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

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

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

Most commonly 3-acyloxy-2,3-dihydro-1*H*-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-1*H*-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 anhydride[7] and reduction of acyloxy(2-nitrophenyl)acetic acid,[8] its ester[9] or amide,[9] followed by a cyclization have been reported to yield compounds (**3**).

We recently reported that 3-hydroxy-1*H*,3*H*-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-1*H*-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

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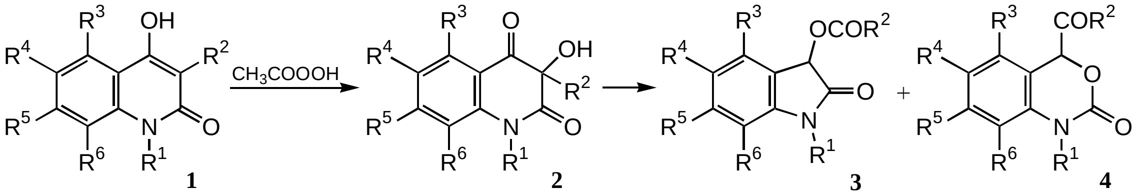
[#] *Dedicated to Professor Thomas Kappe, Professor of Karl Franzens University of Graz, on the occasion of his 70th birthday.*

conditions.[10] Thus, the rearrangement to **3** took place to a significant degree only with 5-substituted 3-hydroxy-1*H*,3*H*-quinoline-2,4-diones (**2**, R^3≠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=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



RESULTS AND DISCUSSION

Starting 3-hydroxy-1*H*,3*H*-quinoline-2,4-diones (**2a**-**s**) (Scheme 1, Table 1) were prepared by condensation of the corresponding anilines with substituted malonates,[10-14] followed by oxidation of 4-hydroxy-1*H*-quinolin-2-ones (**1a**-**s**) with peroxyacetic acid.[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*H*,3*H*-quinoline-2,4-diones (**2**) unsubstituted at the fused benzene ring remained unreacted even after several hours of reflux.[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[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.

Educt **2**	R^1	R^2	R^3	R^4	R^5	R^6	Ph_3P (mol%)	Time (min)	Product	Yield (%)
a	H	C_4H_9	H	H	H	H	20	40	**3a**	28
b	H	CH_2Ph	H	H	H	H	0	50	**3b**	1
							20	50	**3b**	10
c	H	Ph	H	H	H	H	0	40	**3c**	16
							20	40	**3c**	20
d	H	C_4H_9	H	CH_3	H	H	0	20	**3d**	15
							0	60	**3d**	20
							20	20	**3d**	22
e	H	C_4H_9	H	Cl	H	H	0	40	**3e**	15
							20	20	**3e**	21
f	H	C_4H_9	H	H	H	CH_3	20	40	**3f**	19
g	H	C_4H_9	Cl	H	H	CH_3	20	40	**3g**	14
									4g	2
h	H	CH_2Ph	H	H	Cl	CH_3	20	40	**3h**	12
i	CH_3	C_4H_9	H	H	H	H	20	40	**3i**	65
j	CH_3	CH_2Ph	H	H	H	H	20	40	**3j**	33
k	CH_3	Ph	H	H	H	H	0	40	**3k**	72
							20	40	**3k**	82
l	CH_3	C_4H_9	CH_3	H	CH_3	H	0	40	**3l**	56
							20	40	**3l**	72
m	C_2H_5	CH_2Ph	H	H	H	H	20	40	**3m**	20
n	CH_2Ph	C_4H_9	H	H	H	H	20	30	**3n**	55
o	CH_2Ph	CH_2Ph	H	H	H	H	20	40	**3o**	15
p	Ph	C_2H_5	H	H	H	H	0	25	**3p**	33
							20	20	**3p**	41
q	Ph	C_3H_7	H	H	H	H	0	45	**3q**	44
							20	45	**3q**	61
r	Ph	C_4H_9	H	H	H	H	0	80	**3r**	52
							20	80	**3r**	64
s	Ph	Ph	H	H	H	H	0	20	**3s**	72
							20	20	**3s**	67
							0^a	20	**3s**	68
							20^a	20	**3s**	76
							20^b	20	**3s**	78

[a] Hydroquinone (10 mol%) was added. [b] Dibenzoyl 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-1*H*-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-1*H*-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 ^{13}C NMR spectra at 69.1–70.8 ppm (C-3), 170.3–172.5 ppm (O-$\underline{\text{C}}$OR^2) 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-1*H*,3*H*-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-1*H*-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/UV$_{254}$ 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-1*H*-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-1*H*-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; ^{1}H NMR (CDCl$_3$) δ 0.95 (t, 3H, CH$_3$ 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, NCH$_2$), 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 $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.45; H, 6.83; N, 4.64.

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

1-Benzyl-3-butyl-3-hydroxy-1*H*,3*H*-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; ^{1}H NMR (CDCl$_3$) δ 0.84 (t, 3H, CH$_3$ 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, NCH$_2$, *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), 7.50 (ddd, 1H, 7-H, *J* = 8.4, 7.4, 1.6 Hz), 7.95 (dd, 1H, 5-H, *J* = 7.7, 1.6 Hz); ^{13}C NMR (CDCl$_3$) 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 $C_{20}H_{21}NO_3$: 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-1*H*,3*H*-quinoline-2,4-diones (2a-s) to 2-oxo-2,3-dihydro-1*H*-indol-3-yl carboxylates (3a-s) and 5-chloro-8-methyl-4-pentanoyl-1,4-dihydro-2*H*-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-1*H*-indol-3-yl pentanoate (3a). Colorless crystals, mp 71-73 °C (hexane), lit.,[10] mp 72-74 °C (cyclohexane).

2-Oxo-2,3-dihydro-1*H*-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}; ^{1}H NMR δ 3.81 (s, 2H, PhCH$_2$), 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); ^{13}C 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 $C_{16}H_{13}NO_3$: C 71.90; H 4.90; N 5.24. Found: C 72.23; H 4.83; N 5.04.

2-Oxo-2,3-dihydro-1*H*-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; ^{1}H 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); ^{13}C 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 $C_{15}H_{11}NO_3$: 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-1*H*-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, 822, 734, 679, 645 cm^{-1}; ^{1}H NMR δ 0.87 (t, 3H, CH$_3$ 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, ArCH$_3$), 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); ^{13}C 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 $C_{14}H_{17}NO_3$: 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-1*H*-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}; ^{1}H NMR δ 0.87 (t, 3H, CH$_3$ 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); ^{13}C

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-1*H*-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); ^{13}C 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-1*H*-indol-3-yl pentanoate (3g). Colorless crystals, mp 106-113 °C (cyclohexane), lit.,[10] mp 108-113 °C (cyclohexane).

6-Chloro-7-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl phenylacetate (3h). Colorless crystals, mp 190-194 °C (methanol), lit.,[10] mp 190-193 °C (benzene).

1-Methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl pentanoate (3i). Pale yellow oil; IR spectrum is identical with that of the authentic sample.[10]

1-Methyl-2-oxo-2,3-dihydro-1*H*-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); ^{13}C 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-1*H*-indol-3-yl benzoate (3k). Colorless crystals, mp 116-118 °C (cyclohexane), lit.,[18] mp 115 °C (ethanol); IR 3058, 3031, 3004, 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); ^{13}C 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-1*H*-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-1*H*-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-1*H*-indol-3-yl pentanoate (3n). Pale yellow oil; IR 2957, 2931, 2872, 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 13.68, 22.17, 26.95, 33.67, 43.98, 69.83 (3-C), 109.54, 123.06, 124.59, 125.42, 127.32, 127.75, 128.84, 130.11, 135.29, 143.60, 172.47, 173.06. HRMS Calcd for $C_{20}H_{21}NO_3$: 323.1521. Found: 323.1534.

1-Benzyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl phenylacetate (3o). Colorless crystals, mp 99-101 °C (benzene-hexane); IR 3032, 2958, 2914, 1753, 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, $PhCH_2CO$), 4.89 (s, 2H, $PhCH_2N$), 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-1*H*-indol-3-yl propanoate (3p). Pale pink crystals, mp 58-63 °C (benzene-hexane); IR 3052, 2983, 2938, 2924, 2883, 1742, 1731, 1612, 1594, 1500, 1480, 1468, 1455, 1375, 1301, 1234, 1169, 1102, 1082, 1037, 764, 752, 704, 694, 599 cm^{-1}; ^{1}H NMR δ 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-H, 2-, 4-, and 6-H of phenyl), 7.53-7.64 (m, 2H, 3- and 5-H of phenyl); ^{13}C NMR δ 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 . δ 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 δ 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, 2878, 2866, 1741, 1724, 1609, 1593, 1500, 1466, 1371, 1300, 1231, 1178, 1111, 1036, 1020, 780, 758, 744, 700, 592 cm^{-1}; ^{1}H NMR δ 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 δ 13.45, 21.36, 26.47, 32.72, 70.00 (3-C), 109.13, 122.98, 124.23, 124.73, 126.49, 128.15, 129.60, 129.86, 133.91, 144.13, 171.22, 172.21. 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 δ 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 δ 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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