Chemistry of 2-methylene-2,3-dihydro-3-furanones

16.* The reaction of 2-acylmethylene-5-aryl-2,3-dihydro-3-furanones with aromatic amines and *N*-arylideneamines

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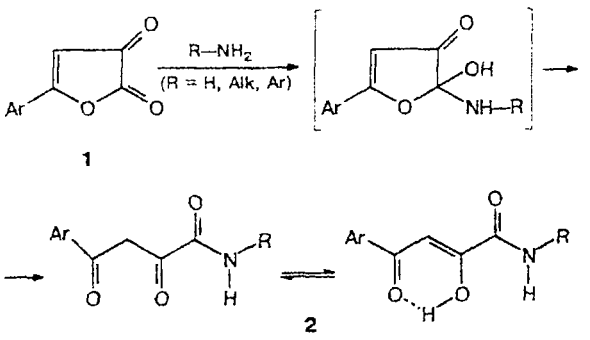
2-*p*-Chlorobenzoylmethylene-5-phenyl-2,3-dihydro-3-furanone reacts with arylamines or *N*-arylideneamines to form the products of ring opening, 1,6-diaryl-1-arylamino-4-hydroxy-1,4-hexadiene-3,6-diones. The reaction of 5-aryl-2-*p*-chlorobenzoylmethylene-2,3-dihydro-3-furanones with *o*-aminophenol afforded 3-*p*-chlorobenzoylmethylene-3,4-dihydro-2*H*-benzo[*b*]-1,4-oxazin-2-one. Nucleophilic attack of amines is directed either to electrophilic centers at the C(5) and C(2) atoms or to the carbonyl group of the 2-phenacylidene substituent of the 3-oxofuran ring.

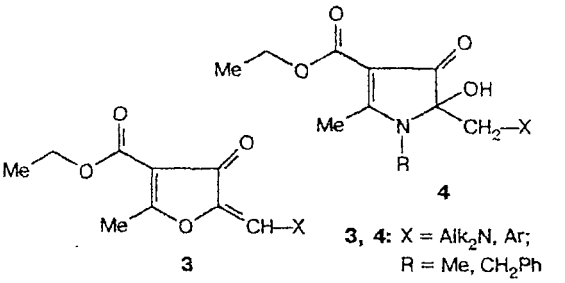
Key words: 5-aryl-2-*p*-chlorobenzoylmethylene-2,3-dihydro-3-furanones, reactions with arylamines, *N*-arylideneamines and *o*-aminophenol.

5-Aryl-2,3-dihydro-2,3-furandiones (**1**) are known to readily undergo ring opening reactions when treated with ammonia and primary alkyl- or arylamines to give aroylpyruvamides (**2**).[2,3] In these reactions, the initial attack of the nucleophile occurs at the lactone carbonyl group[3] (Scheme 1).

Scheme 1



Replacement of the oxygen atom of the lactone carbonyl in 2,3-dihydro-2,3-furandiones **1** by dialkylaminomethylene or arylidene fragments changes the direction of the nucleophilic addition of amines to the corresponding 2-methylene-2,3-dihydro-3-furanones **3**. In reactions with amines, the latter give recyclization products, substituted 2-hydroxy-2,3-dihydro-3-pyrrolones (**4**),[4,5] due to nucleophilic attack by amines at the electrophilic center at the carbon atom in position 5 of the furan cycle.



The introduction of an electron-withdrawing alkoxycarbonyl substituent into the 2-*exo*-methylene fragment of 2-methylene-2,3-dihydro-3-furanones to give compounds **5** causes the relative electrophilicity of the center at the 2-*exo*-methylene carbon atom to become greater than that of the C(5) atom in furanones **3**. This results in the formation of both traditional recyclization products, 2-hydroxy-2,3-dihydro-3-pyrrolones (**6**), and products of the nucleophilic addition of arylamines to the 2-*exo*-methylene bond of the substrates, 5-aryl-2-(arylamino)alkoxycarbonylmethyl-2,3-dihydro-3-furanones (**7**)[6–9] (Scheme 2).

The ratio of compounds **6** and **7** is primarily determined by the polarity of the solvent used, with alcohols favoring the formation of 3-pyrrolones and a hydrocarbon solvent (toluene) favoring the formation of 3-furanones **7**.[8] This might be explained by the polarizing effect of a polar proton-containing solvent on the carbonyl group in position 3 of the ring in 2-alkoxycarbonylmethylene-2,3-dihydro-3-furanone **5**, which increases the relative electrophilicity of the C(5) center by redistributing the electron density towards the electron-deficient C(3) atom, and thereby assists the nucleophilic

*For communication 15, see Ref. 1.

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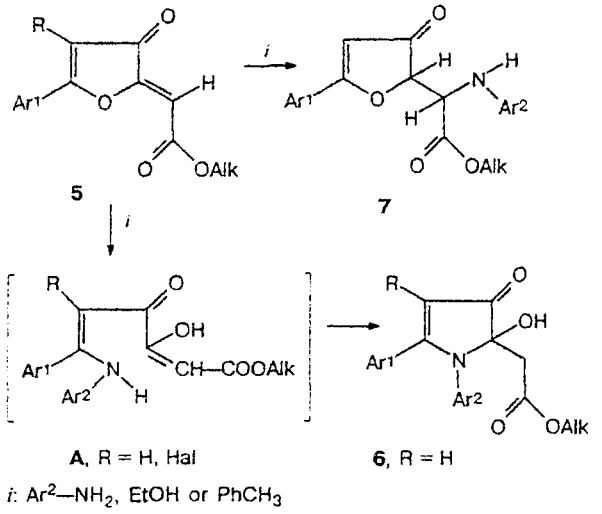
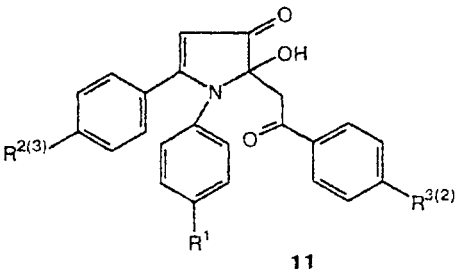
Scheme 2



attack of the amine at the C(5) center to form enaminoketoester (A) as an intermediate. With a nonpolar solvent, the nucleophilic attack of the amine occurs primarily at the electrophilic center at the carbon atom of the 2-*exo*-methylene fragment, which is assisted by the electron-withdrawing effect of the ester group. In this case, the polarizing effect of the solvent on the C(3)=O carbonyl group of the cycle is absent and the main role in the redistribution of the electron density belongs to the alkoxycarbonyl group, which results in the predominant formation of the addition products **7**.[8]

In view of this, it was interesting to study the reaction of amines with the structurally similar 5-aryl-2-aroylmethylene-2,3-dihydro-3-furanones (**10**),[1,10] which differ in the electron-withdrawing substituent at the 2-methylene fragment, and to determine if the C(2), C(5), or C(3) electrophilic centers can participate in the reactions.

The reaction of 2-*p*-chlorobenzoylmethylene-5-phenyl-2,3-dihydro-3-furanone **10a**[1] with aromatic amines (method A) or *N*-arylidene amines (method B) resulted in the formation of 1,6-diaryl-1-arylamino-4-hydroxy-1,4-hexadiene-3,6-diones (**12a—e**)* (Scheme 3) instead of the expected cyclic form, substituted 2-hydroxy-2,3-dihydro-3-pyrrolones (**11**).



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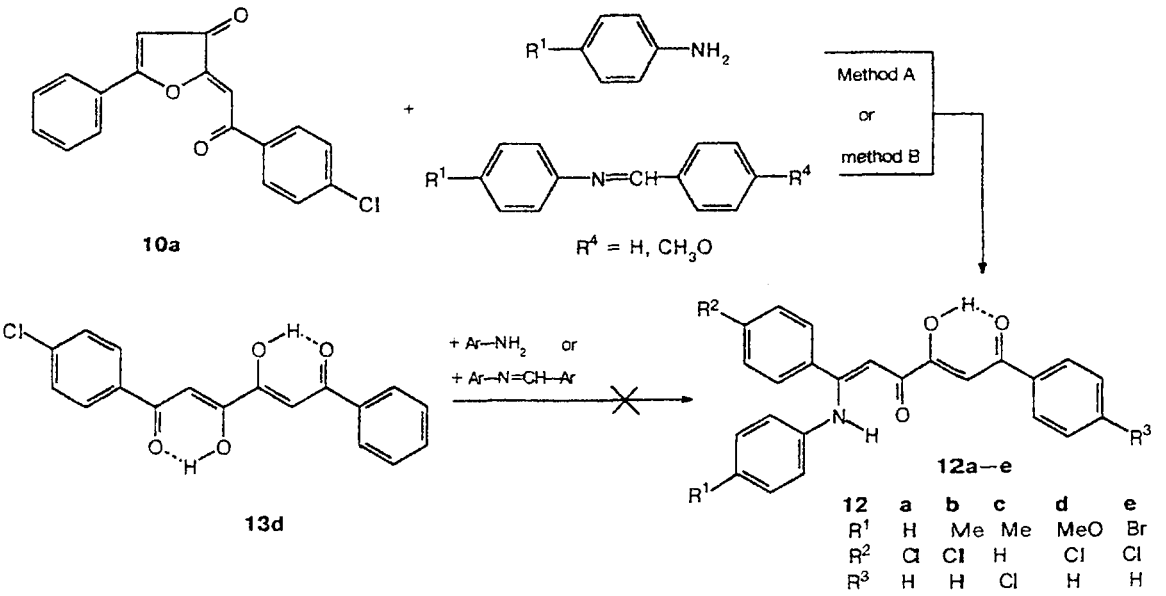
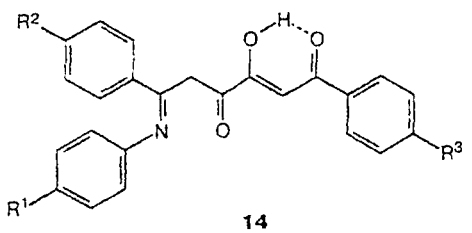
We were unable to perform an independent synthesis of compound **12** by the reaction of the known 6-*p*-chlorophenyl-3,4-dihydroxy-1-phenyl-2,4-hexadiene-1,6-dione (**13d**)[12] with aryl amines or *N*-arylidene amines due to the complete resinification of the reaction mixture.

The absence of the signals of CH_2 groups in the ^1H and ^{13}C NMR spectra of enaminoketones **12a—e** allow us to exclude unambiguously the possible ring (**11**) and chain tautomers (**14**) of all 1,6-diaryl-1-arylamino-4-hydroxy-1,4-hexadiene-3,6-diones (**12a—e**). The ^1H and

*According to preliminary data[11] compounds **12** exhibit moderate antistaphylococcus activity.

Scheme 3





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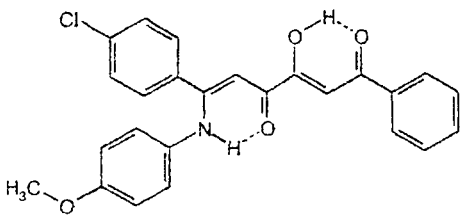
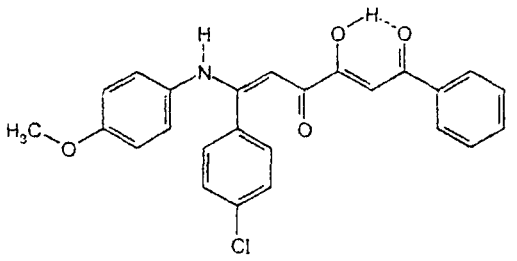
^{13}C NMR spectra of **12d** indicate the existence of two forms that differ insignificantly in the chemical shifts of the majority of the atoms (including those of the proton of the NH group in the ^1H NMR spectrum, in which the signals are separated by 0.95 ppm from each other). These are apparantly isomers with an NH-chelate cycle ((*Z*)-**12d**) and without the cycle ((*E*)-**12d**).

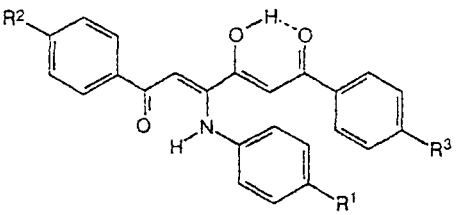


(*Z*)-12d



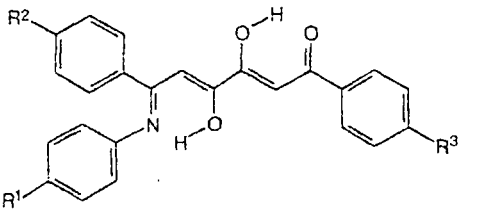
(*E*)-12d

The mass spectrum of **12d** does not contain peaks of the possible *p*-chlorobenzoyl fragment ion (*m/z* 139 and 141). This enabled us to reject the alternative regioisomeric enaminoketone (**12′**) structure as well.



12′

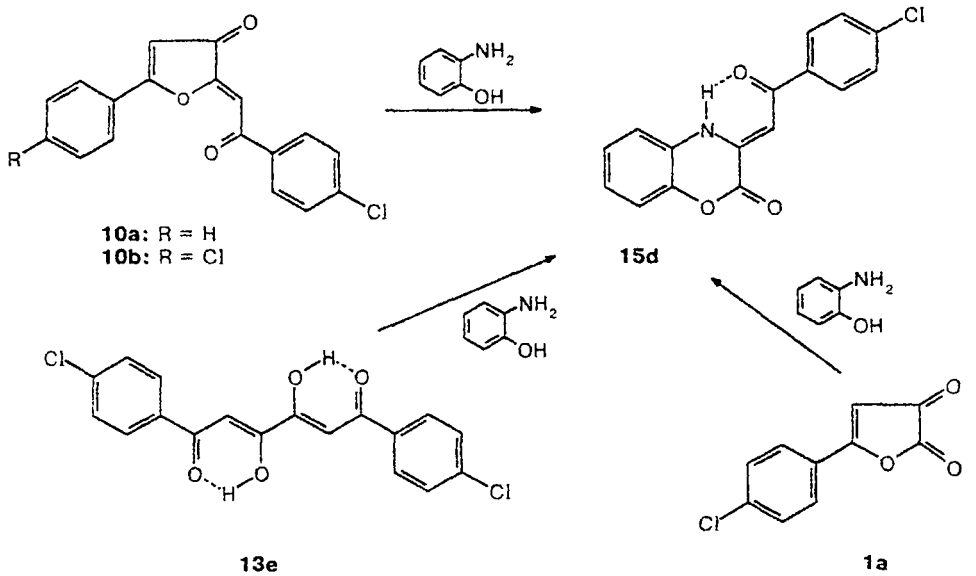
In the ^1H NMR spectra of the possible alternative structure **12″**, the chemical shifts of signals of the protons of the enol hydroxy groups should be not less than 14 ppm (δ(OH) is in the 15.0 — 19.9 interval for similar structures).[13,14] The occurrence of these signals in a stronger field position (12.8—12.88 ppm) allows us to assign them unambiguously to the protons of the NH groups of enaminocarbonyl compounds **12** (see, for example, Ref. 15).



12″

The reactions of 5-aryl-2-*p*-chlorobenzoylmethylene-2,3-dihydro-3-furanones **10a,b**[1] with *o*-aminophenol afforded the same recyclization product, 3-*p*-chloro-

Scheme 4



10a: R = H
10b: R = Cl

15d

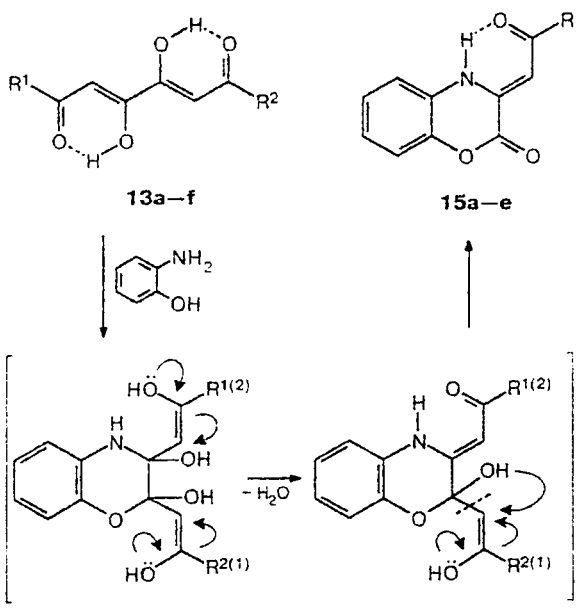
13e

1a

benzoylmethylene-3,4-dihydro-2*H*-benzo[*b*]-1,4-oxazin-2-one (**15d**). The formation of the latter was confirmed by an independent synthesis, *i.e.*, by the reaction of 5-*p*-chlorophenyl-2,3-dihydro-2,3-furandione (**1a**) with *o*-aminophenol (by the known procedure)[3,16] or by the corresponding reaction of this reagent with 1,6-bis-*p*-chlorophenyl-3,4-dihydroxy-2,4-hexadiene-1,6-dione (**13e**) (Scheme 4).

Similarly to compound **13e**, we were able to involve a series of available 1,6-disubstituted 3,4-dihydroxy-2,4-hexadiene-1,6-diones (1,3,4,6-tetraketones) (**13a—d,f**) into the reaction with *o*-aminophenol to afford 3-acylmethylene-3,4-dihydro-2*H*-benzo[*b*]-1,4-oxazin-2-ones (**15a—c,e**)* in preparative yields (Scheme 5).

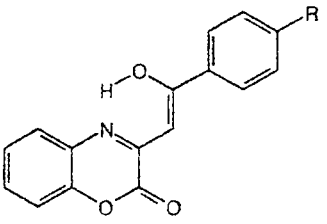
Scheme 5



13: $R^1 = R^2$ = Ph (**a**), 4-MeC_6H_4 (**b**), 4-EtC_6H_4 (**c**), 4-ClC_6H_4 (**e**), Me_3C (**f**); R^1 = Ph, R^2 = 4-ClC_6H_4 (**d**)
15: R = Ph (**a**), 4-MeC_6H_4 (**b**), 4-EtC_6H_4 (**c**), 4-ClC_6H_4 (**d**), Me_3C (**e**)

The alternative structure of enol **15′** was rejected since the signal of the enamine NH group is in a rather strong field (δ 12.85—12.90 ppm) (*cf.*, Ref. 16) (this group can be assigned to the enolic OH group, the common δ values are 15.0—15.9 ppm)[13,14]

Considerable resinification was observed in all reactions of 2-acylmethylene-5-aryl-2,3-dihydro-3-furanones

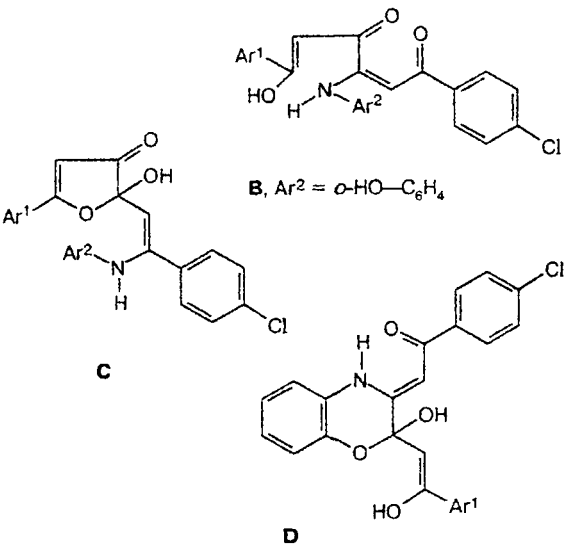


15′

10 with alkylamines (ethylamine, isopropylamine) and benzylamine, and even the use of column chromatography did not make it possible to isolate the products.

Thus, we have found that nucleophilic attack by the amino group of arylamines can occur not only at the electrophilic center at the C(5) carbon atom of the 2-acylmethylene-5-aryl-2,3-dihydro-3-furanone **10** ring (an example of such a process is the formation of compound **12c**) but also at the carbon atom of the carbonyl of the *p*-Cl-phenacylidene fragment, as well as at the C(2) center (to form benzoxazinone **15d**). This results in the formation of different products than in the case of substrates **3** or **5**. We suggest that enaminoketoesters (**B**) (attack at the C(2) atom), which are regioisomeric to the structure **A** or intermediate enamines (**C**) (Scheme 5), can be formed as possible decyclization intermediates. Intermediate (**B**) can subsequently undergo recyclization to give an intermediate benzoxazine (**D**) (Scheme 6). The latter can eliminate arylmethylketones Ar^1COMe under the reaction conditions to give compound **15d**.

Scheme 6



*According to preliminary data[11] compounds **15** exhibit moderate antistaphylococcus activity.

Experimental

IR spectra of the synthesized compounds were recorded on UR-20 and Specord M-80 spectrophotometers in Vaseline oil. ^{1}H NMR spectra were obtained on RYa-2310 (60 MHz) and Bruker WP-200 (200 MHz) instruments in $CDCl_3$ (compounds **10a, 12b—d,** and **15d**) and DMSO-d_6 (compounds **12a,e** and **15a—e**) with HMDS as the internal standard. The ^{13}C NMR spectrum was recorded on a Gemini-200 Varian spectrometer (50.29 MHz for carbon) in $CDCl_3$ (compound **12d**). Mass spectra (EI) were obtained on a Varian MAT-311A spectrometer with direct injection of samples into the ionic source; the accelerating voltage was 3 kV, emission current 1000 μA, ionizing electron energy 70 eV. The course of the reactions and purity of the compounds were monitored on Silufol UV-254 plates in a 10 : 9 : 1 benzene—ether—acetone mixture and visualized with iodine.

The initial 2-*p*-chlorobenzoylmethylene-5-*p*-chlorophenyl-2,3-dihydro-3-furanone (**10b**) was obtained by the previously described procedure,[17] 5-aryl-2,3-dihydro-2,3-furandiones (**1**) were obtained by a modified procedure from Ref. 10, and 1,6-disubstituted 3,4-dihydroxy-2,4-hexadiene-1,6-diones (**13**) were obtained by known procedures.[12,17]

2-*p*-Chlorobenzoylmethylene-5-phenyl-2,3-dihydro-3-furanone (10a). A mixture of 5-phenyl-2,3-dihydro-2,3-furandione **1b** (1.74 g, 10 mmol) and *p*-chlorobenzoylmethylenetriphenylphosphorane (4.15 g, 10 mmol) was refluxed in benzene (50 mL) for 1—2 min (TLC control). The solvent was evaporated, and the residue was crystallized from butyl acetate to yield 1.33 g (43 %) of the (*E*)-isomer, m.p. 151—152 °C. IR, ν/cm^{-1}: 1700 (C(3)=O), 1684 (COPhCl-*p*), 1676, 1642 (C=C, Ar). ^{1}H NMR ($CDCl_3$), δ: 6.35 (s, 1 H, CH_{exo}); 7.00 (s, 1 H, C(4)H); 7.61—7.98 (m, 9 H, Ph, C_6H_4). Found (%): C, 69.21; H, 3.89; Cl, 11.27. $C_{18}H_{11}ClO_3$. Calculated (%): C, 69.58; H, 3.57; Cl, 11.41.

After one day, the precipitate that formed was filtered off from the mother liquor to yield 0.50 g (16 %) of the (*Z*)-isomer, m.p. 151—152 °C. IR, ν/cm^{-1}: 1690 (C(3)=O), 1672 (COPhCl-*p*), 1570—1602 (C=C, Ar). ^{1}H NMR ($CDCl_3$), δ: 6.70 (s, 1 H, CH_{exo}); 7.06 (s, 1 H, C(4)H); 7.45—8.05 (m, H, Ph, C_6H_4). Found (%): C, 69.75 H, 3.32; Cl, 11.63. $C_{18}H_{11}ClO_3$. Calculated (%): C, 69.58; H, 3.57; Cl, 11.41.

1,6-Diaryl-1-arylamino-4-hydroxy-1,4-hexadiene-3,6-diones (12a—e). A mixture of 2-*p*-chlorobenzoylmethylene-5-phenyl-2,3-dihydro-3-furanone **10a** (0.5 g, 1.61 mmol) and the corresponding arylamines (aniline, *p*-toluidine, or *p*-anizidine) (1.61 mmol) (method A) or the corresponding *N*-arylideneamines (benzilideneaniline, *p*-methoxybenzilidene-*p*-tolylamine, benzylidene-*p*-methoxyphenylamine, or benzilidene-*p*-bromophenylamine) (1.61 mmol) (method B) was refluxed in ethanol (50 mL) for 10—20 min (TLC control). The solvent was evaporated, and the residue was crystallized from acetonitrile (compounds **12a,c—e**) or *iso*-PrOH (compounds **12b,d**).

Compound 12a. The yields were 0.15 g (23 %) (method A) and 0.30 g (46 %) (method B), m.p. 169—170 °C. IR, ν/cm^{-1}: 1592, 1562 (wide peaks, $C{=}O_{chelate}$, Ar). ^{1}H NMR (DMSO-d_6), δ: 6.15 (s, 1 H, C(2)H); 6.80—8.71 (m, 15 H, C(5)H, 2 Ph, C_6H_4), 12.85 (br.s, 1 H, NH). Found (%): C, 71.10; H, 4.72; N, 3.66; Cl, 8.24. $C_{24}H_{18}ClNO_3$. Calculated (%): C, 71.38; H, 4.49; N, 3.47; Cl, 8.78.

Compound 12b. The yields were 0.22 g (33 %) (method A) and 0.10 g (15 %) (method B), m.p. 165—166 °C (dec.). IR, ν/cm^{-1}: 1592, 1556 (wide peaks, $C{=}O_{chelate}$, Ar). ^{1}H NMR ($CDCl_3$), δ: 2.20 (s, 3H, Me); 6.28 (s, 1 H, C(2)H); 6.78—8.10 (m, 14 H, C(5)H, Ph, 2 C_6H_4), 12.88 (br.s, 1 H, NH). Found (%): C, 71.54; H, 4.40; N, 3.67; Cl, 8.22. $C_{25}H_{20}ClNO_3$. Calculated (%): C, 71.85; H, 4.82; N, 3.35; Cl, 8.48.

Compound 12c. The yields were 0.35 g (52 %) (method A) and 0.25 g (37 %) (method B), m.p. 183—184 °C (dec.). IR, ν/cm^{-1}: 1605, 1556 (wide peaks, $C{=}O_{chelate}$, Ar). ^{1}H NMR ($CDCl_3$), δ: 2.20 (s, 3 H, Me); 6.25 (s, 1 H, C(2)H); 7.00—8.05 (m, 14 H, C(5)H, Ph, 2 C_6H_4), 12.18 (br.s, 1 H, NH). Found (%): C, 71.42; H, 5.11; N, 3.50; Cl, 8.74. $C_{25}H_{20}ClNO_3$. Calculated (%): C, 71.85; H, 4.82; N, 3.35; Cl, 8.48.

Compound 12d. The yields were 0.55 g (79 %) (method A) and 0.20 g (29 %) (method B), m.p. 138—139 °C (dec.). IR, ν/cm^{-1}: 1596, 1552 (wide peaks, $C{=}O_{chelate}$, Ar). ^{1}H NMR ($CDCl_3$), δ (the signals of the two detected isomers are given): 3.70 (s, 3 H, OMe, *E*-isomer); 3.72 (s, 3 H, OMe, *Z*-isomer), the ratio of the first two signals was 1.5 : 1; 6.28 (s, 1 H, C(2)H); 6.31 (s, 1 H, C(2)H); 6.70—7.92 (m, 2 × 14 H, 2 C(5)H, 2 Ph, 4 C_6H_4), 12.17 (s, 1 H, NH); 13.12 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$) δ, (the signals of the two detected isomers are given): 55.38 (*E*), 55.46 (*Z*) (MeO); 94.06, 94.83, 95.07, 97.66 (C(2) and C(5), unassigned signals of both isomers are given); 114.31 (*E*), 114.68 (*Z*) (C(1)); 124.03, 125.14, 127.25, 128.48, 128.59, 128.76, 128.86, 129.02, 130.09, 131.69, 132.49, 133.06, 134.08, 134.18, 134.87, 137.70, 138.12, 139.33, 156.11, 157.42, 157.59, 164.96 (Ar), (*Z*) + (*E*); 179.96 (*E*), 182.43 (*Z*) (C(3)); 184.18 (*E*), 185.35 (*Z*) (C(4)); 187.68 (*E*), 189.52 (*Z*) (C(6)). Mass spectrum 434 [M$^+$]. Found (%): C, 69.56; H, 4.21; N, 3.07; Cl, 8.49. $C_{25}H_{20}ClNO_4$. Calculated (%): C, 69.21; H, 4.65; N, 3.23; Cl, 8.17.

Compound 12e. The yields were 0.30 g (39 %) (method A) and 0.20 g (26 %) (method B), m.p. 145—146 °C (dec.). IR, ν/cm^{-1}: 1590, 1554 (wide peaks, $C{=}O_{chelate}$, Ar). ^{1}H NMR (DMSO-d_6), δ (poorly soluble): 6.75—7.80 (m, 15 H, C(2)H, C(5)H, Ph, 2 C_6H_4). Found (%): C, 59.43; H, 3.78; N, 3.21. $C_{24}H_{17}BrClNO_3$. Calculated (%): C, 59.71; H, 3.55; N, 2.90.

3-*p*-Chlorobenzoylmethylene-3,4-dihydro-2*H*-benzo[*b*]-1,4-oxazin-2-one (15d). Method A (from **10a,b**). A mixture of 5-aryl-2-*p*-chlorobenzoylmethylene-2,3-dihydro-3-furanones **10a** or **10b** (1.6 mmol) and *o*-aminophenol (0.17 g, 1.6 mmol) was refluxed in ethanol (50 mL) for 30 min (TLC control). The residue was filtered off and crystallized from *iso*-PrOH to yield 0.27 g (56 %) (starting from **10a**) or 0.35 g (73 %) (starting from **10b**) of the product, m.p. 187—188 °C. IR, ν/cm^{-1}: 1756 (C(2)=O), 1628, 1592 (wide peaks, C=O in chelate with NH, Ar). ^{1}H NMR ($CDCl_3$) δ: 6.55 (s, 1 H, CH); 6.88—7.95 (m, 8 H, 2 C_6H_4), 12.90 (br.s, 1 H, NH). ^{1}H NMR (DMSO-d_6), δ: 6.78 (s, 1 H, CH); 7.15—8.05 (m, 8 H, 2 C_6H_4), 12.78 (br.s, 1 H, NH). MS, *m/z* (*I* (%)) (the peaks with *I* > 3 % are given; double fragment [M_x]$^+$ and [M_x+2]$^+$peaks were due to the ions with ^{35}Cl and ^{37}Cl isotopes): 301 (45), 299 (100) [M]$^+$, 272 (36), 270 (64) [M—CO—H]$^+$, 265 (82) [M—Cl+H]$^+$, 264 (3), 258 (3), 256 (7) [M—CO_2—H]$^+$, 237 (31) [M—Cl—CO+H]$^+$, 236 (57) [M—Cl—CO], 222 (4), 188 (4), 160 (79) [M—*p*-ClPh—CO]$^+$, 159 (10) [M—*p*-ClPh—CO—H]$^+$, 141 (20), 139 (58) [*p*-ClPh—C≡O]$^+$, 123 (4), 122 (8), 119 (4), 118 (5), 113 (13), 111 (40) [*p*-ClPh]$^+$, 106 (5), 105 (44) [Ph—C≡O]$^+$, 104 (10), 103 (5), 102 (4), 92 (3), 89 (4), 78 (9), 77 (77) [Ph]$^+$, 76 (12), 75 (13), 68 (5), 65 (22), 64 (18). Found (%): C, 64.48; H, 3.59; N, 4.95; Cl, 11.27. $C_{16}H_{10}ClNO_3$. Calculated (%): C, 64.12; H, 3.36; N, 4.67; Cl, 11.83.

3-Aroylmethylene-3,4-dihydro-2*H*-benzo[*b*]-1,4-oxazin-2-ones (15a—d). Method B (starting from **13a—e**). A mixture of the corresponding disubstituted 3,4-dihydroxy-2,4-hexadiene-1,6-diones (**13a—e**) (5.0 mmol) and *o*-aminophenol (0.55 g, 5.0 mmol) was refluxed in ethanol (50—100 mL) for 0.5—2 h

(TLC control). The residue was filtered off and crystallized from acetonitrile (compounds **15a—b**) or toluene (compound **15d**).

Compound 15a. Yield 1.10 g (83 %), m.p. 184—185 °C (*cf.* Ref. 14: 203—204 °C). IR, ν/cm^{-1}: 1754 (C(2)=O), 1602, 1590 (wide peaks, C=O in chelate with NH, Ar). ^1H NMR (DMSO-d_6), δ: 7.13 (s, 1 H, CH); 7.48—8.10 (m, 9 H, Ph, C_6H_4); a distinct signal of the NH group proton was not found in the spectrum. Found (%): C, 72.13; H, 4.34; N, 5.40. $C_{16}H_{11}NO_3$. Calculated (%): C, 72.45; H, 4.18; N, 5.28.

Compound 15b. Yield 1.20 g (86 %), m.p. 189—190 °C (*cf.* Ref. 14: 193—194 °C). IR, ν/cm^{-1}: 1760 (C(2)=O), 1615, 1600 (wide peaks, C=O in chelate with NH, Ar). ^1H NMR (DMSO-d_6), δ: 2.36 (s, 3 H, Me); 6.82 (s, 1 H, CH); 7.10—7.82 (m, 8 H, 2 C_6H_4); a distinct signal of the NH group proton was not found in the spectrum. Found (%): C, 73.52; H, 4.88; N, 4.79. $C_{17}H_{13}NO_3$. Calculated (%): C, 73.11; H, 4.69; N, 5.02.

Compound 15c. Yield 0.90 g (61 %), m.p. 164—165 °C. IR, ν/cm^{-1}: 1755 (C(2)=O), 1620, 1600 (wide peaks, C=O in chelate with NH, Ar). ^1H NMR (DMSO-d_6), δ: 1.32 (t, 3 H, $\underline{CH_3}CH_2$); 4.08 (q, 2 H, $CH_3\underline{CH_2}$); 6.85 (s, 1 H, CH); 7.05—7.95 (m, 8 H, 2 C_6H_4), 12.85 (br.s, 1 H, NH). Found (%): C, 73.60; H, 5.43; N, 4.47. $C_{18}H_{15}NO_3$. Calculated (%): C, 73.71; H, 5.15; N, 4.78.

Compound 15d. Yield 1.15 g (77 %), m.p. 187—188 °C.

3-Pivaloylmethylene-3,4-dihydro-2*H*-benzo[*b*]-1,4-oxazin-2-one (15e).[18] A mixture of 5,6-dihydroxy-2,2,9,9-tetramethyl-4,6-decadiene-3,8-dione (**13f**) (1.27 g) and *o*-aminophenol (0.55 g, 5.0 mmol) was heated in ethanol (50 mL) until dissolution. The solvent was evaporated, and the residue was crystallized from ethanol to yield 1.10 g (90 %) of **15e**, m.p. 80—81 °C. IR, ν/cm^{-1}: 1766 (C(2)=O), 1628, 1605 (wide peaks, C=O in chelate with NH, Ph). ^1H NMR (DMSO-d_6), δ: 1.13 (s, 9 H, Me_3C), 6.37 (s, 1 H, CH); 6.70—7.45 (m, 4 H, C_6H_4), 12.33 (br.s, 1 H, NH). Found (%): C, 68.89; H, 5.94; N, 5.38. $C_{14}H_{15}NO_3$. Calculated (%): C, 68.56; H, 6.16; N, 5.71.

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