

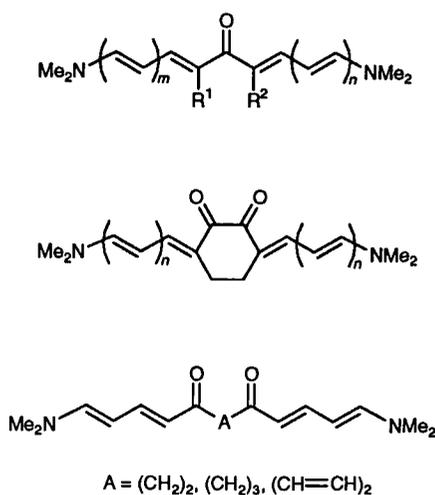
## Synthesis of Novel Substituted Phenols by Condensation of $\alpha,\beta$ -Unsaturated $\beta$ -Dimethylaminoaldehyde Aminals with Triketones

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Condensation of  $\alpha,\beta$ -unsaturated  $\beta$ -dimethylaminoaldehydes with heptane-2,4,6-trione unexpectedly affords a new type of substituted phenols (**4a-c**; **5a,c**) due to intramolecular cyclization accompanied by 1,6-deamination.

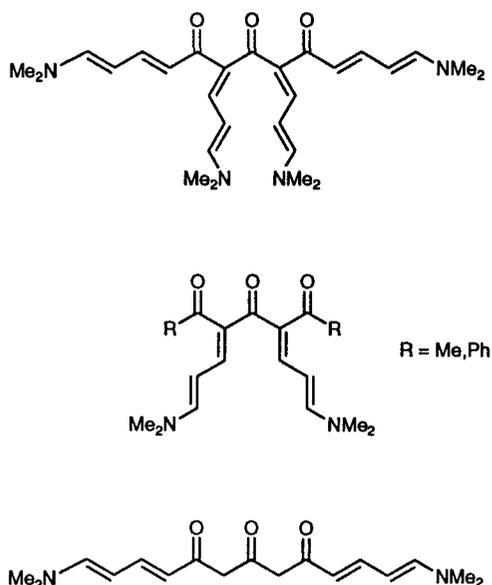
Earlier<sup>1-5</sup> we studied the interaction of aminals of conjugated  $\omega$ -dimethylaminoaldehydes with cyclic and acyclic ketones and diketones of various structures. The bis( $\omega,\omega'$ -dimethylamino-polyenyl)ketones and diketones resulting from this condensation contained two  $\omega$ -aminopolyenic chromophores separated by one or two C=O groups:



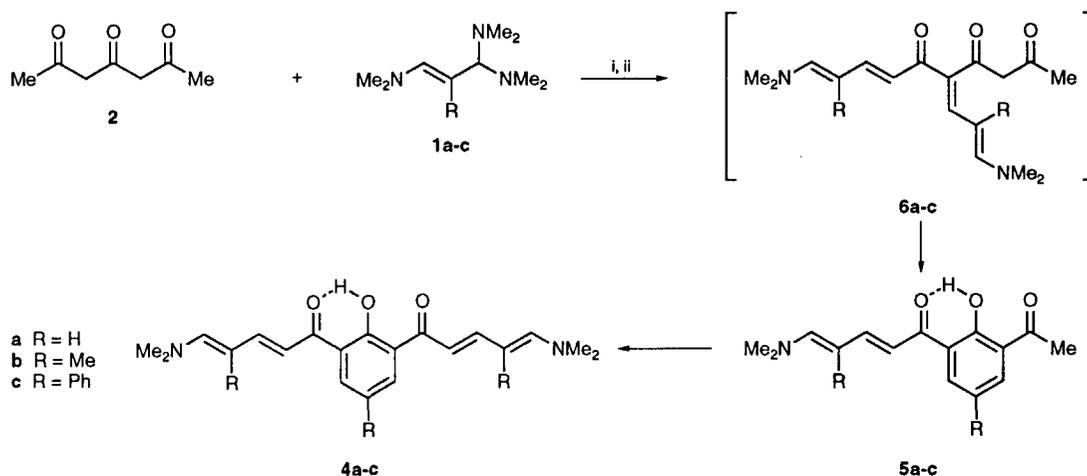
The investigation of these compounds has shown that they possess a number of specific properties, *viz.* solvatochromy, thermochromism, fluorescence, *etc.*<sup>6,7</sup>

The aim of this work was to study the interaction of aminals **1** (Scheme 1), where R=H (**1a**), Me (**1b**) or Ph (**1c**) with the following triketones: heptane-2,4,6-trione (**2**)<sup>8</sup> and 1,5-diphenylpentane-1,3,5-trione (**3**).<sup>9</sup>

The presence of reactive methyl and methylene groups in the triketones led us to believe that condensation with aminals **1a-c** would afford polyenic  $\omega$ -dimethylaminotriketones of various structures:



Unexpectedly, it appeared that condensation of aminals **1a-c** with triketone **2** in the ratio **1a-c**:**2** of 3:1 afforded 2,6-bis(5'-dimethylaminopenta-2',4'-dienoyl)phenols **4a-c**. Condensation of aminals **1a** and **1c** with triketone **2** in the ratio 2:1 allowed us to obtain 2-(5'-dimethylaminopenta-2',4'-dienoyl)-6-acetylphenol **5a** in low yield (Scheme 1).



**Scheme 1** Reagents and conditions: i (1a-c):2 = 3:1, benzene, 60–70 °C, 0.5 h; **4a** 70%, **4b** 62%, **4c** 50%; ii, (1a,c):2 = 2:1; 60–70 °C, 0.5 h; **5a** 19%, **5c** 22%.

It is likely that the reaction of **1a-c** with triketone **2** initially gives bis( $\omega,\omega'$ -dimethylaminopropenylidene)triketones **6a-c**; the latter undergo intramolecular cyclization accompanied by 1,6-deamination to afford phenols **5a,c**. If excess amination is present in the reaction mixture, phenols **4a-c** are formed from phenols **5a-c**.

The phenols **4a-c** and **5a,c** thus synthesized represent a new type of substituted phenol. These phenols are crystalline, yellowish-brown compounds. It follows from the  $^1\text{H}$  NMR spectral data that they have a *trans*-configuration of methine protons and exist as *S-trans*-conformers. The substituted phenols **4a-c** and **5a,c** are chelates stabilized by an intramolecular hydrogen bond; the latter was deduced from the  $^1\text{H}$  NMR spectra.

It should be noted that the  $\lambda_{\text{max}}$  values in the UV-spectra of the respective bis- and mono( $5'$ -dimethylaminopenta- $2',4'$ -dienyl)-substituted phenols **4a** and **5a**, **4c** and **5c** are very close, and the spectra differ only in the appearance of a short-wave shoulder (400–410 nm) in the spectra of the bis-substituted phenols.<sup>†</sup>

<sup>†</sup> General procedure and spectral characteristics.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  ( $^1\text{H}$  250 MHz). The assignment of methine protons was made based on the double resonance data.

A mixture of triketone **2** (0.5 g, 3.4 mmol) and amination **1a** (1.75 g, 10.2 mmol) in 5 ml of absolute benzene was warmed for 30 min at 60–70 °C. Benzene was evaporated, the residue was ground in absolute ether, and the deposit was filtered to afford 0.8 g (70%) of **4a**, m.p. 185–186 °C (MeOH).

Compound **4a**:  $^1\text{H}$  NMR  $\delta$  2.95 (s, 12H,  $\text{NMe}_2$ ), 5.35 (t, 2H,  $\text{H}_\gamma$ ,  $J$  12.5 Hz), 6.66 (d, 2H,  $\text{H}_\alpha$ ,  $J$  15 Hz), 6.81 (d, 2H,  $\text{H}_\beta$ ,  $J$  12.5 Hz), 7.61 (dd, 2H,  $\text{H}_\beta$ ,  $J$  12.5 Hz and  $J$  15.0 Hz), 6.85 (t, 1H,  $\text{H}^4$ -Ph,  $J$  8.0 Hz), 7.79 (d, 2H,  $\text{H}^3$  and  $\text{H}^5$ -Ph,  $J$  8.0 Hz), 14.48 (br.s, 1H, OH); MS  $m/z$  340 ( $\text{M}^+$ ); UV  $\lambda_{\text{max}}/\text{nm}$  (EtOH): 400 sh ( $\epsilon$  37740), 464 ( $\epsilon$  77520).

Compound **4b**: m.p. 139–141 °C (EtOH);  $^1\text{H}$  NMR  $\delta$  2.0 (s, 6H, Me), 2.31 (s, 3H,  $\text{Me}^n$ ), 3.07 (s, 12H,  $\text{NMe}_2$ ), 6.52 (s, 2H,  $\text{H}_\beta$ ), 6.57 (d, 2H,  $\text{H}_\alpha$ ,  $J$  14.5 Hz), 7.55 (d, 2H,  $\text{H}_\beta$ ,  $J$  14.5 Hz), 7.62 (s, 2H,  $\text{H}^3$  or  $\text{H}^5$ -Ph), 14.48 (br.s, 1H, OH); UV  $\lambda_{\text{max}}/\text{nm}$  (EtOH): 400 sh ( $\epsilon$  37138), 460 ( $\epsilon$  74230).

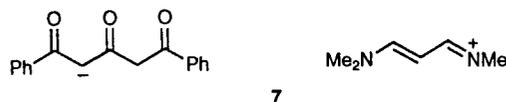
Compound **4c**: m.p. 190–193 °C;  $^1\text{H}$  NMR  $\delta$  2.73 (s, 12H,  $\text{NMe}_2$ ), 6.17 (d, 2H,  $\text{H}_\alpha$ ,  $J$  14.5 Hz), 6.73 (s, 2H,  $\text{H}_\beta$ ), 7.72 (d, 2H,  $\text{H}_\beta$ ,  $J$  14.5 Hz), 7.75 (s, 2H,  $m$ -Ph), 7.2–7.4 (m, 15H, Ph), 14.4 (br.s, 1H, OH); UV  $\lambda_{\text{max}}/\text{nm}$  (EtOH): 410 sh ( $\epsilon$  22700), 480 ( $\epsilon$  53000).

Compound **5a**: m.p. 138–140 °C;  $^1\text{H}$  NMR  $\delta$  2.73 (s, 3H, Me), 3.02 (s, 6H,  $\text{NMe}_2$ ), 5.42 (t, 1H,  $\text{H}_\gamma$ ,  $J$  12.5 Hz), 6.65 (d, 1H,  $\text{H}_\alpha$ ,  $J$  14.0 Hz), 6.94 (d, 1H,  $\text{H}_\beta$ ,  $J$  12.5 Hz), 7.76 (t, 1H,  $\text{H}_\beta$ ,  $J$  12.5 and 14.0 Hz), 6.88 (t, 1H,  $\text{H}^4$ -Ph,  $J$  8.0 Hz), 7.92 (m, 2H  $\text{H}^3$  and  $\text{H}^5$ -Ph,  $J$  8.0 Hz), 14.9 (br.s, 1H, OH); MS  $m/z$  259 ( $\text{M}^+$ ); UV  $\lambda_{\text{max}}/\text{nm}$  (EtOH): 460.

Compound **5c**: m.p. 178–180 °C (EtOH);  $^1\text{H}$  NMR  $\delta$  2.75 (s, 3H, Me), 2.78 (s, 6H,  $\text{NMe}_2$ ), 6.21 (d, 1H,  $\text{H}_\beta$ ,  $J$  14.0 Hz), 7.20–7.48 (m, 10H, Ph), 7.81 (s, 1H,  $\text{H}^3$ -Ph), 8.18 (s, 1H,  $\text{H}^5$ -Ph), 14.93 (br.s, 1H, OH); MS  $m/z$  411 ( $\text{M}^+$ ); UV  $\lambda_{\text{max}}/\text{nm}$  (EtOH): 245 ( $\epsilon$  32600), 475 ( $\epsilon$  52000).

Compound **7**: m.p. 143–146 °C;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  3.1 (s, 6H,  $\text{NMe}_2$ ), 3.28 (s, 6H,  $\text{NMe}_2$ ), 6.54 (t, 1H,  $\text{H}_\beta$ ), 7.38–7.60 (m, 9H,  $\text{Ph}^n$ ,  $\text{CH}_\alpha$  and  $\text{H}_\gamma$ ), 7.85 (d, 4H,  $o$ -Ph); UV  $\lambda_{\text{max}}/\text{nm}$  (EtOH): 312 ( $\epsilon$  65300).

In the case of the reaction of amination **1a** with triketone **3** no polyenic  $\omega$ -dimethylaminotriketones mentioned above were obtained either, since the reaction resulted only in the trimethine salt **7**:



The structure of the salt **7** was confirmed by  $^1\text{H}$  NMR and UV spectra. As shown earlier, trimethine salts are produced as intermediates in the formation of  $\delta$ -aminodienones from amination and  $\text{CH}$ -acids or ketones. However, it has been observed that with strong  $\text{CH}$ -acids, whose anions have low nucleophilicity (*e.g.*, tetrionic acid, hexafluoroacetylacetone, and some others), the reaction ceased at the stage of formation of a trimethine salt.<sup>10,11</sup>

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