Formylation of $\alpha\beta$-acidic Compounds via the Anilinomethylene Derivatives

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Three component condensation of active methylene compounds with aniline and trialkyl orthoformate gives anilinomethylene-1,3-dicarboxyls, which can be hydrolysed with aqueous $\text{K}_2\text{CO}_3$, $\text{KOH}$ or $\text{HCl}$, depending on the sensitivity of the hydroxymethylene derivative thus formed. The reaction sequence is fairly generally applicable: Cyclohexan-1,3-diones, pyrimin-3,5-diones (including barbituric acids), pyrazolones and pyrazolin-3,5-diones, indan-1,3-dione, (thio)phthalide, indoxyl, oxindole, anthrone, 2,6- and 2,7-dihydroxynaphthalene, and pentan-2,4-dione have been formylated. Using orthoacetate or orthopropionate, tetronic acid, pyrazolones and pyrazolin-3,5-diones, resp., could also be acylated by this method.

To introduce a formyl (or its tautomeric hydroxymethylene) group into CH$_2$-acidic compounds only a limited number of methods is known [2], which contrasts the variety of possibilities at aromatic systems. The reaction of orthoformates with CH$_2$-acidic molecules like diethyl malonate [3], 2,4-pentandione [3], malononitrile [4] or ethyl nitroacetate [5] to form their ethoxymethylene derivatives is a useful and the most direct method [6].

Unfortunately many cyclic $\beta$-diketones tend to give bis- and tris-condensation products with orthoformates [6, 7], thus prohibiting their direct formylation.

We wish to report more details on a simple two step procedure for synthesis of hydroxymethylene-1,3-dicarboxyls and related compounds, using orthoesters [8]. No condensing agent like $\text{POCl}_3$, which may lead to chlorinated byproducts, is required. The method is of particular utility for the formylation of cyclic $\beta$-diketones and related systems, but does also work with activated aromatic molecules like dihydroxynaphthalenes [11]. It fails in the case of phenol or anisole.

Three component condensation of an aromatic primary amine with trialkyl orthoformate and a cyclic active methylene compound ($pK_a$ lower than 10) gives anilinomethylene-1,3-dicarboxyls [1, 7–10]. This reaction proceeds smoothly at 50–70 °C in various solvents like alcohols, aromatic hydrocarbons, glycoles, dialkylformamides or glacial acetic acid, unless they contain more than 1% of water. Compounds 1a, c, e, g, 2a, e, 3a, c, 4a, 5a, 6a and 7a have been prepared this way. Less reactive CH$_2$-acidic molecules and those having intramolecular hydrogen bonds require more drastic reaction conditions (120–160 °C). 8a, e, 9a, e, 10a, c, 11a and 12a have been synthesized at these temperatures in good yields. When orthoacetates or orthopropinates are used instead of orthoformates, only five ring dicarboxyls give the desired products (4c, e, 5e, e, 6c, e). When cyclohexan-1,3-dione was heated with aniline and excess of triethylorthoacetate, 3-anilino-cyclohex-2-en-1-one was isolated instead of the desired $\beta\beta$-diacylenamine. The attempted three component condensation between triethylorthoacetate, aniline and 4-hydroxycou...
marin (or barbituric acid) gave no crystallizable products at all. Using alkyl amines instead of anilines is not advantageous, since the yields on N-alkylaminomethylene derivatives are consider- able lower. Steam volatile anilines, such as p-toluidine or p-chloroaniline, may also be used and sometimes give even better yields than aniline itself. It is known, that enamines can be used in many reactions instead of the free, less stable hydroxy- methylene-1,3-dicarbonyls [9, 10, 12, 13]. However in some cases the synthesis the β,β-diacylenoles is desirable. Several methods have been investigated for the hydrolysis of β,β-diacylenamines. Dilute aqueous NaOH or KOH (0.5–2 N) seems to be the most generally applicable reagents, but aqueous Na₂CO₃ or better K₂CO₃ may also be used, particularly when sensitive functional groups (e.g. cyclic esters) are present. Nitrile functions may undergo secondary reactions under these conditions, however. So, an attempted preparation of hydroxymethylenemalononitrile or ethyl cyanoacetate gives, in a complex reaction sequence, aminopyridones. More details on this interesting reaction will be reported later.

For small scale preparations of hydroxymethylene from anilinomethylene the latter (A) is heated with a base (K₂CO₃, KOH) in an open flask, until the odour of aniline can no more be detected. This usually is the case after 30–90 min. Alternatively, hydrolysis can be performed in a steam distillation apparatus; the liberated aniline may then be recovered from the distillate in over 90% yield.

Acidification of the relatively stable salts B is a crucial step and has to be performed at temperatures below 10 °C. Otherwise side reactions have to be expected.

Unlike their sodium salts many hydroxymethylene-1,3-dicarboxyls (C) (for instance 2b, 6b, 7b, 11b) are sensitive to heat and suffer decarbonylation (C→D). Therefore they must not be recrystallized from high boiling solvents. Decarbonylation of C leads to the starting diketone D, which can react with unchanged C to form deeply coloured and sparingly soluble oxonoles (E). Hydroxymethylenecyclohexane-1,3-diones form tris compounds [7] under these conditions, and the latter often contami- nate the isolated hydroxymethylene.

These findings prevent an enam hydrolysis using strong mineral acids in many cases. Nevertheless, the more stable enoles 4b, 5b, d and 10b, d could alternatively be prepared by acidic saponification. Generally fair yields have been obtained, with the exception of the very sensitive [14] hydroxy- methylene-anthrone 11b (12%). No product could be isolated either by alkaline or acidic hydrolysis of 5a, although acidified reaction mixtures gave greenish-brown colorations FeCl₃ solutions, indicating the presence of an enolic system.
As to the tautomeric equilibria between formyl and hydroxymethylene structure, an easy differentiation can be made using PMR spectroscopy: The \( =\text{CHO}-\text{OH} \) proton resonances in the \( \delta = 7.5 \) to 8.2 ppm region, often as a dublet [15]. The \( -\text{CHO} \) proton resonances in the 9 to 10 ppm region as a singlet. According to the PMR spectra only 10b, d and partially 11b exist in the aldehyde form. A detailed PMR spectroscopic study on hydroxymethylene-1,3-dicarboxylenes [15] and on amino-methylene-1,3-dicarboxylenes [16] has been performed.

Experimental

For the instrumental equipment see ref. [1]. Melting points are uncorrected. Chemical shifts are given in \( \delta \)-units (tetramethylsilane = 0). The synthesis of compounds 1a, c, e, g [10] and 2a, e [17] has been described.

2-Hydroxymethylene-cyclohexane-1,3-dione (1b)

2.15 g (10 mmol) 2-anilinomethylene-cyclohexane-1,3-dione is suspended in 200 ml 5% aqueous \( \text{K}_2\text{CO}_3 \) solution and 30 ml 2-propanol and heated in an open flask, until the odour of aniline can no more be detected (1–2 h, NaOCl-paper). During this time a yellow solution is formed, which, after cooling to room temperature, is once extracted with 40 ml \( \text{CHCl}_3 \) and then acidified with conc. HCl under cooling (ice pieces) to pH 2. Exhaustive extraction with four 50 ml portions diethyl ether, washing the ethereal phase with 10 ml water, drying \( (\text{Na}_2\text{SO}_4) \) and concentrating the solution in vacuo leaves a yellow oil (1.0 g, 71%) of over 90% purity (tlc), which is of sufficient quality for most purposes. It gives a dark red coloration with aqueous \( \text{FeCl}_3 \). The oil may be recrystallized from ethereal extraction in 98% yield. Derivatives 2d and 2f have been prepared similarly.

5-Anilinomethylene-1,2,3,4,5,6-hexahydropyrimidine-2,4,6-trione (2b)

2.21 g (10 mmol) 5-anilinomethylene-1,2,3,4,5,6-hexahydropyrimidine-2,4,6-trione [8] is dissolved in 200 ml 1 N KOH and steam distilled for half an hour. The cooled solution is filtered and acidified (conc. HCl). The crystals are collected and recrystallized from \( \text{AcOH} \). Yield 1.42 g (91%), m.p. 275 °C (decomp.).

5-Anilinomethylene-1,2,3,4,5,6-tetrahydro-pyrimidine-4,6-dione (3a)

5.6 g (50 mmol) 4,6-dihydroxy pyrimidine (commercial), 4.6 g (50 mmol) aniline and 8.9 g (60 mmol) triethoxymethane are carefully mixed at room temp. and then heated in a 160 °C oil bath for one hour. A dark brown mass is formed, which is treated with 5 ml DMFA, cooled, filtered by suction and recrystallized from DMFA/DMSO (1:1). Yellow, fluorescent crystals of m.p. 340 °C (decomp.), yield 7.9 g (73%).

5-Anilinomethylene-3,4,5,6-tetrahydro-pyrimidine-4,6-dione (3b)

Was prepared in analogy to the method given for 2b, in 64% yield. Slightly yellow crystals of m.p. 246–248 °C (decomp.).

5-Anilinomethylene-3,4,5,6-tetrahydro-pyrimidine-4,6-dione (3b)

1.6 g (10 mmol) 1-phenyl-1,2,3,4,5,6-hexahydropyrimidine-2,4,6-trione (1-phenyl-barbituric acid), suspended in 10 ml glacial acetic acid, is dropped at 70–80 °C a mixture of 0.93 g (10 mmol) aniline and 3.0 g (20 mmol) triethoxymethane (triethyl orthoformate). Stirring and heating to 100 °C for 10 min produces a voluminous precipitate, which, from acetic acid, gives yellowish crystals of m.p. 265–266 °C (decomp.) in 85% yield (2.6 g).

C\(_2\)H\(_2\)N\(_2\)O\(_3\) (307.3)

Calcd C 66.44 H 4.26 N 13.67,

Found C 66.70 H 4.20 N 13.50.

4-Anilinomethylene-1,2-diphenyl-pyrazolidin-3,5-dione (4a)

2.52 g (10 mmol) 1,2-Diphenylpyrazolidine-3,5-dione and 0.93 g (10 mmol) aniline in 5 ml \( \text{AcOH} \) are warmed to 60 °C. To this is added dropwise, under good stirring, 1.48 g (10 mmol) triethoxy-
methane. The temp. is then raised to 100 °C. After 1 h the mixture is cooled, concentrated in vacuo and left for crystallization. Yellow leaflets of m.p. 178 °C (from 2-PrOH), yield 84% (3.0 g).

\[
\text{C}_{22}\text{H}_{17}\text{N}_{3}\text{O}_{2} \quad (355.4)
\]

Calcd C 74.35 H 4.82 N 11.82,

Found C 74.22 H 4.76 N 12.00.

When an excess of orthoester is used, formation of the yellow methinylbispyrazolone (oxonole) of m.p. 301-302 °C has to be expected as a side reaction.

4b, c have been synthesized similarly, using 1,1,1-triethoxyethane (triethylorthoacetate) and 1,1,1-triethoxypropane (triethylorthopropionate), resp., instead of triethoxymethane (see Table I).

Table I. Data of compounds 1-12.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Systematic name</th>
<th>Formula (molmass)</th>
<th>m.p. [°C]</th>
<th>Crystall. solvent</th>
<th>Yield [%]</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>1d</td>
<td>5,5-Dimethyl-2-hydroxymethylene-cyclohexan-1,3-dione</td>
<td>C9H12O3 (168.2)</td>
<td>80-81</td>
<td>Et2O</td>
<td>76</td>
<td>[15]</td>
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<tr>
<td>1f</td>
<td>2-Hydroxyethylene-5-phenyl-cyclohexane-1,3-dione</td>
<td>C13H12O3 (216.2)</td>
<td>71</td>
<td>50% EtOH</td>
<td>64b</td>
<td>—</td>
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<tr>
<td>1h</td>
<td>3-Hydroxymethyl-1-oxaspiro-[5,5]undecane-2,4-dione</td>
<td>C13H12O4 (210.2)</td>
<td>110</td>
<td>50% EtOH</td>
<td>76</td>
<td>—</td>
</tr>
<tr>
<td>2d</td>
<td>1,3-Dimethyl-5-hydroxymethylene-1,2,3,4,5,6-hexahydropyrimidine-2,4,6-trione</td>
<td>C2H4N2O4 (184.2)</td>
<td>123</td>
<td>MeOH</td>
<td>85</td>
<td>e</td>
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<tr>
<td>2f</td>
<td>5-Hydroxymethylene-1-phenyl-1,2,3,4,5,6-hexahydropyrimidine-2,4,6-trione</td>
<td>C11H12N2O4 (232.3)</td>
<td>255</td>
<td>DMFA</td>
<td>78</td>
<td>[19]</td>
</tr>
<tr>
<td>3e</td>
<td>5-Anilinomethylene-2-methyl-3,4,5,6-tetrahydropyrimidine-4,6-dione</td>
<td>C12H11N3O2 (229.2)</td>
<td>&gt; 300</td>
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<td>68</td>
<td>[19]</td>
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<td>3d</td>
<td>5-Hydroxymethylene-2-methyl-3,4,5,6-tetrahydropyrimdin-4,6-dione</td>
<td>C12H11N3O2 (154.1)</td>
<td>235-240</td>
<td>DMFA</td>
<td>68</td>
<td>[19]</td>
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<tr>
<td>4c</td>
<td>4(α-Anilinoethylidene)-1,2-diphenylpyrazolidine-3,5-dione</td>
<td>C9H12N3O3 (369.4)</td>
<td>158</td>
<td>CH3CN</td>
<td>72</td>
<td>[21]</td>
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<tr>
<td>4e</td>
<td>4(α-Anilinopropylidene)-1,2-diphenylpyrazolidine-3,5-dione</td>
<td>C9H12N3O2 (383.5)</td>
<td>162</td>
<td>2-PrOH</td>
<td>71</td>
<td>—</td>
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<tr>
<td>4f</td>
<td>4(α-Hydroxypropylidene)-1,2-diphenylpyrazolidine-3,5-dione</td>
<td>C14H15N3O3 (308.3)</td>
<td>128</td>
<td>EtOH</td>
<td>69</td>
<td>—</td>
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<tr>
<td>5e</td>
<td>3(α-Anilinopropylidene)-2,3,4,5-tetrahydrofuran-2,4-dione</td>
<td>C14H12N3O (231.3)</td>
<td>154</td>
<td>CH2COOH</td>
<td>68</td>
<td>—</td>
</tr>
<tr>
<td>5f</td>
<td>3(α-Hydroxypropylidene)-2,3,4,5-tetrahydrofuran-2,4-dione</td>
<td>C14H12O4 (156.1)</td>
<td>95</td>
<td>C6H12</td>
<td>58</td>
<td>e</td>
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<tr>
<td>6a</td>
<td>4-Anilinomethylene-3-methyl-1-phenylpyrazoline-5-one</td>
<td>C12H13N3O (277.3)</td>
<td>154</td>
<td>toluene</td>
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<td>6b</td>
<td>4-Hydroxyethylene-3-methyl-1-phenylpyrazole-5-one</td>
<td>C13H12N3O2 (202.2)</td>
<td>180</td>
<td>EtOH</td>
<td>68</td>
<td>g</td>
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<tr>
<td>6c</td>
<td>4(α-Anilinoethylidene)-3-methyl-1-phenylpyrazole-5-one</td>
<td>C14H17N3O (291.4)</td>
<td>183</td>
<td>C6H6</td>
<td>69</td>
<td>—</td>
</tr>
<tr>
<td>6d</td>
<td>4(α-Hydroxyethylidene)-3-methyl-1-phenylpyrazole-5-one</td>
<td>C12H12N3O2 (216.2)</td>
<td>58</td>
<td>EtOH</td>
<td>84</td>
<td>h</td>
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<td>6e</td>
<td>4(α-Anilinopropylidene)-3-methyl-1-phenylpyrazoline-5-one</td>
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<td>131</td>
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<td>66</td>
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<td>6f</td>
<td>4(α-Hydroxypropylidene)-3-methyl-1-phenylpyrazoline-5-one</td>
<td>C14H14N2O2 (230.3)</td>
<td>68</td>
<td>EtOH</td>
<td>85</td>
<td>—</td>
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</table>
Table I (contd.).

<table>
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<tr>
<th>Compound</th>
<th>Systematic name</th>
<th>Formula (molmass)</th>
<th>m.p. [°C]</th>
<th>Crystall. solvent</th>
<th>Yield [%]</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>7a</td>
<td>2-Anilinomethylene-indan-1,3-dione</td>
<td>C16H11N02 (249.3)</td>
<td>191</td>
<td>2-Butanon</td>
<td>63</td>
<td>i</td>
</tr>
<tr>
<td>7b</td>
<td>2-Hydroxymethylene-indan-1,3-dione</td>
<td>C10H6O3 (174.2)</td>
<td>142</td>
<td>benzene</td>
<td>86</td>
<td>i</td>
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<tr>
<td>7c</td>
<td>2(α-Anilinoethylidene)-indan-1,3-dione</td>
<td>C17H12N02 (263.3)</td>
<td>138</td>
<td>EtOH</td>
<td>42</td>
<td>—</td>
</tr>
<tr>
<td>7d</td>
<td>2(α-Hydroxyethylidene)-indan-1,3-dione</td>
<td>C17H13O3 (188.2)</td>
<td>110</td>
<td>MeOH</td>
<td>71</td>
<td>m</td>
</tr>
<tr>
<td>8a</td>
<td>3-Anilinomethylene-2,3-dihydro-[1H]indole-2-one</td>
<td>C16H12N02 (236.3)</td>
<td>254 (decomp.)</td>
<td>CH3COOH</td>
<td>84</td>
<td>n</td>
</tr>
<tr>
<td>8b</td>
<td>3-Hydroxymethylene-2,3-dihydro-[1H]indole-2-one</td>
<td>C16H12O3 (161.2)</td>
<td>212</td>
<td>EtOH</td>
<td>72</td>
<td>o</td>
</tr>
<tr>
<td>8c</td>
<td>3-Anilinomethylene-2,3-dihydrobenzo[a]-furan-2-one</td>
<td>C22H14N03 (263.3)</td>
<td>164</td>
<td>EtOH</td>
<td>64</td>
<td>—</td>
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<tr>
<td>8d</td>
<td>3-Hydroxymethylene-2,3-dihydrobenzo[a]-furan-2-one</td>
<td>C22H14O3 (146.1)</td>
<td>147-150</td>
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<td>86</td>
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<tr>
<td>8e</td>
<td>3-Anilinomethylene-2,3-dihydrobenzo[a]-thiophen-2-one</td>
<td>C22H14N03 (263.3)</td>
<td>184</td>
<td>EtOH</td>
<td>70</td>
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<tr>
<td>8f</td>
<td>3-Hydroxymethylene-2,3-dihydrobenzo[a]-thiophen-2-one</td>
<td>C14H9O2 (178.2)</td>
<td>130</td>
<td>EtOH</td>
<td>68</td>
<td>—</td>
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<tr>
<td>8g</td>
<td>3-Anilinomethylene-1-methyl-2,3-dihydro-[1H]indole-2-one</td>
<td>C16H14N02 (250.3)</td>
<td>141</td>
<td>EtOH</td>
<td>74</td>
<td>—</td>
</tr>
<tr>
<td>8h</td>
<td>3-Hydroxymethylene-1-methyl-2,3-dihydro-[1H]indole-2-one</td>
<td>C16H14O2 (175.2)</td>
<td>186</td>
<td>MeOH/H2O</td>
<td>74</td>
<td>—</td>
</tr>
<tr>
<td>9a</td>
<td>2-Anilinomethylene-2,3-dihydro-[1H]indole-3-one</td>
<td>C16H12N02 (236.3)</td>
<td>195 (decomp.)</td>
<td>CH3COOH</td>
<td>64</td>
<td>—</td>
</tr>
<tr>
<td>9b</td>
<td>2-Hydroxymethylene-2,3-dihydro-[1H]indole-3-one</td>
<td>C16H12O2 (161.2)</td>
<td>162</td>
<td>EtOH</td>
<td>51</td>
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<tr>
<td>10a</td>
<td>1-Anilinomethylene-6-hydroxy-1,2-dihydro-naphthalene-2-one</td>
<td>C27H12N02 (263.3)</td>
<td>241 (decomp.)</td>
<td>2-Butanon</td>
<td>62</td>
<td>[11]</td>
</tr>
<tr>
<td>10b</td>
<td>2,6-Dihydroxy-naphthalene-1-carbaldehyde</td>
<td>C11H6O3 (188.2)</td>
<td>193-194</td>
<td>EtOH</td>
<td>42</td>
<td>[11]</td>
</tr>
<tr>
<td>10c</td>
<td>1-Anilinomethylene-7-hydroxy-1,2-dihydro-naphthalene-2-one</td>
<td>C27H12N02 (263.3)</td>
<td>220 (decomp.)</td>
<td>2-Butanon</td>
<td>56</td>
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<td>10d</td>
<td>2,7-Dihydroxynaphthalene-1-carbaldehyde</td>
<td>C11H6O3 (188.2)</td>
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<td>EtOH</td>
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<td>11a</td>
<td>Anilinomethyleneanthrone</td>
<td>C21H15N0 (297.4)</td>
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<td>CH3COOH</td>
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<td>12a</td>
<td>3-Anilinomethylene-pentane-2,4-dione</td>
<td>C23H13N02 (203.2)</td>
<td>90</td>
<td>ligroin</td>
<td>46</td>
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</table>

a All compounds gave satisfactory C, H and/or N analyses.

b On cooling the hot solution prior to acidification the potassium salt of I crystallizes (m. p. 225-229 °C, decomp.) and can be separated.

j Decrystallization from water gives only the red oxonol of m. p. 303 °C.
k Deeply colored byproducts are formed and crystallization requires several days.
The cooled mixture is filtered, and concentrated in vacuo to 20-30 ml. The precipitate is collected and recrystallized from methanol to give 2.0 g (68%) product of m.p. 117 °C.

C₆H₁₂N₂O₃ (294.3)
Calcd C 69.38 H 4.79 N 9.52,
Found C 69.45 H 4.83 N 9.60.

4f may be obtained from 4e by the same procedure.

3-Anilinoethylene-2,3,4,5-tetrahydrofuran-2,4-dione (5a)
1.0 g (10 mmol) tetrone acid [22], 5 ml glacial acetic acid, 1.6 g (11 mmol) triethoxymethane and 0.93 g (10 mmol) aniline are heated to 100 °C for 10 min. The mixture becomes clear, and soon a precipitate is formed. The product is filtered, washed with methanol and recrystallized from little DMFA to give 1.48 g (73%) slightly yellow crystals of m.p. 171-172 °C.

IR (KBr): 3260, 3065, 1737, 1661-1670, 1641 and 1590 cm⁻¹.
PMR (CDCl₃): 2.50 (s, 3H); 4.00 (2s, 2H).

C₁₂H₁₁NO₃ (217.2)
Calcd C 65.02 H 4.47 N 6.89,
Found C 65.14 H 4.40 N 6.78.

It is useful to add the orthoester prior to the aniline to avoid the formation of 4-anilino-2,5-dihydrofuran-2-one of m.p. 218 °C as a byproduct.

3(a-Acetyl tetronic acid)

To 2.0 g (20 mmol) tetrone acid [22] in 20 ml dioxane is dropped at 70 °C over a 30 min period under stirring a mixture of 1.86 g (20 mmol) aniline and 4.86 g (30 mmol) 1,1,1-triethoxymethane. Then the temperature is slowly raised to 100 °C. Cooling after 1 h, concentrating at diminished pressure and crystallization affords, 2.82 g (65%) product of m.p. 188 °C (from AcOH).

C₁₂H₁₄N₂O₃ (294.3)
Calcd C 69.45 H 4.83 N 9.60,
Found C 69.54 H 4.79 N 9.52.

5f and 5e were prepared according to the directions given for 5c and 5d (Table I). Compounds 6a-f and 7a-d were synthesized analogous to 5a-f.

General method for the synthesis of 8a, e, e, g and 9a
Equimolar amounts (10-20 mmol) of the active methylene compound, aniline and orthoester are carefully mixed with 5 ml AcOH in an open flask and heated in a 140 °C oilbath. The contents become clear, and after 20' the exothermic reaction has completely ceased. Addition of 20 ml ethanol to the cooled solution causes crystallization. Further data are given in Table I.

Hydrolysis of these enamines to form 8b, d, f, h and 9b was accomplished by the methods given for 4b and 4d.

General method for the synthesis of the enamines 10a, 10c and 11a, 12a
The active methylene compound, triethoxymethane and aniline are mixed in a 1:1:1 molar ratio (for 12a 1.3:1:1), and heated slowly over a one hour period to 160 °C. After 2 h at this temperature, the mixture is cooled and treated with methanol to induce crystallization. After some time the precipitate is collected (10a, e are yellow, 11a is red, 12a colorless) and recrystallized from an appropriate solvent (Table I).

10b and 10d were prepared by the steam distillation process [11], as given for 4b.

Hydroxyazomethyleneanthrone [14] (11b)
3.0 g (10 mmol) 11a were stirred in 100 ml 2N KOH for 6 h at room temperature. The solution was filtered, extracted with diethylether, and carefully acidified with acetic acid at 0 °C. A yellow precipitate (0.27 g = 12%) of m.p. 200-202 °C is formed, which is carefully dried over P₂O₅ and may be recrystallized under big losses from benzene.

C₁₅H₁₅O₃ (222.3)
Calcd C 81.05 H 4.53,
Found C 80.80 H 4.60.

3-Hydroxyazomethylene-pentane-2,4-dione [24] (12b)
10 g (50 mmol) 12a were heated under reflux with 100 ml 1 N KOH for 4 h. After cooling, extraction with ether (2 x 50 ml) and acidification with conc. HCl (at 10 °C) the solution was exhaustively extracted with ether again. Washing with water (2 x 10 ml), drying (CaCl₂) and removal of the solvent left an yellow oil, which was distilled (b.p. = 86 °C) to give an almost colorless, unstable solid of m.p. 47 °C (5.6 g = 87%).

C₅H₆O₂ (128.1)
Calcd C 56.24 H 6.29,
Found C 56.01 H 6.04.

C₅H₆O₂ (142.1)
Calcd C 50.71 H 4.26,
Found C 50.54 H 4.39.