THERMAL REARRANGEMENT OF 3-HYDROXY-1H,3H-QUINOLINE-2,4-DIONES TO 3-ACYLOXY-2,3-DIHYDRO-1H-INDOL-2-ONES

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Abstract - 3-Alkyl/aryl-3-hydroxy-1H,3H-quinoline-2,4-diones (2) were transformed into isomeric 3-acyloxy-2,3-dihydro-1H-indol-2-ones (3) by thermally induced molecular rearrangement. All products were characterized by their 1H NMR, 13C NMR, and IR spectra.

Despite possessing interesting biological activity, exemplified by antihypoxic 3-acetoxy-5-bromo-2,3-dihydro-1H-indol-2-one,1 relatively few methods2-10 for the preparation of 3-acyloxy-2,3-dihydro-1H-indol-2-ones (3) have been described in the literature.2-10

Most commonly 3-acyloxy-2,3-dihydro-1H-indol-2-ones are accessed by acylation of dioxindoles with carboxylic acid anhydrides or acyl chlorides. A relatively limited selection of other methods is based either on a modification of substituted indoles or a ring formation starting from the appropriate o-disubstituted benzenes. Examples to the former are chlorine substitution in methyl 3-(3-chloro-2-oxo-2,3-dihydro-1H-indol-3-yl)propionate by acetoxy group in the presence of tetrabutylammonium acetate,2 reduction of 4,7-dimethoxyisatine with Zn/Cu in acetic acid,3 oxidative transformation of 1-benzenesulfonyl-3-methylindole with manganese(III) acetate,4 and reduction of isatines with zinc in acetic acid/acetic anhydride.5,6 Cyclization of o-aminomandelic acids by the action of acetic anhydride7 and reduction of acyloxy(2-nitrophenyl)acetic acid,8 its ester9 or amide,9 followed by a cyclization have been reported to yield compounds (3).

We recently reported that 3-hydroxy-1H,3H-quinoline-2,4-diones (2) rearranged through the action of various organic bases as catalysts in boiling xylene or cyclohexanol to the isomeric 3-acyloxy-2,3-dihydro-1H-indol-2-ones (3) and/or 4-acyl-1,4-dihydro-3,1-benzoxazin-2-ones (4) (Scheme 1).10 The course of the rearrangement depended on the choice of the substituents rather than the reaction

# Dedicated to Professor Thomas Kappe, Professor of Karl Franzens University of Graz, on the occasion of his 70th birthday.
conditions.\textsuperscript{10} Thus, the rearrangement to 3 took place to a significant degree only with 5-substituted 3-hydroxy-1\textit{H},3\textit{H}-quinoline-2,4-diones (2, \(R^3\neq H\)). The yield of 3 also slightly depended on \(R^6\), with 8-protio analogues being lower. Compounds (2) unsubstituted at the fused benzene ring reacted only to a minor degree or did not react at all. Interestingly, 3-phenyl substituted 2 (\(R^2=\text{Ph}\)) reacted to benzoxazinones (4) as major or even sole products. The rearrangement of 2 also took place in the absence of catalysts but the conversions were generally low.

In our present study we have tried to obtain further information on the conversion of 2 to 3 and/or 4. We have endeavored to find reaction conditions that would lead to increased yields in the rearrangement of substances (2) unsubstituted at the fused benzene ring, as well as conditions for a selective formation of 3 or 4.

**Scheme 1**

\[
\begin{align*}
\text{Scheme 1} & \quad \text{NO}_2\text{R}_1\text{OH} \quad \text{NO}_2\text{R}_1\text{O} \quad \text{R}_2\text{OH} \\
& \quad \text{R}_2\text{O} \quad \text{R}_3\text{R}_4\text{R}_5\text{R}_6 \quad \text{R}_5\text{R}_4\text{R}_3\text{R}_6 \\
& \quad \text{N} \quad \text{O} \quad \text{R}_1\text{COR}_2 \quad \text{R}_6 \quad \text{R}_5 \quad \text{R}_4 \quad \text{R}_3 \quad \text{R}_6 \quad \text{R}_5 \quad \text{R}_4 \quad \text{R}_3 \quad \text{N} \quad \text{R}_1\text{O} \quad \text{OCOR}_2 \quad + \\
& \quad \text{CH}_3\text{COOOH} \quad 1 \quad 2 \quad 3 \quad 4
\end{align*}
\]

**RESULTS AND DISCUSSION**

Starting 3-hydroxy-1\textit{H},3\textit{H}-quinoline-2,4-diones (2a-s) (Scheme 1, Table 1) were prepared by condensation of the corresponding anilines with substituted malonates,\textsuperscript{10-14} followed by oxidation of 4-hydroxy-1\textit{H}-quinolin-2-ones (1a-s) with peroxycetic acid.\textsuperscript{10,14,15}

In our preliminary experiments we determined an optimal reaction temperature for the rearrangement of 2. To this end we heated solid (2a-s) at different temperatures using a melting point apparatus, and monitored the reactions by a semi quantitative TLC. Most of the substrates reacted within a temperature interval of 150-270 °C, whereas at higher temperatures decomposition to complex reaction mixtures took place in most cases. Next we turned to the investigation of the rearrangements on a preparative scale. Based on the above preliminary results we decided to conduct the reactions in boiling cyclohexylbenzene, at 250 °C.

Previously, we have demonstrated that in boiling xylene 3-hydroxy-1\textit{H},3\textit{H}-quinoline-2,4-diones (2) unsubstituted at the fused benzene ring remained unreacted even after several hours of reflux.\textsuperscript{10} On the contrary, in boiling cyclohexylbenzene complete conversion of these compounds is observed within 20-40 min and products (3) were isolated in moderate to good yields (Table 1).

To be able to compare these results with those previously described\textsuperscript{10} we decided to conduct the experiments also in the presence of catalytic triphenylphosphine. Addition of 20 mol% of triphenylphosphine to the reaction mixture slightly increased the yields of 3. However, this increase is
caused not only by the catalytic activity of triphenylphosphine, but mainly by the fact that, under its presence, the quantity of intensely colored side-products is diminished in most cases. This facilitates chromatographic separation of the reaction mixture and, consequently, increases the yields of 3. Further suppression of the colored side-products formation can be achieved also by the addition of hydroquinone or dibenzoyl peroxide to the reaction mixture (see rearrangement of 2s in Table 1).

Table 1. Rearrangement of 2a-s in boiling cyclohexylbenzene.

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<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>R⁵</th>
<th>R⁶</th>
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ₐHydroquinone (10 mol%) was added. ᵇDibenzoyl peroxide (3 mol%) was added.

In both cases, whether the catalyst was present or not, the exclusive products of the rearrangements of 2 were 3-acyloxy-2,3-dihydro-1H-indol-2-ones (3). Merely in a single case of 2g a minute quantity of
isomeric benzoxazinone derivative (4g) was isolated together with substance (3g). This result shows that at a given reaction temperature thermodynamic control of the reaction definitely prevails, resulting in thermodynamically more stable products (3). It may thus be assumed that if the reaction is conducted toward increasing yield of substances (4), it will be probably necessary to work at a lower temperature employing highly basic catalysts. Experiments in this respect are planned.

As can be seen from Table 1, the yields of 3 depend on the character of the lactam nitrogen atom. Provided the lactam group in 2 is secondary, as in the case of 2a-h, the yields of 3 are modest (10-20%). Despite that it is noteworthy that under the reaction conditions, previously used in the literature,10 these compounds did not react at all. Unfortunately, our attempts to increase the yields of 3a-h by prolonged reflux in cyclohexylbenzene failed. Instead, large amounts of side-products were formed. On the other hand, starting compounds (2i-s) with a tertiary lactam group rearranged in boiling cyclohexylbenzene smoothly to give the corresponding 3-acyloxy-2,3-dihydro-1H-indol-2-ones (3i-s) in good to very good yields.

The presence of benzyl group at 3-position of starting substances (2) reduced the yields of 3 due to the formation of side-products. On the other hand, much better yields of 3 were obtained with substances (2p-s) having phenyl group on lactam nitrogen atom. The phenyl group obviously contributes to the migration capability of carbon atom C-2 through its mesomeric effect.

IR spectra of 3 exhibit absorption bands characteristic for both ester group (1725–1753 cm⁻¹) and lactam group (1696–1731 cm⁻¹). The dioxindole structure of 3 has been unequivocally confirmed by the presence of characteristic resonance in ¹³C NMR spectra at 69.1–70.8 ppm (C-3), 170.3–172.5 ppm (O-COR²) and 171.1–173.8 ppm (C-2).10 In the case of phenyl esters, the ester carbonyl signal shifted to a region of 164.85–164.92 ppm.

In conclusion, the described thermally induced rearrangement of 3-hydroxy-1H,3H-quinoline-2,4-diones (2) is not only interesting from a theoretical point of view, but owing to good yields particularly with compounds substituted at the lactam nitrogen, can become a valuable preparative tool for the synthesis of 3-acyloxy-2,3-dihydro-1H-indol-2-ones (3). Easily available precursors (2) and simple reaction conditions make this protocol an attractive alternative for the synthesis of dioxindoles and isatines, especially N-substituted isatins, which are known to be prepared by the classical Sandmeyer synthesis in relatively low yields.16

EXPERIMENTAL

Melting points were determined on a Kofler block or Gallencamp apparatus. IR (KBr) spectra were recorded on a Mattson 3000 Spectrometer. NMR spectra were recorded on a Bruker DPX-300 spectrometer in hexadeuteriodimethyl sulfoxide (unless otherwise indicated). Chemical shifts are given on the δ scale (ppm) and are referred to internal TMS. MS spectra were obtained on a VG-Analytical
AutospecQ instrument. Column chromatography was carried out on silica gel (Merck, grade 60, 70-230 mesh) using benzene and then successive mixtures of benzene-ethyl acetate (from the rations of 99:1 to 8:2) as eluent (solvent system S). The course of separation and also the purity of substances were monitored by TLC (elution systems benzene-ethyl acetate 4:1, and chloroform-ethanol 9:1 and/or 19:1) on Alugram® SIL G/UV254 foils (Macherey-Nagel). Elemental analyses (C, H, N) were performed with a Perkin-Elmer 2400 CHN Analyser and EA 1108 Elemental Analyzer (Fisons Instrument).

4-Hydroxy-1H-quinoline-2-ones (1a-s) were prepared by condensation of the corresponding anilines with substituted diethyl malonates according to the described procedure.14

1-Benzyl-3-butyl-4-hydroxy-1H-quinoline-2-one (1n). Colorless crystals, mp 156-157 °C (ethanol), yield 91%; IR 2800-3500 (br), 2959, 2930, 2875, 1630, 1605, 1580, 1500, 1458, 1440, 1410, 1335, 1300, 1288, 1160, 1030, 1009, 978, 944, 910, 880, 851, 757, 739, 703, 675; 1H NMR (CDCl3) δ 0.95 (t, 3H, CH3 of butyl, J = 7.2 Hz), 1.39-1.52 (m, 2H, 3-H of butyl), 1.58-1.67 (m, 2H, 2-H of butyl), 2.74 (t, 2H, 1-H of butyl, J = 7.7 Hz), 5.56 (s, 2H, NCH2), 6.13 (s, 1H, OH), 7.15-7.31 (m, 7H, 6-H, 8-H and phenyl protons), 7.40 (ddd, 1H, 7-H, J = 8.5, 7.2, 1.5 Hz), 7.98 (dd, 1H, 5-H, J = 8.0, 1.5 Hz). Anal. Calcd for C20H21NO2: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.45; H, 6.83; N, 4.64.

3-Hydroxy-1H,3H-quinoline-2,4-diones (2a-s) were prepared by oxidation of 4-hydroxy-1H-quinolin-2-ones (1a-s) with peroxyacetic acid according to the described procedure.15

1-Benzyl-3-butyl-3-hydroxy-1H,3H-quinoline-2,4-dione (2n). Colorless crystals, mp 112-114 °C (methanol), yield 70%; IR 3464, 2955, 2920, 2870, 1710, 1675, 1600, 1490, 1469, 1370, 1355, 1305, 1211, 1183, 1160, 1114, 1090, 1058, 1018, 954, 785, 762, 740, 703; 1H NMR (CDCl3) δ 0.84 (t, 3H, CH3 of butyl, J = 7.4 Hz), 1.18-1.52 (m, 4H, 3-H and 2-H of butyl), 1.83-2.04 (m, 2H, 1-H of butyl), 3.92 (s, 1H, OH), 4.95 and 5.57 (two d, 2H, NCH2, J = 16.6 Hz), 7.05 (d, 1H, 8-H, J = 8.4 Hz), 7.16 (ddd, 7.4, 0.5 Hz, 1H, 6-H, J = 7.7), 7.20-7.39 (m, 5H, phenyl protons), 7.40 (ddd, 1H, 7-H, J = 8.4, 7.4, 1.6 Hz), 7.95 (dd, 1H, 5-H, J = 7.7, 1.6 Hz); 13C NMR (CDCl3) δ 13.78, 22.42, 24.93, 40.98, 46.93, 82.85, 115.90, 120.80, 123.83, 126.39, 127.72, 128.11, 129.04, 135.67, 136.04, 141.99, 172.78, 194.82. Anal. Calcd for C20H21NO3: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.02; H, 6.60; N, 4.58.

General procedure for the rearrangement of 3-hydroxy-1H,3H-quinoline-2,4-diones (2a-s) to 2-oxo-2,3-dihydro-1H-indol-3-yl carboxylates (3a-s) and 5-chloro-8-methyl-4-pentanoyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (4g). A mixture of 2 (3 mmol) and additives (Table 1) in cyclohexylbenzene (10 mL) was refluxed for 20-80 min (Table 1). After cooling, the precipitated unreacted starting material (2) was filtered off with suction (in only several cases). Filtrate or crude reaction mixture were separated by
column chromatography using solvent system S as eluent. For yields of 3 see Table 1. For physical and spectroscopic data of compounds (3a,g,h,i and 4g) see literature.¹⁰

2-Oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3a). Colorless crystals, mp 71-73 °C (hexane), lit.,¹⁰ mp 72-74 °C (cyclohexane).

2-Oxo-2,3-dihydro-1H-indol-3-yl phenylacetate (3b). Colorless crystals, mp 104-108 °C (benzene-hexane); IR 3212, 3117, 3031, 2931, 2875, 1736, 1696, 1622, 1599, 1494, 1469, 1391, 1350, 1328, 1303, 1293, 1233, 1182, 1123, 1105, 1039, 900, 768, 720, 694 cm⁻¹; ¹H NMR δ 3.81 (s, 2H, PhCH₂), 5.93 (s, 1H, 3-H), 6.84 (d, 1H, 7-H, J = 7.5 Hz), 6.95 (t, 1H, 5-H, J = 7.3 Hz), 7.17 (d, 1H, 4-H, J = 7.0 Hz), 7.21-7.38 (m, 6H, ArH and 6-H), 10.59 (br s, 1H, NH); ¹³C NMR δ 70.54 (3-C), 109.87, 121.77, 124.69, 124.82, 126.87, 128.31, 129.21, 129.84, 133.76, 142.81, 170.38, 173.14. Anal. Calcd for C₁₆H₁₃NO₃: C 71.90; H 4.90; N 5.24. Found: C 72.23; H 4.83; N 5.04.

2-Oxo-2,3-dihydro-1H-indol-3-yl benzoate (3c). Colorless crystals, mp 136-138 °C (benzene), lit.,¹⁷ mp 134 °C; IR 3164, 3092, 3064, 3034, 2961, 2894, 2845, 1742, 1721, 1619, 1599, 1473, 1451, 1338, 1256, 1236, 1208, 1178, 1103, 1096, 1070, 1027, 871, 778, 755, 726, 701, 682, 658; ¹H NMR δ 6.18 (s, 1H, 3-H), 6.91 (d, 1H, 7-H, J = 7.6 Hz), 6.98 (t, 1H, 5-H, J = 7.4 Hz), 7.23-7.25 (m, 2H, 4-H and 6-H), 7.56 (m, 2H, 3-H of phenyl), 7.71 (m, 1H, 4-H of phenyl), 8.02 (m, 2H, 2-H of phenyl), 10.70 (s, 1H, NH); ¹³C NMR δ 70.94 (3-C), 109.99, 121.87, 124.83, 124.86, 128.57, 128.87, 129.41, 129.94, 133.87, 142.95, 164.86, 173.28. Anal. Calcd for C₁₅H₁₁NO₃: C 71.14; H 4.38; N 5.53. Found: C 71.15; H 4.19; N 5.57.

5-Methyl-2-oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3d). Colorless crystals, mp 82-83 °C (hexane); IR 3318, 2962, 2932, 2873, 1748, 1728, 1627, 1492, 1467, 1386, 1349, 1268, 1204, 1180, 1137, 1125, 1037, 1007, 734, 679, 645 cm⁻¹; ¹H NMR δ 0.87 (t, 3H, CH₃ of butyl, J = 7.3 Hz), 1.24-1.38 (m, 2H, 3-H of butyl), 1.48-1.60 (m, 2H, 2-H of butyl), 2.23 (s, 3H, ArCH₃), 2.41 (t, 2H, 1-H of butyl, J = 7.3 Hz), 5.87 (s, 1H, 3-H), 6.73 (d, 1H, 7-H, J = 7.8 Hz), 7.04 (s, 1H, 4-H), 7.06 (d, 1H, 6-H, J = 8.3 Hz), 10.47 (br s, 1H, NH); ¹³C NMR δ 13.46, 20.45, 21.38, 26.49, 32.79, 70.13 (3-C), 109.61, 125.09, 125.32, 129.95, 130.73, 140.33, 172.15, 173.28. Anal. Calcd for C₁₄H₁₇NO₃: C 68.00; H 6.93; N 5.66. Found: C 68.24; H 7.04; N 5.73.

5-Chloro-2-oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3e). Colorless crystals, mp 112-114 °C (benzene); IR 3203, 2959, 2930, 2870, 1737, 1698, 1621, 1473, 1443, 1302, 1234, 1227, 1179, 1156, 1107, 1034, 833, 723, 565 cm⁻¹; ¹H NMR δ 0.87 (t, 3H, CH₃ of butyl, J = 7.3 Hz), 1.24-1.38 (m, 2H, 3-H of butyl), 1.48-1.59 (m, 2H, 2-H of butyl), 2.43 (t, 2H, 1-H of butyl, J = 7.3 Hz), 5.90 (s, 1H, 3-H), 6.86 (d, 1H, 7-H, J = 8.2 Hz), 7.28 (br s, 1H, 4-H), 7.32 (dd, 1H, 6-H, J = 8.3, 2.0 Hz), 10.70 (s, 1H, NH); ¹³C
NMR δ 13.45, 21.37, 26.40, 32.66, 70.03 (3-C), 111.28, 124.69, 125.68, 127.08, 129.49, 141.67, 172.10, 173.09. Anal. Calcd for C_{13}H_{14}NO_3Cl: C 58.32; H 5.27; N 5.23. Found: C 58.52; H 5.21; N 5.27.

7-Methyl-2-oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3f). Colorless crystals, mp 116-123 °C (cyclohexane); IR 3168, 3094, 3036, 2957, 2930, 2873, 1748, 1721, 1628, 1609, 1492, 1466, 1437, 1384, 1348, 1266, 1216, 1164, 1113, 1058, 814, 765, 733, 562 cm^{-1}; ^1H NMR δ 0.87 (t, 3H, CH_3 of butyl, J = 7.3 Hz), 1.24-1.37 (m, 2H, 3-H of butyl), 1.48-1.59 (m, 2H, 2-H of butyl), 2.20 (s, 3H, ArCH_3), 2.41 (t, 2H, 1-H of butyl, J = 7.3 Hz), 5.90 (s, 1H, 3-H), 6.88 (t, 1H, 5-H, J = 7.5 Hz), 7.03 (d, 1H, 4-H, J = 7.4 Hz), 7.08 (d, 1H, 6-H, J = 7.6 Hz), 10.61 (s, 1H, NH); ^13C NMR δ 13.46, 16.14, 21.37, 26.52, 32.79, 70.38 (3-C), 119.27, 121.75, 121.94, 124.69, 130.99, 141.33, 172.12, 173.79. Anal. Calcd for C_{14}H_{17}NO_3: C 68.00; H 6.93; N 5.66. Found: C 68.22; H 7.02; N 5.84.

4-Chloro-7-methyl-2-oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3g). Colorless crystals, mp 106-113 °C (cyclohexane), lit., mp 108-113 °C (cyclohexane).

6-Chloro-7-methyl-2-oxo-2,3-dihydro-1H-indol-3-yl phenylacetate (3h). Colorless crystals, mp 190-194 °C (methanol), lit., mp 190-193 °C (benzene).

1-Methyl-2-oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3i). Pale yellow oil; IR spectrum is identical with that of the authentic sample.

1-Methyl-2-oxo-2,3-dihydro-1H-indol-3-yl phenylacetate (3j). Colorless crystals, mp 63-65 °C (benzene-hexane), IR 3092, 3059, 2932, 1735, 1727, 1616, 1494, 1469, 1454, 1376, 1354, 1338, 1243, 1144, 1093, 1023, 894, 852, 758, 749, 731, 695 cm^{-1}; ^1H NMR δ 3.11 (s, 3H, N-CH_3), 3.81 (s, 2H, PhCH_2), 6.00 (s, 1H, 3-H), 6.95-7.07 (m, 2H, 5-H and 7-H), 7.21-7.40 (m, 7H, 4-H, 6-H and phenyl protons); ^13C NMR δ 26.00, 40.29, 70.04 (3-C), 108.81, 122.41, 124.08, 124.36, 126.88, 128.31, 129.21, 129.96, 133.69, 144.26, 170.39, 171.42. Anal. Calcd for C_{17}H_{15}NO_3: C 72.58; H 5.37; N 4.98. Found: C 72.59; H 5.29; N 5.07.

1-Methyl-2-oxo-2,3-dihydro-1H-indol-3-yl benzoate (3k). Colorless crystals, mp 116-118 °C (cyclohexane), IR 3058, 3031, 2966, 2937, 1722, 1711, 1612, 1494, 1472, 1449, 1378, 1354, 1318, 1271, 1249, 1129, 1111, 1094, 1067, 1032, 752, 707, 684, 637, 630 cm^{-1}; ^1H NMR δ 3.19 (s, 3H, N-CH_3), 6.26 (s, 1H, 3-H), 7.02-7.12 (m, 2H, 5-H and 7-H), 7.34-7.45 (m, 2H, 4-H and 6-H), 7.57 (m, 2H, 3-H of phenyl), 7.74 m (1H, 4-H of phenyl), 8.01 (m, 2H, 2-H of phenyl); ^13C NMR δ 26.12, 70.45 (3-C), 108.92, 122.52, 124.13, 124.51, 128.45, 128.88, 129.43, 130.06, 133.92, 144.40, 164.85, 171.57. Anal. Calcd for C_{16}H_{13}NO_3: C 71.90; H 4.90; N 5.24. Found: C 72.14; H 4.70; N 5.41.
1,4,6-Trimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3l). Colorless crystals, mp 72-73 °C (hexane); IR 2958, 2928, 2870, 1743, 1725, 1712, 1621, 1609, 1460, 1381, 1372, 1349, 1305, 1164, 1098, 1032, 983, 874, 841, 610, 587 cm\(^{-1}\). \(^1\)H NMR δ 0.86 (t, 3H, CH\(_3\) of butyl, \(J = 7.3\) Hz), 1.22-1.37 (m, 2H, 3-H of butyl), 1.47-1.58 (m, 2H, 2-H of butyl), 2.13 (s, 3H, ArCH\(_3\)), 2.29 (s, 3H, ArCH\(_3\)), 2.40 (t, 2H, 1-H of butyl, \(J = 7.3\) Hz), 3.08 (s, 3H, N-CH\(_3\)), 6.03 (s, 1H, 3-H), 6.68 (s, 1H, Ar-H), 6.69 (s, 1H, Ar-H); \(^{13}\)C NMR δ 13.44, 17.26, 21.25, 21.39, 26.01, 26.52, 32.65, 69.10 (3-C), 107.17, 119.10, 124.41, 134.39, 139.64, 144.52, 171.69, 171.78. Anal. Calcd for C\(_{16}\)H\(_{21}\)NO\(_3\): C 69.79; H 7.69; N 5.09. Found: C 70.08; H 7.73; N 5.17.

1-Ethyl-2-oxo-2,3-dihydro-1H-indol-3-yl phenylacetate (3m). Pale yellow oil; IR 2923, 2851, 1729, 1615, 1490, 1468, 1371, 1237, 1212, 1135, 1095, 1027, 936, 753, 724, 699 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) δ 1.28 (t, 3H, CH\(_3\) of ethyl, \(J = 7.2\) Hz), 3.68-3.83 (m, 2H, 1-H of ethyl), 3.76 (m, 2H, PhCH\(_2\)), 5.93 (s, 1H, 3-H), 6.83 (d, 1H, 7-H, \(J = 7.8\) Hz), 7.00 (t, 1H, 5-H, \(J = 7.5\) Hz), 7.22-7.36 (m, 7H, 4-H, 6-H and phenyl protons); \(^{13}\)C NMR (CDCl\(_3\)) δ 12.42, 29.72, 34.97, 40.77, 70.34 (3-C), 108.62, 122.86, 124.52, 125.66, 127.29, 128.65, 129.32, 130.25, 133.31, 143.63, 170.98, 171.74. HRMS Calcd for C\(_{18}\)H\(_{17}\)NO\(_3\): 295.1208. Found: 295.1217.

1-Benzyl-2-oxo-2,3-dihydro-1H-indol-3-yl pentanoate (3n). Pale yellow oil; IR 2957, 2851, 1734, 1731, 1615, 1489, 1468, 1379, 1366, 1236, 1172, 1160, 1103, 1007, 752, 698 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) δ 0.92 (t, 3H, CH\(_3\) of butyl, \(J = 7.2\) Hz), 1.32-1.46 (m, 2H, 3-H of butyl), 1.60-1.75 (m, 2H, 2-H of butyl), 2.41-2.56 (m, 2H, 1-H of butyl), 4.90 (s, 2H, PhCH\(_2\)), 6.03 (s, 1H, 3-H), 6.69 (d, 1H, 7-H, \(J = 7.7\) Hz), 7.01 (t, 1H, 5-H, \(J = 7.3\) Hz), 7.13-7.39 (m, 7H, 4-H, 6-H and phenyl protons); \(^{13}\)C NMR (CDCl\(_3\)) δ 12.68, 22.17, 26.95, 33.67, 43.98, 69.83 (3-C), 109.54, 123.06, 124.59, 125.42, 127.32, 128.65, 129.32, 130.25, 133.31, 143.63, 170.98, 171.74. HRMS Calcd for C\(_{20}\)H\(_{21}\)NO\(_3\): 323.1521. Found: 323.1534.

1-Benzyl-2-oxo-2,3-dihydro-1H-indol-3-yl phenylacetate (3o). Colorless crystals, mp 99-101 °C (benzene-hexane); IR 3032, 2958, 2914, 1753, 1739, 1719, 1618, 1491, 1471, 1384, 1372, 1357, 1215, 1176, 1144, 995, 751, 730, 699, 547 cm\(^{-1}\). \(^1\)H NMR δ 3.85 (s, 2H, PhCH\(_2\)CO), 4.89 (s, 2H, PhCH\(_2\)N), 6.14 (s, 1H, 3-H), 6.87 (d, 1H, 7-H, \(J = 7.6\) Hz), 7.01 (t, 1H, 5-H, \(J = 7.4\) Hz), 7.20-7.39 (m, 12H, 4-H, 6-H and phenyl protons); \(^{13}\)C NMR δ 39.18, 42.70, 70.28 (3-C), 109.41, 122.51, 124.17, 124.41, 126.90, 127.12, 127.32, 128.22, 128.33, 128.49, 129.22, 129.75, 133.70, 135.84, 143.14, 170.34, 171.68. Anal. Calcd for C\(_{23}\)H\(_{19}\)NO\(_3\): C 77.29; H 5.36; N 3.92. Found: C 77.65; H 5.31; N 4.03.

2-Oxo-1-phenyl-2,3-dihydro-1H-indol-3-yl propanoate (3p). Pale pink crystals, mp 58-63 °C (benzene-hexane); IR 3032, 2958, 2914, 1753, 1739, 1719, 1618, 1491, 1471, 1384, 1372, 1357, 1215, 1176, 1144, 995, 751, 730, 699, 547 cm\(^{-1}\). \(^1\)H NMR δ 3.85 (s, 2H, PhCH\(_2\)CO), 4.89 (s, 2H, PhCH\(_2\)N), 6.14 (s, 1H, 3-H), 6.87 (d, 1H, 7-H, \(J = 7.6\) Hz), 7.01 (t, 1H, 5-H, \(J = 7.4\) Hz), 7.20-7.39 (m, 12H, 4-H, 6-H and phenyl protons); \(^{13}\)C NMR δ 39.18, 42.70, 70.28 (3-C), 109.41, 122.51, 124.17, 124.41, 126.90, 127.12, 127.32, 128.22, 128.33, 128.49, 129.22, 129.75, 133.70, 135.84, 143.14, 170.34, 171.68. Anal. Calcd for C\(_{23}\)H\(_{19}\)NO\(_3\): C 77.29; H 5.36; N 3.92. Found: C 77.65; H 5.31; N 4.03.
1375, 1301, 1234, 1169, 1082, 1037, 764, 752, 704, 694, 599 cm$^{-1}$; $^1$H NMR $\delta$ 1.08 (t, 3H, CH$_3$ of ethyl, $J = 7.3$ Hz), 2.48 (q, 2H, CH$_2$ of ethyl, $J = 7.3$ Hz), 6.14 (s, 1H, 3-H), 6.73 (d, 1H, 7-H, $J = 7.8$ Hz), 7.11 (t, 1H, 5-H, $J = 7.3$ Hz), 7.31 (t, 1H, 6-H, $J = 7.6$ Hz), 7.35-7.51 (m, 4H, 4-, 2-, 4-, and 6-H of phenyl), 7.53-7.64 (m, 2H, 3- and 5-H of phenyl); $^{13}$C NMR $\delta$ 8.80, 26.43, 70.00 (3-C), 109.11, 123.00, 124.23, 124.82, 126.51, 128.17, 129.61, 129.87, 133.92, 144.14, 171.25, 172.95. Anal. Calcd for C$_{17}$H$_{15}$NO$_3$: C 72.58; H 5.37; N 4.98. Found: C 72.81; H 5.28; N 5.07.

2-Oxo-1-phenyl-2,3-dihydro-1$^H$-indol-3-yl butanoate (3q). Colorless crystals, mp 43-47 °C (benzene-hexane); IR 3064, 2967, 2933, 2877, 1737, 1731, 1611, 1595, 1500, 1480, 1467, 1372, 1300, 1247, 1233, 1216, 1180, 1102, 1043, 759, 701, 587 cm$^{-1}$; $^1$H NMR $\delta$ 0.91 (t, 3H, CH$_3$ of propyl, $J = 7.4$ Hz), 1.56-1.64 (m, 2H, 2-H of propyl), 2.44 (t, 2H, 1-H of propyl, $J = 7.3$ Hz), 6.14 (s, 1H, 3-H), 6.75 (d, 1H, 7-H, $J = 7.8$ Hz), 7.11(t, 1H, 5-H, $J = 7.5$ Hz), 7.28-7.62 (m, 7H, 4- H, 6-H and phenyl protons); $^{13}$C NMR $\delta$ 13.18, 17.95, 34.86, 70.01 (3-C), 109.15, 123.00, 124.27, 124.77, 126.52, 128.17, 129.62, 129.88, 133.94, 144.16, 171.25, 172.11. Anal. Calcd for C$_{18}$H$_{17}$NO$_3$: C 73.20; H 5.80; N 4.74. Found: C 73.22; H 5.75; N 4.81.

2-Oxo-1-phenyl-2,3-dihydro-1$^H$-indol-3-yl pentanoate (3r). Pale pink crystals, mp 81-82 °C (benzene-hexane); IR 3057, 2951, 2895, 2866, 2866, 1741, 1724, 1609, 1593, 1500, 1466, 1371, 1300, 1231, 1178, 1111, 1036, 1020, 780, 758, 744, 700, 592 cm$^{-1}$; $^1$H NMR $\delta$ 0.88 (t, 3H, CH$_3$ of butyl, $J = 7.3$ Hz), 1.25-1.38 (m, 2H, 3-H of butyl), 1.50-1.62 (m, 2H, 2-H of butyl), 2.49 (t, 2H, 1-H of butyl, $J = 7.3$ Hz), 6.13 (s, 1H, 3-H), 6.73 (d, 1H, 7-H, $J = 7.9$ Hz), 7.11 (t, 1H, 5-H, $J = 7.5$ Hz), 7.31 (t, 1H, 6-H, $J = 7.7$ Hz), 7.35-7.63 (m, 6H, 4-H and phenyl protons); $^{13}$C NMR $\delta$ 13.18, 17.95, 34.86, 70.01 (3-C), 109.15, 123.00, 124.27, 124.77, 126.52, 128.17, 129.62, 129.88, 133.94, 144.16, 171.25, 172.11. Anal. Calcd for C$_{19}$H$_{19}$NO$_3$: C 73.77; H 6.19; N 4.53. Found: C 73.89; H 6.17; N 4.62.

2-Oxo-1-phenyl-2,3-dihydro-1$^H$-indol-3-yl benzoate (3s). Colorless crystals, mp 133-136 °C (benzene-hexane), lit., 18 mp 137 °C (ethanol); IR 3063, 3033, 2931, 1737, 1721, 1618, 1596, 1501, 1468, 1375, 1349, 1277, 1179, 1107, 1070, 749, 721, 696 cm$^{-1}$; $^1$H NMR $\delta$ 6.41 (s, 1H, 3-H), 6.79 (d, 1H, 7-H, $J = 7.9$ Hz), 7.12 (t, 1H, 5-H, $J = 7.5$ Hz), 7.34 (t, 1H, 6-H, $J = 7.7$ Hz), 7.42-7.68 (m, 8H, 4-H, 3- and 5-H of benzoyl and N-phenyl protons), 7.72 (t, 1H, 4-H of benzoyl, $J = 7.4$ Hz), 8.06 (d, 2H, 2- and 6-H of benzoyl, $J = 7.3$ Hz); $^{13}$C NMR $\delta$ 70.82 (3-C), 109.25, 123.10, 124.07, 124.90, 126.55, 128.22, 128.39, 128.91, 129.52, 129.64, 130.03, 133.96, 134.01, 144.28, 164.92, 171.19. Anal. Calcd for C$_{21}$H$_{15}$NO$_3$: C 76.58; H 4.59; N 4.25. Found: C 76.80; H 4.52; N 4.40.

5-Chloro-8-methyl-4-pentanoyl-1,4-dihydro-2$^H$-3,1-benzoxazin-2-one (4g). Colorless crystals, mp 174-180 °C (benzene), lit., 10 mp 173-188 °C (cyclohexane).
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