Chemistry of Heterocyclic Compounds, Vol. 40, No. 2, 2004

ISOMERIZATION OF (HET)ARYL-BENZOINS IN BASIC MEDIA

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The α→β isomerization of the hetaryl analogs of unsymmetrical benzoins on heating in basic media is a convenient preparative method for the production of α-hydroxyacyl derivatives of π-excessive heterocycles. The motivating force here for the isomerization is the formation of a thermodynamically more stable product. It was established that α→β isomerization is promoted by increase in the difference between the electron-donating characteristics of the (het)aryl residues.

Keywords: benzoins, π-excessive heterocycles, isomerization.

The benzoin condensation is a convenient method for the synthesis of benzoins both with symmetrical and with unsymmetrical structures [1]. With thiazolium salts as catalysts it was possible not only to increase the overall yield and optical purity of the benzoins but also to use the reaction as a model to study the formation of the C–C bond in natural systems, catalyzed by enzymes (thiamine diphosphate) [2-11]. Study of the mechanism of the benzoin condensation and determination of the role of the acyl carbanion as intermediate made it possible to obtain the less stable unsymmetrical α-benzoins as a result of a two-stage reaction [12-17], which is impossible under the conditions of the classical benzoin condensation [1]. However, the α-benzoins are formed here with low yields, while only the furan and pyridine derivatives are obtained from the hetaryl analogs [17]. The aldehydes of π-excessive heterocycles are inactive under the conditions of the benzoin condensation [18]. Therefore, for example, electrophilic acylation, requiring a few more stages for the production of the benzoins, was used in the case of the synthesis of α-hydroxyacylindoles, which have pharmacological activity [19, 20].

4'-Dimethylaminobenzoin (the α-isomer) can be isomerized to the corresponding β-isomer in basic media [1], and it was interesting to use α→β isomerization for the production of the more stable hetarylbenzoins.

The starting compounds were the hetaryl analogs of α-benzoins, which can be easily obtained by hydroxymethylation of the respective π-excessive heterocycles with arylglyoxals [21].

We found that the isomerization of α-benzoins **1-13** takes place smoothly in the presence of triethylamine as base in boiling alcohol. As a result high yields of the corresponding hetaryl analogs of β-benzoins **14-26** were obtained (Scheme 1).

In our opinion α→β isomerization of benzoins takes place as intramolecular migration of a hydrogen atom between the oxygen atoms in the anion **A**, formed as a result of removal of a proton by the base from the carbon atom of the hydroxymethyl group. In fact, use of the O-deuterated α-benzoin **27** in isomerization under the indicated conditions gave the β-benzoin **28**, in which the deuterium atom was preserved to the extent of 100%. The ^{1}H NMR spectrum of the β-benzoin **28** does not contain the signals in the region of 5.70 and 11.88 ppm that in the spectrum of the β-benzoin **20** correspond to the OH and NH protons, while the signals of

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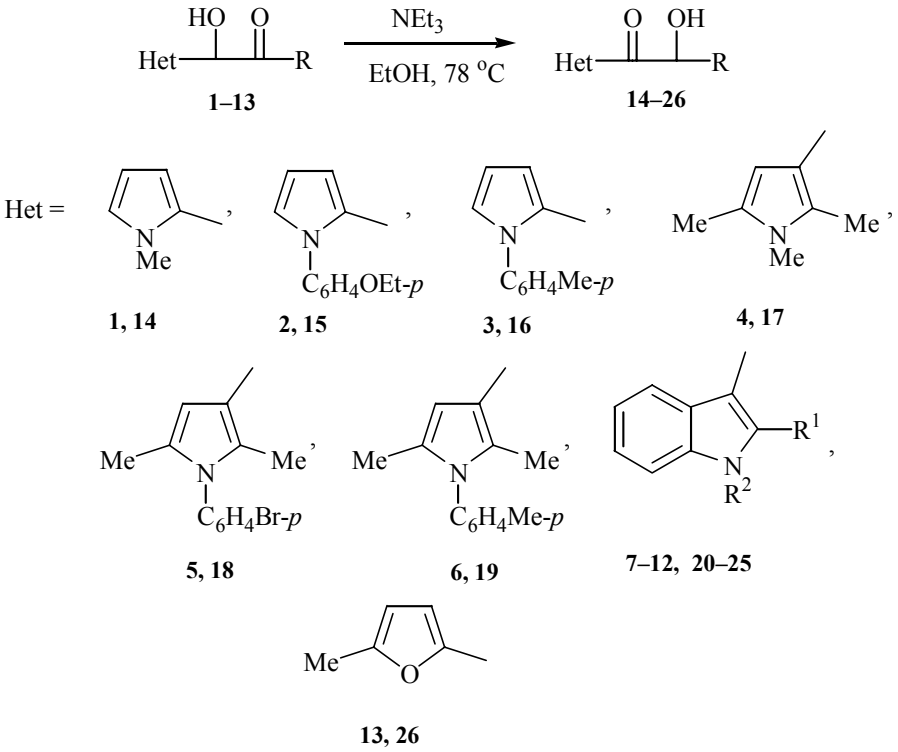
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 187-194, February, 2004. Original article submitted November 14, 2003.

 0009-3122/04/4002-0154

Scheme 1



R = Ph (**1–11, 13–24, 26**), 2-thienyl (**12, 25**)

R^1 = H (**7, 12, 20, 25**), Me (**8, 9, 21, 22**), Ph (**10, 23**), *t*-Bu (**11, 24**)
R^2 = Me (**9, 22**), H (all other cases)

CHOD and H(2) Ind are in the form of singlets, in contrast to the doublets in the ^{1}H NMR spectrum of **20**. In the IR spectrum of compound **28** the vibrations of the N–D and O–D bonds appear in the region of 2580-2490 cm^{-1} respectively. The presence of the deuterium at the oxygen atom and not at the carbon atom in the β-benzoin **28**

Scheme 2

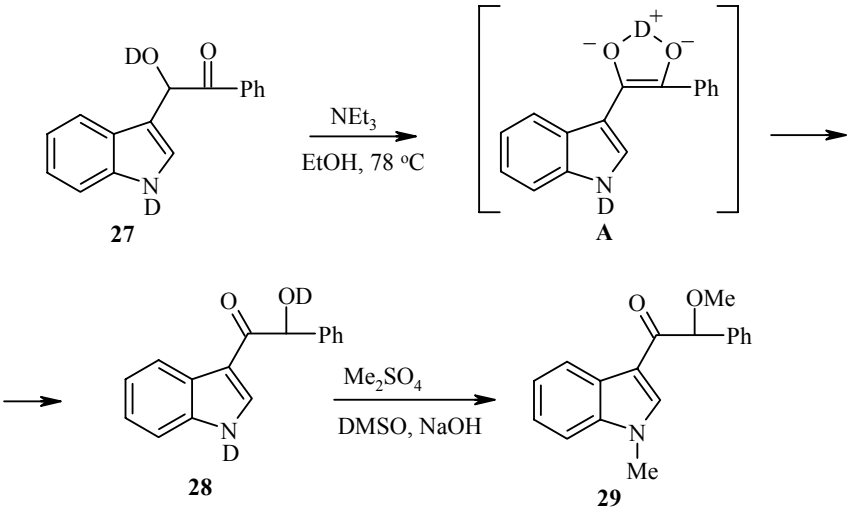


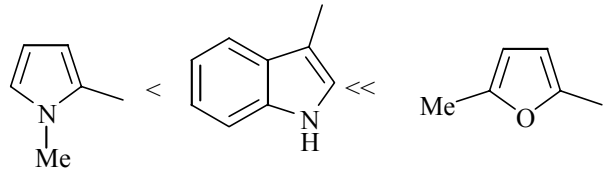
TABLE 1. The Duration of the Isomerization of α-Benzoins

Compound	Duration, h*	Compound	Duration, h*	Compound	Duration, h*
1	1.5	**6**	12	**11**	9
2	3.5	**7**	3	**12**	5
3	4	**8**	5	**13**	6.5
4	11.5	**9**	5	**27**	3
5	12	**10**	9		

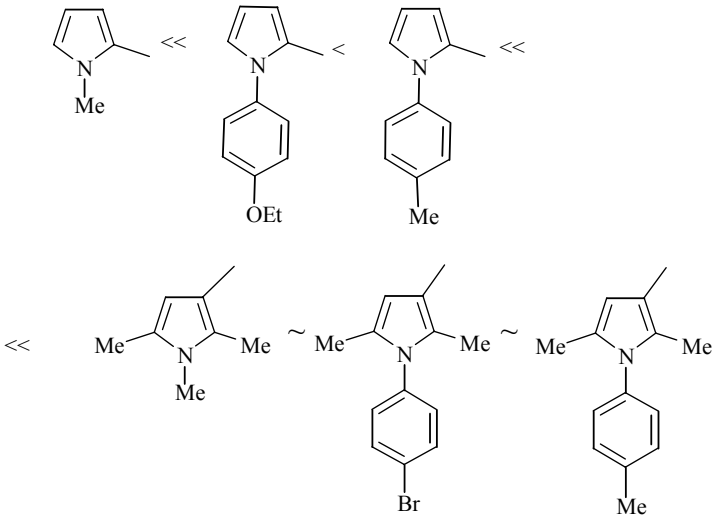
* The duration was determined from the disappearance of the spot for the initial compound in TLC (every 30 min).

was also proved by the alkylation of **28** with dimethyl sulfate in DMSO. In fact, the ^{1}H NMR spectrum of the isolated bis-O,N-alkylated product **29** contains a singlet at 5.32 ppm as also in the ^{1}H NMR spectrum of the β-benzoin **28**, indicating the presence of a proton at the carbon atom.

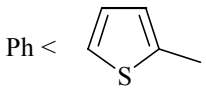
The formation of the thermodynamically more stable β-isomer, determined by the electronic nature of the hetaryl residue, is in our opinion the motivating force of the isomerization, and an increase in the duration of the isomerization is therefore observed with decrease of the electron-donating power in the following order (for R = Ph):



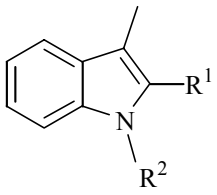
The substantial decrease in the electron-donating power of the furan ring compared with the pyrrole rings leads to the result that the α-benzoin **13** is less active than the α-benzoins **1** and **7**. In the case of the pyrrole derivatives it was established that the decrease in the electron-donating power of the position of the heterocycle reduces the duration of isomerization in the following order (for R = Ph):



The most active is the α-benzoin **1**, in which the reaction center is attached to the most electron-donating group. Replacement of the alkyl group at the nitrogen atom by a less electron-donating aryl group increases the duration of isomerization, and the reaction center here is sensitive to the electronic effect of the substituent in the aryl ring. The pyrrole **2** is therefore somewhat more active than **3**. In the case of the pyrroles **4-6** the hydroxy ketone group is attached to the less electron-donating β-position of the heterocycle. The duration of isomerization is therefore increased, while the influence of the electronic effect of the substituent at the nitrogen atom is levelled out. The opposite effect from the electron-donating characteristics is observed for (het)aryl groups in the righthand part of the benzoin molecule. Thus, the isomerization rate decreases with increase in the donating power (for Het = Ind), i.e., the greater the difference in the electron-donating characteristics of the (het)aryl substituents in the benzoin molecule, the more readily the isomerization takes place.



The increase in the size of the substituent at the *o*-position to the α-hydroxy ketone group in the hetaryl moiety in the series of 2-alkylindole derivatives (for R = Ph) leads to a reduction in the rate of α→β isomerization, due to steric hindrances to removal of the proton at the carbon atom by the base. In our opinion the increase in the duration of the isomerization of the 2-phenylindole derivative is due in addition to the electron-accepting effect of the phenyl ring.



R^1 = H < Me< Ph ~ *t*-Bu

In the ^{1}H NMR spectra of the obtained β-benzoins it is possible to detect the following relationship: the doublets of the *o*-protons of the unsubstituted phenyl ring are shifted upfield by 0.5-0.6 ppm compared with those in the spectra of the initial α-benzoins [21]. This relationship can be used to determine the structure of isomeric benzoins, since the position and form of the signals of these protons are similar for isomers of the same series [22].

EXPERIMENTAL

The ^{1}H NMR spectra were obtained in DMSO-d_6 on a Varian VXR-300 instrument (300 MHz) with TMS as internal standard. The reaction was monitored by TLC on Silufol UV-254 plates in the 5:1 benzene–acetone system with development in iodine vapor.

We described the α-benzoins **1-10**, **12**, and **13** in [21].

The α-benzoins **11** and **27** were obtained by the general procedure in [21].

2-(2-*tert*-Butyl-1H-indol-3-yl)-2-hydroxy-1-phenylethanone (11). A solution of 2-*tert*-butylindole (5.00 mmol) in benzene (4 ml) was added to a solution of phenylglyoxal (5.00 mmol) in benzene (4 ml). The obtained solution was kept at room temperature for 24 h. The precipitate was filtered off and crystallized from benzene. Yield 66.3%, colorless crystals; mp 142-144°C. ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.49 (s, 9H, *t*-Bu);

5.29 (d, 1H, CHOH, J = 5.4); 6.41 (d, 1H, CHOH, J = 5.4); 6.76 (t, 1H, H(6) Ind, J = 8.4); 6.92 (t, 1H, H(5) Ind, J = 8.4); 7.19 (d, 1H, H(7) Ind, J = 8.4); 7.25 (d, 1H, H(4) Ind, J = 8.4); 7.34 (t, 1H, H(3) and H(5) Ar, J = 6.9); 7.46 (d, 1H, H(4) Ar, J = 6.9); 7.82 (d, 2H, H(2) and H(6) Ar, J = 6.9); 10.72 (s, 1H, NH). Found, %: C 78.11; H 6.87. $C_{20}H_{21}NO_2$. Calculated, %: C 78.15; H 6.89.

O,N-Dideutero-2-hydroxy-2-(1H-indol-3-yl)-1-Phenylethanone (27). A solution of phenylglyoxal deuteroxide (5.00 mmol), indole (5.00 mmol), and deuterium oxide (0.1 ml) in benzene (8 ml) was boiled for 2 h and cooled. The precipitate was filtered off and crystallized from toluene. Yield 58.0%, colorless crystals; mp 180-182°C. ^{1}H NMR spectrum, δ, ppm, J (Hz): 6.39 (s, 1H, CHOD); 7.00 (t, 1H, H(6) Ind, J = 8.1); 7.08 (t, 1H, H(5) Ind, J = 8.1); 7.32 (d, 1H, H(7) Ind, J = 8.1); 7.35 (s, 1H, H(2) Ind); 7.40 (d, 1H, H(7) Ind, J = 8.1); 7.51 (t, 2H, H(3) and H(5) Ph, J = 7.8); 7.67 (d, 1H, H(4) Ph, J = 7.8); 8.02 (d, 2H, H(2) and H(6) Ph, J = 7.8). Found, %: C 75.73; N 5.52. $C_{16}H_{11}D_2NO_2$. Calculated, %: C 75.87; N 5.53.

General Procedure for the Isomerization of α-Benzoins 1-13 and 27 (Table 1, Schemes 1 and 2). A solution of the α-benzoin (1.50 mmol) and triethylamine (0.21 ml, 1.80 mmol) in ethanol (6 ml) was boiled for the time indicated in the table. The obtained solution was evaporated under vacuum, and the residue was crystallized. The following compounds were obtained in this way.

2-Hydroxy-1-(1-methyl-1H-pyrrol-2-yl)-2-phenylethanone (14). Yield 50.5%, colorless prisms; mp 107-108 (hexane). ^{1}H NMR spectrum, δ, ppm, J (Hz): 3.84 (s, 3H, NMe); 5.58 (d, 1H, CHOH, J = 5.7); 5.70 (d, 1H, CHOH, J = 5.7); 6.05 (dd, 1H, H(4) Pyr, J = 3.9, J = 2.4); 7.05 (d, 1H, H(5) Pyr, J = 2.4); 7.20 (d, 1H, H(4) Ph, J = 6.9); 7.21 (d, 1H, H(3) Pyr, J = 3.9); 7.27 (t, 2H, H(3) and H(5) Ph, J = 6.9); 7.42 (d, 2H, H(2) and H(6) Ph, J = 6.9). Found, %: C 72.53; H 6.10. $C_{13}H_{13}NO_2$. Calculated, %: C 72.54; H 6.09.

1-[1-(4-Ethoxyphenyl)-2-hydroxy-1H-pyrrol-2-yl]-2-phenylethanone (15). Yield 80.4%, light-yellow powder; mp 78-79°C (80% ethanol). ^{1}H NMR spectrum, δ, ppm, J (Hz): 1.40 (t, 3H, CH_3CH_2, J = 7.0); 4.10 (q, 2H, CH_3CH_2), J = 7.0); 5.60 (d, 1H, CHOH, J = 5.6); 5.64 (d, 1H, CHOH, J = 5.6); 5.88 (dd, 1H, H(4) Pyr, J = 3.9, J = 2.4); 6.04 (d, 1H, H(5) Pyr, J = 2.4); 6.87 (d, 1H, H(3) Pyr, J = 3.9); 7.04 (d, 2H, H(2) and H(6) Ar, J = 8.7); 7.36 (d, 1H, H(4) Ph, J = 7.8); 7.45 (d, 2H, H(3) and H(6) Ar, J = 8.7); 7.47 (t, 2H, H(3) and H(5) Ph, J = 7.8); 7.58 (d, 2H, H(2) and H(6) Ph, J = 7.8). Found, %: C 74.79; H 5.99. $C_{20}H_{19}NO_3$. Calculated, %: C 74.75; H 5.96.

2-Hydroxy-1-(1-(*p*-tolyl)-1H-pyrrol-2-yl)-2-phenylethanone (16). Yield 70.3%, oil from hexane. ^{1}H NMR spectrum, δ, ppm, J (Hz): 2.38 (s, 3H, 4-MeAr); 5.71 (d, 1H, CHOH, J = 6.3); 5.82 (d, 1H, CHOH, J = 6.3); 6.30 (dd, 1H, H(4) Pyr, J = 3.9, J = 3.9); 6.93 (d, 2H, H(2) and H(6) Ar, J = 9.0); 7.17 (d, 2H, H(3) and H(5) Ar, J = 9.0); 7.25 (d, 1H, H(5) Pyr, J = 3.9); 7.29 (d, 1H, H(3) Pyr, J = 3.9); 7.31 (d, 1H, H(4) Ph, J = 8.1); 7.34 (t, 2H, H(3) and H(5) Ph, J = 8.1); 7.44 (d, 2H, H(2) and H(6) Ph, J = 8.1). Found, %: C 78.27; H 5.59. $C_{19}H_{17}NO_2$. Calculated, %: C 78.33; H 5.88.

2-Hydroxy-1-(1,2,5-trimethyl-1H-pyrrol-3-yl)-2-phenylethanone (17). Yield 64.7%, colorless plates; mp 135-136°C (benzene). ^{1}H NMR spectrum, δ, ppm, J (Hz): 2.08 (s, 3H, 5-MePyr); 2.45 (s, 3H, 2-MePyr); 3.31 (s, 3H, 1-MePyr); 5.26 (d, 1H, CHOH, J = 5.7); 5.53 (d, 1H, CHOH, J = 5.7); 6.29 (s, 1H, H(4) Pyr); 7.18 (d, 1H, H(4) Ph, J = 6.9); 7.27 (t, 2H, H(3) and H(5) Ph, J = 6.9); 7.36 (d, 2H, H(2) and H(6) Ph, J = 6.9). Found, %: C 74.01; H 7.04. $C_{15}H_{17}NO_2$. Calculated, %: C 74.05; H 7.04.

1-[1-(4-Bromophenyl)-2,5-dimethyl-1H-pyrrol-3-yl]-2-hydroxy-2-phenylethanone (18). Yield 92.6%, light-yellow powder; mp 160-161°C (80% ethanol). ^{1}H NMR spectrum, δ, ppm, J (Hz): 1.91 (s, 3H, 5-MePyr); 2.25 (s, 3H, 2-MePyr); 5.39 (d, 1H, CHOH, J = 5.7); 5.55 (d, 1H, CHOH, J = 5.7); 6.44 (s, 1H, H(4) Pyr); 7.22 (d, 1H, H(4) Ph, J = 7.5); 7.23 (d, 2H, H(2) and H(6) Ar, J = 8.4); 7.31 (t, 2H, H(3) and H(5) Ph, J = 7.5); 7.42 (d, 2H, H(2) and H(6) Ph, J = 7.5); 7.68 (d, 2H, H(3) and H(5) Ar, J = 8.4). Found, %: C 62.53; H 4.71. $C_{20}H_{18}BrNO_2$. Calculated, %: C 62.51; H 4.72.

2-Hydroxy-1-[2,5-dimethyl-1-(*p*-tolyl)-1H-pyrrol-3-yl]-2-phenylethanone (19). Yield 85.8%, light-yellow powder; mp 126-127°C (80% ethanol). ^{1}H NMR spectrum, δ, ppm, J (Hz): 1.89 (s, 3H, 5-MePyr); 2.24 (s, 3H, 4-MeAr); 2.40 (s, 3H, 2-MePyr); 5.29 (d, 1H, CHOH, J = 6.3); 5.52 (d, 1H, CHOH, J = 6.3); 6.37 (s,

1H, H(4) Pyr); 7.09 (d, 2H, H(2) and H(6) Ar, *J* = 8.1); 7.21 (d, 1H, H(4) Ph, *J* = 6.9); 7.28 (d, 2H, H(3) and H(5) Ar, *J* = 8.1); 7.30 (t, 2H, H(3) and H(5) Ph, *J* = 6.9); 7.41 (d, 2H, H(2) and H(6) Ph, *J* = 6.9). Found, %: C 78.98; H 6.65. $C_{21}H_{21}NO_2$. Calculated, %: C 78.97; H 6.63.

2-Hydroxy-1-(1H-indol-3-yl)-2-phenylethanone (20). Yield 85.9%, colorless prisms; mp 194-196°C (toluene). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 5.70 (d, 1H, CHOH, *J* = 4.2); 5.77 (d, 1H, CHOH, *J* = 4.2); 7.12 (t, 1H, H(6) Ind, *J* = 8.1); 7.15 (t, 1H, H(5) Ind, *J* = 8.1); 7.20 (d, 1H, H(4) Ph, *J* = 7.3); 7.28 (t, 2H, H(3) and H(5) Ph, *J* = 7.3); 7.40 (d, 1H, H(7) Ind, *J* = 8.1); 7.51 (d, 2H, H(2) and H(6) Ph, *J* = 7.3); 8.18 (d, 1H, H(4) Ind, *J* = 8.1); 8.43 (d, 1H, H(2) Ind, *J* = 3.0); 11.88 (d, 1H, H(l) Ind, *J* = 3.0). Found, %: C 76.47; H 5.21. $C_{16}H_{13}NO_2$. Calculated, %: C 76.48; H 5.21.

2-Hydroxy-1-(2-methyl-1H-indol-3-yl)-2-phenylethanone (21). Yield 71.4%, colorless crystals; mp 175-176°C (benzene). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.41 (s, 3H, Me); 5.72 (d, 1H, CHOH, *J* = 6.0); 5.90 (d, 1H, CHOH, *J* = 6.0); 7.16 (t, 1H, H(6) Ind, *J* = 7.2); 7.22 (t, 1H, H(5) Ind, *J* = 7.2); 7.24 (d, 1H, H(4) Ph, *J* = 7.8); 7.30 (t, 2H, H(3) and H(5) Ph, *J* = 7.8); 7.45 (d, 1H, H(7) Ind, *J* = 7.2); 7.54 (d, 2H, H(2) and H(6) Ph, *J* = 7.8); 7.83 (d, 1H, H(4) Ind, *J* = 7.2); 11.88 (s, 1H, H(l) Ind). Found, %: C 76.87; H 5.73. $C_{17}H_{15}NO_2$. Calculated, %: C 76.96; H 5.70.

2-Hydroxy-1-(1,2-dimethyl-1H-indol-3-yl)-2-phenylethanone (22). Yield 73.9%, colorless crystals; mp 185°C ethanol. ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.50 (s, 3H, 2-MeInd); 3.70 (s, 3H, l-MeInd); 5.69 (d, 1H, CHOH, *J* = 5.9); 5.94 (d, 1H, CHOH, *J* = 5.9); 7.19 (t, 1H, H(6) Ind, *J* = 8.1); 7.22 (t, 1H, H(5) Ind, *J* = 8.1); 7.27 (d, 1H, H(4) Ph, *J* = 6.3); 7.37 (t, 2H, H(3) and H(5) Ph, *J* = 6.3); 7.43 (d, 1H, H(7) Ind, *J* = 8.1); 7.49 (d, 2H, H(2) and H(6) Ph, *J* = 6.3); 8.04 (d, 1H, H(4) Ind, *J* = 8.1). Found, %: C 77.35; H 6.06. $C_{18}H_{17}NO_2$. Calculated, %: C 77.40; H 6.13.

2-Hydroxy-2-phenyl-1-(2-phenyl-1H-indol-3-yl)ethanone (23). Yield 90.9%, white powder; mp 151-152°C (benzene–hexane). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 5.79 (d, 1H, CHOH, *J* = 6.0); 5.83 (d, 1H, CHOH, *J* = 6.0); 7.17 (t, 1H, H(6) Ind, *J* = 6.9); 7.21 (t, 1H, H(5) Ind, *J* = 6.9); 7.23 (d, 1H, H(4) Ph, *J* = 7.9); 7.30 (t, 2H, H(3) and H(5) Ph, *J* = 7.9); 7.35-7.40 (m, 5H, 2-PhInd); 7.45 (d, 1H, H(7) Ind, *J* = 6.9); 7.53 (d, 2H, H(2) and H(6) Ph, *J* = 7.9); 7.77 (d, 1H, H(4) Ind, *J* = 6.9); 11.51 (s, 1H, H(1) Ind). Found, %: C 80.59; H 5.18. $C_{22}H_{17}NO_2$. Calculated, %: C 80.71; H 5.23.

1-(2-*tert*-Butyl-1H-indol-3-yl)-2-hydroxy-2-phenylethanone (24). Yield 80.0%, colorless prisms; mp 222-224°C (benzene). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.61 (s, 9H, *t*-Bu); 5.97 (d, 1H, CHOH, *J* = 8.1); 6.22 (d, 1H, CHOH, *J* = 8.1); 7.17 (t, 1H, H(6) Ind, *J* = 7.2); 7.21 (t, 1H, H(5) Ind, *J* = 7.2); 7.24 (d, 1H, H(4) Ph, *J* = 7.9); 7.30 (t, 2H, H(3) and H(5) Ph, *J* = 7.9); 7.45 (d, 1H, H(7) Ind, *J* = 7.2); 7.54 (d, 2H, H(2) and H(6) Ph, *J* = 7.9); 7.83 (d, 1H, H(4) Ind, *J* = 7.2); 12.10 (s, 1H, H(1) Ind). Found, %: C 78.09; H 6.77. $C_{20}H_{21}NO_2$. Calculated, %: C 78.15; H 6.89.

2-Hydroxy-1-(1H-indol-3-yl)-2-(2-thienyl)ethanone (25). Yield 52.7%, colorless needles; mp 162-163°C (ethanol). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 6.06 (d, 1H, CHOH, *J* = 4.5); 6.13 (d, 1H, CHOH, *J* = 4.5); 6.93 (t, 1H, H(4) Th, *J* = 4.8); 7.13 (d, 1H, H(3) Th, *J* = 4.8); 7.20 (t, 1H, H(6) Ind, *J* = 7.8); 7.22 (t, 1H, H(5) Ind, *J* = 7.8); 7.40 (d, 1H, H(5) Th, *J* = 4.8); 7.48 (d, 1H, H(7) Ind, *J* = 7.8); 8.19 (d, 1H, H(4) Ind, *J* = 7.8); 8.57 (s, 1H, H(2) Ind); 12.05 (s, 1H, H(1) Ind). Found, %: C 65.34; H 4.27. $C_{14}H_{11}NO_2S$. Calculated, %: C 65.35; H 4.31.

2-Hydroxy-1-(5-methyl-2-furyl)-2-phenylethanone (26). Yield 90.3%, colorless needles; mp 150-151°C (ethanol). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.33 (s, 3H, 5-MeFur); 5.63 (d, 1H, CHOH, *J* = 3.9); 5.94 (d, 1H, CHOH, *J* = 3.9); 6.24 (d, 1H, H(4) Fur, *J* = 3.0); 7.21 (d, 1H, H(4) Ph, *J* = 7.5); 7.29 (t, 2H, H(3) and H(5) Ph, *J* = 7.5); 7.43 (d, 2H, H(2) and H(6) Ph, *J* = 7.5); 7.46 (d, 1H, H(3) Fur, *J* = 3.0). Found, %: C 72.19; H 5.62. $C_{13}H_{12}O_3$. Calculated, %: C 72.21; H 5.59.

O,N-Dideuterio-2-hydroxy-1-(1H-indol-3-yl)-2-phenylethanone (28). Yield 80.9%, colorless prisms; mp 198-200°C (toluene). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 5.80 (s, 1H, CHOD); 7.16 (t, 1H, H(6) Ind, *J* = 9.6); 7.19 (t, 1H, H(5) Ind, *J* = 9.6); 7.23 (d, 1H, H(4) Ph, *J* = 8.1); 7.30 (t, 2H, H(3) and H(5) Ph, *J* = 8.1);

7.46 (d, 1H, H(7) Ind, J = 9.6); 7.54 (d, 2H, H(2) and H(6) Ph, J = 8.1); 8.21 (d, 1H, H(4) Ind, J = 9.6); 8.54 (s, 1H, H(2) Ind). Found, %: C 75.84; N 5.49. $C_{16}H_{11}D_2NO_2$. Calculated, %: C 75.87; N 5.53.

2-Methoxy-1-(1-methyl-1H-indol-3-yl)-2-phenylethanone (29). To a stirred solution of the α-benzoin **28** (380 mg, 1.50 mmol) in DMSO (5 ml) a 10% aqueous solution of sodium hydroxide (0.60 ml, 1.50 mmol) and dimethyl sulfate (0.57 ml, 6.00 mmol) were added successively. The obtained mixture was stirred, 20 ml of water was added, and the precipitate was filtered off and crystallized from 80% ethanol. Yield 51.8%, light-yellow powder; mp 132-133°C. ^{1}H NMR spectrum, δ, ppm, J (Hz): 3.40 (s, 3H, NMe); 3.88 (s, 3H, OMe); 5.33 (s, 1H, CHOMe); 7.18 (t, 1H, H(6) Ind, J = 8.4); 7.21 (t, 1H, H(5) Ind, J = 8.4); 7.25 (d, 1H, H(7) Ind, J = 8.4); 7.30 (t, 2H, H(3) and H(5) Ph, J = 7.5); 7.46 (d, 1H, H(4) Ph, J = 7.5); 7.51 (d, 2H, H(2) and H(6) Ph, J = 7.5); 8.19 (d, 1H, H(4) Ind, J = 8.4); 8.57 (s, 1H, H(2) Ind). Found, %: C 77.36; H 6.10; N 5.00. $C_{18}H_{17}NO_2$. Calculated, %: C 77.40; H 6.13; N 5.01.

The work was carried out with financial support from the Ministry of Education and Science of Ukraine (No. 0101U00159).

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