximum (λ 450 nm) present in the UV spectrum of the mother liquor obtained after the separation of compound **10**. However, condensation of aminals **2** and **3** with compound **4** gives oxanine salts **12** and **13** in 58 and 20 % yield, respectively (Scheme 1).

Scheme 1



The interaction of aminals **1** and **2** with malonamides **5** and **6** affords only δ-dimethylaminodienediones (**14—17**) in good yields (see Table 1, Scheme 2).

According to the data from the ^{1}H NMR and UV spectra (see Table 2), compounds **16** and **17** exist only as the open-chain dienedione form **D**, in contrast to the

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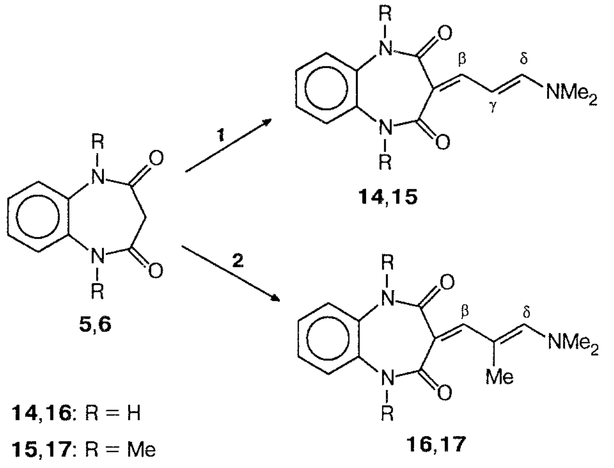
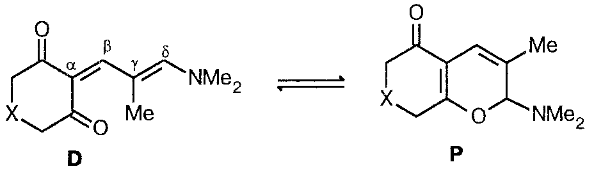
Scheme 2



14,16: R = H

15,17: R = Me

previously studied γ-methyl substituted δ-dimethylaminodienediones (**18—20**), which exist in an equilibrium with 2-dimethylamino-2*H*-pyrans **P**, with the latter substantially predominating:[2]



18: X = CH_2

19: X = CMe_2

20: X = CH_2CH_2

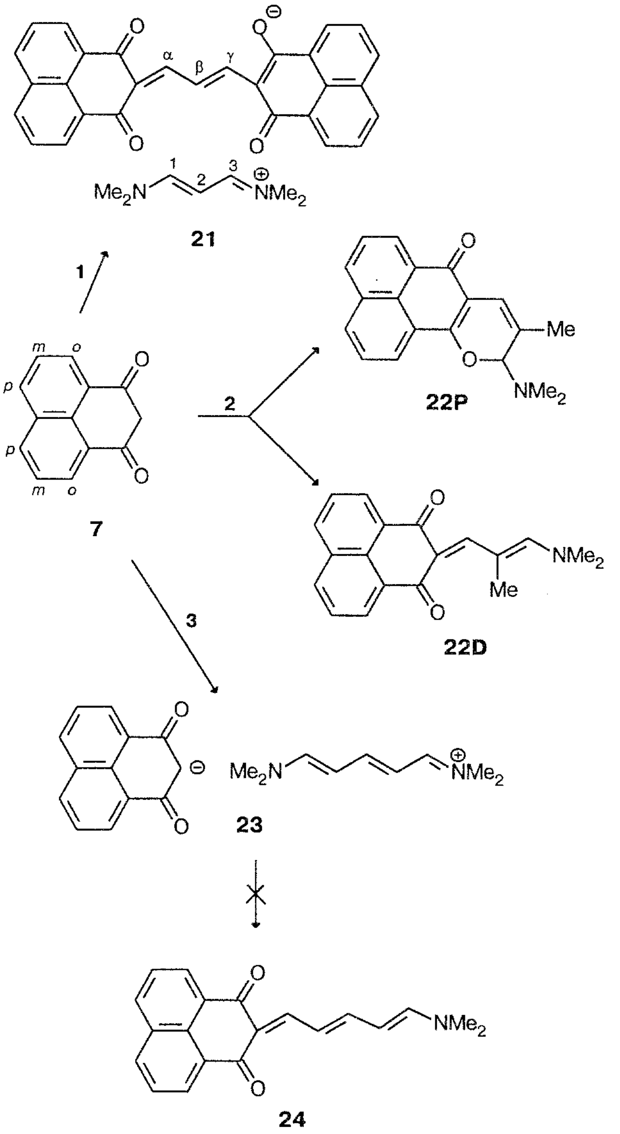
Condensation of compound **7** with aminal **1** affords the oxanine salt (**21**), and in the reaction with aminal **2** only substituted 2*H*-pyran (**22P**) is formed. According to the data from ^1H NMR and UV spectra, compound **22** exists as only the 2*H*-pyran form **22P**, irrespective of the solvent, and does not contain the open-chain dienedione form **22D**.

The reaction of compound **3** with **7** gives only the pentamethine salt (**23**), whose structure has been confirmed by ^1H NMR and UV spectra. Salt **23** cannot be converted to the trienedione (**24**). As has been shown previously, type **23** polymethine salts are intermediate products in the formation of ω-aminopolyenones from aminals and CH-acids, although in some cases the reaction is stopped at the step of the formation of the salt[2,7] (Scheme 3).

The reaction of aminals **1** and **2** with 1,3-cyclopentanedione **8** (unlike 1,3-cyclohexanedione) yields only resinous products.

δ-Dimethylaminodienediones **10** and **14—17** are dark-red crystalline solids. According to ^1H NMR spectra (J = 12÷13 Hz), in dienediones **10**, **14**, and **15**, *trans*-orientation of the methine protons and an *S-trans* conformation are realized.

Scheme 3

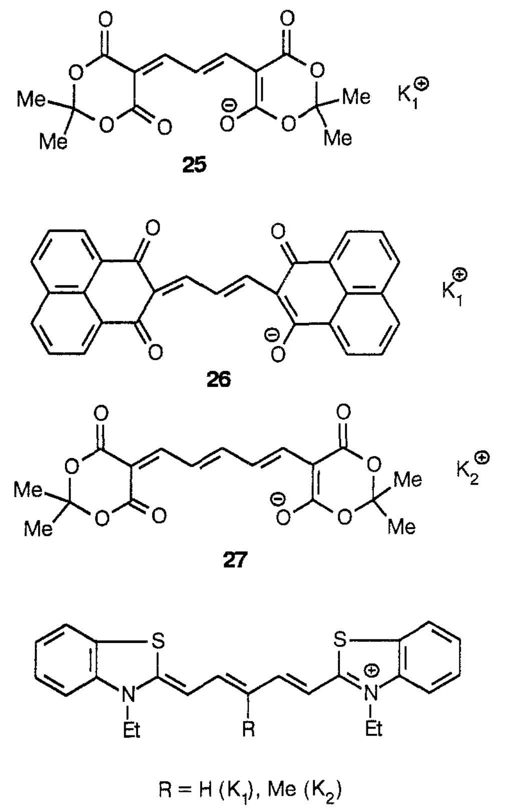


Oxanine salts **12**, **13**, and **21** readily undergo an exchange with the $K_1^{\oplus}$ and $K_2^{\oplus}$ cations of a cyanine dye to afford cyanine dyes, containing chromophores in both the cation and the anion and exhibit two absorption maxima with high extinction coefficients corresponding to the cationic and the anionic constituents. For instance, from salts **12** and **21**, dyes **25** and **26** were prepared, and salt **13** gave dye **27** (Scheme 4).

Experimental

UV spectra were recorded on a Specord UV-VIS instrument, ^1H NMR spectra were run on a Bruker WM-250 spectrometer (^1H 250 MHz) with TMS as the internal stand-

Scheme 4



ard. Signals for the methine protons were assigned using double resonance.

Reaction conditions, yields, and characteristics of compounds **10**, **14—17** are given in Tables 1 and 2.

For the isolation of compound **10**, the reaction mixture was cooled to 20 °C and dissolved in abs. MeOH. After cooling to −10 °C, the precipitate was separated and recrystallized from abs. MeOH. To isolate compound **14**, the precipitate was separated, washed with abs. ether and then with MeOH with stirring, and filtered off. For the isolation of compound **15**, benzene was evaporated, and the residue was triturated with abs. ether, filtered off, and washed with abs. ether and abs. EtOH. For the isolation of compound **16**, the reaction mixture was twice washed with ether and triturated with abs. EtOH, and the precipitate was filtered off and washed with abs. EtOH. To isolate compound **17**, the reaction mixture was triturated with abs. ether, and the precipitate was filtered off and washed with abs. ether.

3-Dimethylamino-2-methyl-2-propenylidenedimethylammonium salt of bis(4,6-dioxo-2,2-dimethyl-1,3-dioxane)-2′-methyltrimethineoxanine (12). A mixture of 0.45 g of compound **4** and 0.54 g of compound **2** was kept for 24 h at 20 °C and then diluted with abs. ether. The precipitate was separated and recrystallized from acetone to give 0.43 g (58 %) of salt **12** as an orange-colored solid, m.p. 167—168 °C. Found (%): C, 59.90; H, 7.22; N, 5.83. $C_{24}H_{34}N_2O_8$. Calculated (%): C, 60.23; H, 7.11; N, 5.85. UV (EtOH), λ_{max}/nm: 260 (ε 16000), 324 (ε 73300), 465 (ε 127500). ^{1}H NMR (CD$_3$OD), δ: anion 1.64 (s, 12 H, Me); 2.1 (s, 3 H, Me); 7.82 (s, 2 H, CH); cation 1.8 (s, 3 H, Me); 3.23 (s, 12 H, NMe$_2$); 7.18 (s, 2 H, CH).

5-Dimethylamino-2,4-pentadienylidenedimethylammonium salt of bis(4,6-dioxo-2,2-dimethyl-1,3-dioxane)pentamethineoxanine (13). A mixture of 0.17 g of compound **4** and 0.28 g of compound **3** in 5 mL of abs. ether was kept for 48 h at 20 °C and then washed with abs. ether. The precipitate was separated and recrystallized from dry acetone to give 0.06 g (20 %) of salt **13** as a violet-colored solid, m.p. 199—201 °C. UV (EtOH), λ_{max}/nm: 413 (ε 111000), 560 (ε 170000). ^{1}H NMR (CDCl$_3$), δ: for the anion: 1.68 (s, 12 H, Me); 7.2—7.4 (m, 3 H, H(β—δ)); 7.76 (d, 2 H, H(α,ε)); for the cation: 3.31 and 3.06 (s, 12 H, NMe$_2$); 5.62 (t, 2 H, H-2′,4′); 7.2—7.4 (m, 3 H, H-1′,3′,5′); $J_{2',1'} = J_{2',3'} = J_{3',4'} = J_{4',5'} =$ 12 Hz, $J_{\alpha\beta} = J_{\delta\varepsilon} =$ 13 Hz.

3-Dimethylamino-2-propenylidenedimethylammonium salt of bis(2,3-dihydrophenalenedione-1,3)-2-trimethineoxanine (21). A mixture of 2 g of compound **7** and 1.75 g of **1** in 5 mL of abs. benzene was boiled with stirring for 13 h. Benzene was evaporated, and the residue was washed with abs. ether and recrystallized from MeOH to give 1 g (35 %) of salt **21** as a red solid, m.p. 192—195 °C. UV (EtOH), λ_{max}/nm: 235 (ε 130000), 312 (ε 66500), 565 (ε 135000). ^{1}H NMR (DMSO), δ: for the anion: 7.56 (t, 1 H, H(β)), 8.07 (d, 2 H, H(α) and H(γ)); 7.75 (t, 4 H, H-*m*); 8.27 (d, 4 H, H-*o*); 8.42 (d, 4 H, H-*p*); for the cation 3.02 and 3.21 (s, 12 H, NMe$_2$); 5.35 (m, 1 H, H-2); 7.65 (d, 2 H, H-1 and H-3); $J_{1,3} = J_{2,3}$ = 12.6 Hz.

Table 1. Characteristics of compounds **10**, **14—17**

Compound	Reaction temp./°C (time/h),	Yield (%)	M.p. /°C	M$^+$, *m/z*	Molecular formula	Found/Calculated (%)		
						C	H	N
10	60 (0.25) 80 (1.5)	45	198—199*	225	$C_{11}H_{15}NO_4$	58.60 58.66	6.74 6.66	6.69 6.22
14	80 (2.5)**	86	240	257	$C_{14}H_{15}N_3O_2$			
15	80 (8)**	35	240	285	$C_{16}H_{19}N_3O_2$	67.36 67.37	6.79 6.67	15.0 14.74
16	100 (0.3)	50	214—216	271	$C_{15}H_{17}N_3O_2$	66.61 66.42	6.39 6.27	15.72 15.50
17	100—120 (0.3)	90	118—122	299	$C_{17}H_{21}N_3O_2$	68.27 68.23	7.10 7.02	14.35 14.05

* From MeOH. ** Abs. C_6H_6.

Table 2. UV and ^{1}H NMR spectra of compounds **10**, **14—17**

	UV, λ_{max}/nm (ε)			^{1}H NMR ($CDCl_3$, δ)		
Compound	EtOH	$CHCl_3$	NMe_2	Olefinic protons	Other protons	J/Hz
10	383 (58613)	380	3.15 3.30	7.97 (β); 6.90 (γ) 7.38 (δ)	1.7 (6 H, Me)	13 (β,γ); 12 (γ,δ)
14	220 (94700) 395 (9550)	395	2.95^a	7.29 (β+δ); 6.0 (γ)	7.0 (4 H, Ph); 9.35 (1H, NH); 9.55 (1 H, NH)	12.5 (β,γ),(γ,δ)
15	218 (40300) 390 (44600)	385	2.9	7.2 (β); 5.9 (γ); 6.75 (δ)	3.41 (3 H, Me); 3.35 (3 H, Me); 7.18 (4 H, Ph)	13 (β,γ),(γ,δ)
16	410 (60400)	405	3.09	6.55 (δ); 7.13 (β)	2.05 (3 H, Me); 7.75 (1 H, H-5^b); 7.0—7.15 (3 H, H-3, H-4, H-2^b); 8.23 (1 H, NH); 8.90 (1 H, NH)	
17	218 (30300) 380 (29100) 355 (hexane)	370	2.99	6.95 (β); 6.41 (δ)	3.34 (3 H, Me); 3.42 (3 H, Me); 1.69 (3 H, Me); 7.2 (4 H, Ph)	

^{a} The spectrum was recorded in DMSO. ^{b} The assignment of the ^{1}H NMR signals to H-2 and H-5 was arbitrary.

Table 3. Yields, characteristics, and UV spectral data for the cationic-anionic dyes **25—27**

Compound	Yield (%)	M.p. /°C	Molecular formula	Found / Calculated (%)				UV (EtOH), λ_{max}/nm
				C	H	N	S	($\varepsilon \cdot 10^{-4}$)
25	80	206—208	$C_{39}H_{40}N_2O_8S_2 \cdot 0.5H_2O$	63.32 63.52	5.81 5.56		8.72 8.68	465 (8.4)* 661 (18.0)
26	65	197—199	$C_{52}H_{38}N_2O_4S_2$					565 (9.5) 665 (10.5)
27	67	145—148	$C_{41}H_{42}N_2O_8S_2 \cdot H_2O$	63.92 63.73	5.55 5.69	3.42 3.63		560 (17.0) 658 (25.4)

* In CH_2Cl_2.

The reaction of aminal 3 with compound 7. A mixture of 0.5 g of **7** and 0.5 g of **3** in 3 mL of abs. benzene was boiled for 10 h. The UV spectrum of the reaction mixture: λ_{max} 235 and 420 nm. After evaporation of benzene, the residue was washed with abs. ether to afford 0.45 g of salt **23**, m.p. 105—110 °C. UV (EtOH), λ_{max}/nm: 235 (ε 28320), 420 (ε 52700). ^{1}H NMR (DMSO-d_6), δ: 2.95 and 3.17 (s, 12 H, NMe_2); 5.65 (t, 2 H, H-2,4); 7.1—7.3 (m, 3 H, H-1,3,5); 7.78 (t, 2 H, H-*m*); 8.2—8.45 (m, 4 H, H-*o,p*).

The reaction of aminal 2 with compound 7. A mixture of 0.5 g of **7** and 0.45 g of **2** was boiled with stirring for 2 h. After evaporation of benzene, the orange precipitate was washed with abs. ether and recrystallized from abs. MeOH to give 0.3 g (40 %) of 2*H*-pyran **22P**, m.p. 158—161 °C. Found (%): C, 78.42; H, 5.60; N, 4.79. $C_{19}H_{17}NO_2$. Calculated (%): C, 78.35; H, 5.84; N, 4.81. UV (EtOH), λ_{max}/nm: 218 (ε 49470), 240 (ε 46560), 295 (ε 24250), 355 (ε 21340), shoulder 370 (ε 16490); ($CHCl_3$), λ_{max}/nm: 290 (ε 17460), 355 (ε 14550), shoulder 370 (ε 1224); (hexane, λ_{max}/nm): 218 (ε 28876), 240 (ε 23500), 285 (ε 11640), 345 (ε 8960), shoulder 360 (ε 8050). ^{1}H NMR ($CDCl_3$), δ: 1.95 (s, 3 H, Me); 2.46 (s, 6 H, NMe_2); 5.78 (s, 1 H, H-2); 6.95 (s, 1 H, H-4); 8.61 (1 H, H-*o*); 7.6—7.8 (2 H, H-*o,m*); 8.0—8.3 (m, 3 H, H-*m,p*); (CD_3OD), δ: 1.98 (s, 3 H, Me); 2.5 (s, 6 H, NMe_2); 5.9 (s, 1 H, H-2); 6.85 (s, 1 H, H-4); 7.7—7.85 (m, 2 H, H-*o,m*); 8.2—8.45 (m, 3 H, H-*m,p*). MS, *m/z*: 291.

The cation-anionic dyes (25—27). Equimolar amounts of oxanine salt **12**, **13**, or **21** and a cyanine dye tosylate ($TsOK_1$ or $TsOK_2$) were separately dissolved without heating in minimum amounts of MeOH or EtOH. The solutions were filtered, combined, and cooled to −10 °C. After 1 h the resulting precipitate of the dye was separated and washed with alcohol and ether. The yields, characteristics of the compounds, and UV spectral data are given in Table 3.

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