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Synthesis of New Carbamate Derivatives of Indole and Their Modification

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Abstract—Oximation of indoles having a methoxycarbonylamino group on C^5 and an acyl group on C^3 with hydroxylamine hydrochloride in the presence of pyridine gave the corresponding oximes. The reduction of the 3-C=O group with sodium tetrahydridoborate in the presence of sodium hydroxide was accompanied by removal of the methoxycarbonyl group at the pyrrole nitrogen atom with formation of racemic alcohols. 1,4-Addition of 1-(pyridin-3-yl)butane-1,3-dione to dimethyl 1,4-benzoquinone diimine *N*,*N*′-dicarboxylate in dioxane in the presence of sodium methoxide, followed by heating in boiling 22% hydrochloric acid, afforded methyl 2-methyl-5-(methoxycarbonylamino)-3-(pyridin-3-ylcarbonyl)-1*H*-indole-1-carboxylate. 3-(Dimethylamino)-1-(4-methyl-1,2,5-oxadiazol-3-yl)prop-2-en-1-one reacted with *N*,*N*′-bis(methoxycarbonyl)- and *N*,*N*′-bis(phenylsulfonyl)-1,4-benzoquinone diimines in methylene chloride and acetic acid, respectively, in the presence of $BF_3 \cdot Et_2O$ to produce indoles having a 1,2,5-oxadiazolylcarbonyl group on C^3.

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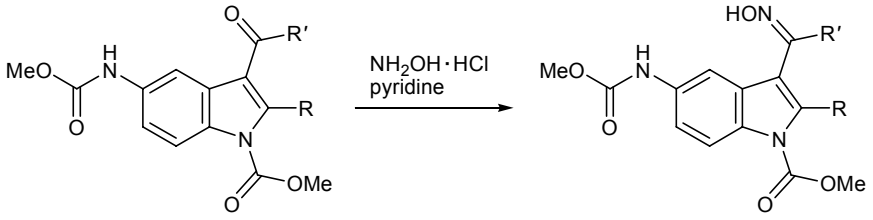
One of the most fruitful and extensively developing fields in the chemistry of heterocyclic compounds is chemical modification of natural and synthetic biologically active substances. Nitrogen-containing heterocycles are traditional compounds exhibiting various kinds of biological activity.

We previously reported on the synthesis of indole derivatives possessing a carbamate group on C^5 [1–3]. However, poor solubility of these compounds is a considerable drawback which reduces their pharmacological value. Therefore, their modification with a view to improve their solubility and introduce new pharmacophoric groups seemed to be important. The presence of a carbonyl group on C^3 in indoles obtained by the Michael reaction of *N*,*N*′-bis(methoxycarbonyl)-1,4-benzoquinone diimine with β-diketones implies the possibility for transformation of that group into oxime or hydroxy. The oxime group in indole compounds is responsible for their antiarrhythmic, hypotensive, antidepressant, psychotropic, antiphlogistic, and antiviral activity [4]. Furthermore, oxime group may be reduced to amino. Hydroxy group is a structural unit of a large number of natural and synthetic biologically active substances [5]. Nitro-substituted carbamate derivatives of indole can find specific application, or they may be used as intermediate products in the synthesis of other polyfunctional compounds. The above stated determined perspectives in the corresponding modifications of carbamate indole derivatives.

Indolyl ketones **Ia** and **Ib** were subjected to oximation by the action of hydroxylamine hydrochloride in the systems NaOH–EtOH, AcONa–dioxane, and pyridine–EtOH, as well as in the presence of pyridine [6]. The best results were obtained in pyridine on heating at 50°C over a period of 1.5 h (Scheme 1). The IR spectra of oximes **IIa** and **IIb** are hardly suitable for identification of their structure, for stretching vibrations of the C=N bond give rise to absorption in the region 1640–1630 cm^{-1}; analogous absorption band of nonconjugated oximes is located at about 1640 cm^{-1}. The structure of compounds **IIa** and **IIb** was confirmed by their ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of oxime **IIa** we observed a double set of signals belonging to protons in the methyl group on C^2 (δ 2.58 and 2.24 ppm for the *syn* and *anti* isomers, respectively), methyl group in the oxime residue (δ_{syn} 2.25, δ_{anti} 2.16 ppm), and hydroxy group (δ_{syn} 10.32, δ_{anti} 9.69 ppm), indicating the presence of two isomers (*s-cis–trans* or *syn–anti* isomerism). The 4-H proton resonates in a weaker field (δ 8.31 ppm) relative to the corresponding signal of indole (δ 8.25 ppm), so that we presumed conservation of the

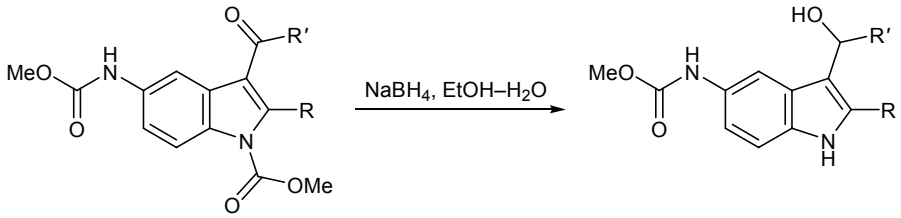
Scheme 1.



Ia, **Ib** **IIa**, **IIb**

R = R′ = Me (**a**); RR′ = $CH_2CMe_2CH_2$ (**b**).

Scheme 2.



Ia–Ic **IIIa–IIIc**

R = R′ = Me (**a**); RR′ = $CH_2CMe_2CH_2$ (**b**); R = Me, R′ = Ph (**c**).

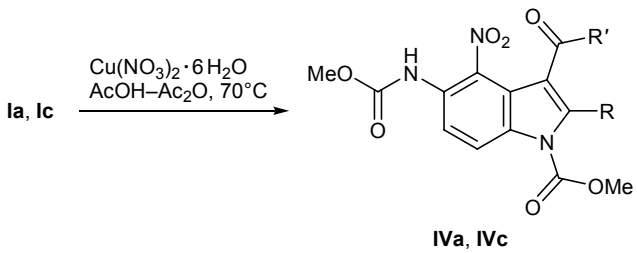
s-trans conformation and the presence of two forms was ascribed to *syn–anti* isomerism [7].

The ^{13}C NMR spectrum of oxime **IIb** having fixed *s-trans* conformation also contained signals from two isomers which may differ only in the orientation of the oxime hydroxy group. Here, γ-effect of the hydroxy group is clearly observed: the difference in the chemical shifts of the methylene and quaternary carbon atoms is 14.80 and 3.30 ppm, respectively. This fact also counts in favor of *syn–anti* isomerism of oxime **IIb**. The predominant formation of oximes **IIa** and **IIb** as *syn-s-trans* isomers may be rationalized in terms of steric repulsion between the oxime OH group and proton on C^4 in the *anti-s-trans* isomer.

We tried to reduce the carbonyl group in indoles **Ia**–**Ic** to hydroxy with sodium tetrahydridoborate in aqueous ethanol in the presence of sodium hydroxide [8]. It was found that the reaction occurs fairly readily at 60–70°C (in 1 h) and that it is accompanied by reductive elimination of the methoxycarbonyl group at the pyrrole nitrogen atom to give the corresponding racemic alcohols **IIIa**–**IIIc** in good yields (Scheme 2). The structure of compounds **IIIa**–**IIIc** was confirmed by IR and ^1H NMR spectra. The ^1H NMR spectra of **IIIa**–**IIIc** lacked singlets typical of the methoxycarbonyl group on the pyrrole nitrogen atom in the initial indoles (δ 4.07–4.02 ppm), whereas signals from the methoxycarbonylamino group on C^5 were observed at δ 3.72–3.65 ppm; in addition, a signal from the hydroxy proton appeared in the region δ 5.90–3.55 ppm.

Indoles **Ia** and **Ic** were subjected to nitration according to the procedure described in [9], i.e., using copper(II) nitrate hexahydrate in a mixture of acetic acid with acetic anhydride. The reaction mixtures were heated for 1 h at 70°C. Analysis by thin-layer chromatography and ^1H NMR data showed that the nitration was regioselective. The products were the corresponding 4-nitro derivatives **IVa** and **IVc** (Scheme 3). Isomeric 6-nitro derivatives should display in the ^1H NMR spectra two singlets from aromatic protons on C^4 and C^7. The spectra of the products contained two doublets at δ 7.45–7.55 and 8.25–.38 ppm, indicating formation of just 4-nitroindoles **IVa** and **IVc**.

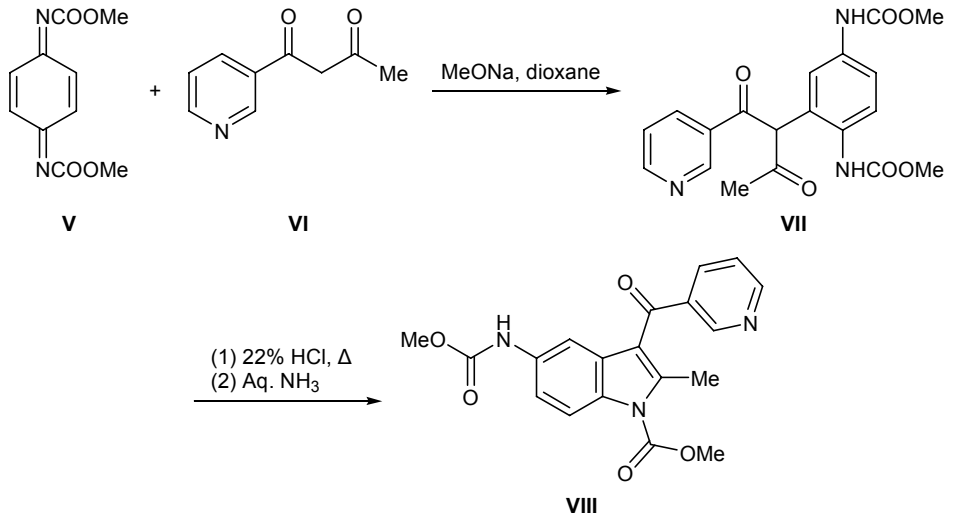
Scheme 3.



Ia, **Ic** **IVa**, **IVc**

We also made an attempt to synthesize carbamate indole derivatives possessing a pyridine fragment. For this purpose, we examined the reaction of *N*,*N*′-bis-(methoxycarbonyl)-1,4-benzoquinone diimine (**V**) with

Scheme 4.



V **VI** **VII** **VIII**

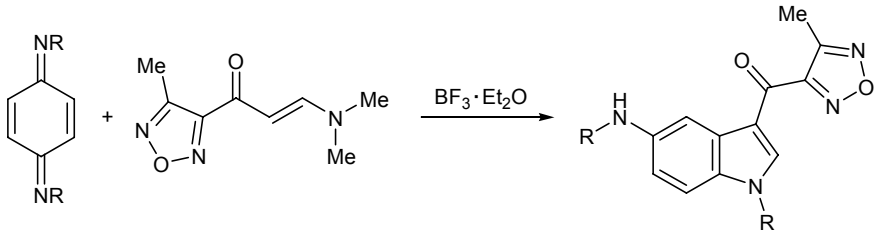
1-(pyridin-3-yl)butane-1,3-dione (**VI**) in dioxane in the presence of sodium methoxide. The reaction mixture was kept for 8 h at 20°C, and the product was the corresponding Michael adduct with aromatic structure. The structure of dimethyl 2-[1,3-dioxo-1-(pyridin-3-yl)butan-2-yl]-1,4-phenylenedicarbamate (**VII**) was confirmed by IR spectroscopy. Treatment of compound **VII** with boiling 22% hydrochloric acid over a period of 2 h, followed by neutralization with 25% aqueous ammonia gave substituted indole derivative **VIII** (Scheme 4). The ^{1}H NMR spectrum of methyl 5-(methoxycarbonylamino)-2-methyl-3-(pyridin-3-ylcarbonyl)-1*H*-indole-1-carboxylate (**VIII**) contained singlets from protons in the methyl group on C^2, $NHCO_2$**Me** and NCO_2Me groups, and 4-H at δ 2.64 (3H), 3.73 (3H), 3.96 (3H), and 8.48 ppm (1H), respectively, as well as a multiplet at δ 8.08–8.19 ppm from the aromatic protons, a doublet from 4′-H at δ 8.58 ppm (J = 5.2 Hz), a singlet from 2′-H at δ 8.85 ppm, and a broadened singlet from the NH proton at δ 8.65 ppm.

Nenițsescu reaction provides one of the most important methods for the synthesis of 5-hydroxyindols [10–12]. We previously showed [13] that *N*,*N*′-bis(methoxycarbonyl)-1,4-benzoquinone diimine (**V**) is capable of reacting with some enamino ketones. In continuation of these studies we examined the reactions of 3-dimethylamino-1-(4-methyl-1,2,5-oxadiazol-3-yl)prop-2-en-1-one (**X**) with compound **V** in methylene chloride and with *N*,*N*′-bis(phenylsulfonyl)-1,4-benzoquinone diimine (**IX**) in acetic acid in the presence of $BF_3 \cdot Et_2O$. Unlike bis-sulfonamide **IX**, the reaction of **X** with bis-carbamate **V** cannot be carried out in acetic acid because of concurrent 1,4-addition of acetic acid at the N=C–C=C conjugated bond system with formation of the corresponding acetoxyphenol [14]. By Nenițsescu reaction of compounds **V** and **IX** with **X** we obtained indole derivatives **XI** and **XII** in good yields (77–85%), and the product structure was confirmed by IR, ^{1}H NMR, and mass spectra.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-400 spectrometer at 400.13 MHz using tetramethylsilane as internal reference. The ^{13}C NMR spec-

Scheme 5.



V, **IX** **X** **XI**, **XII**

V, **IX**, R = CO_2Me; **XI**, **XII**, R = SO_2Ph.

tra were obtained on a Bruker WM-400 instrument at 100 MHz with complete decoupling from protons. The IR spectra were measured in the frequency range from 4000 to 400 cm^{-1} on IKS-29 and Infra-LUM FT-02 spectrometers from samples dispersed in mineral oil (except for **XI** and **XII**). The mass spectra (electron impact, 70 eV) were recorded on a Finnigan MAT INCOS 50 instrument. The purity of the products was checked by thin-layer chromatography on Silufol UV-254 plates.

Initial indolylcarbamates **Ia**–**Ic** and bis-sulfonamide **IX** were synthesized by known methods [1, 15].

Methyl 3-(1-hydroxyiminoethyl)-5-(methoxycarbonylamino)-2-methyl-1*H*-indole-1-carboxylate (IIa). A mixture of 0.88 g (2.89 mmol) of methyl 3-acetyl-5-(methoxycarbonylamino)-2-methyl-1*H*-indole-1-carboxylate (**Ia**), 0.20 g (2.89 mmol) of hydroxylamine hydrochloride, and 5 ml of anhydrous pyridine was heated for 1.5 h at 50°C (on a water bath). The mixture was cooled and poured into ice water, and the precipitate was filtered off, washed on a filter with water (20 ml), dried in air, and recrystallized from ethanol. Yield 0.59 g (64%), colorless crystals, mp 178–179°C. IR spectrum, ν, cm^{-1}: 3345 (NH, OH); 1720 (C=O); 1630 (C=N); 1615, 1570, 1545 (C=C, C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.16 s and 2.25 s (3H, MeC=N), 2.28 s and 2.58 s (3H, 2-Me), 3.74 s (3H, $NHCO_2$**Me**), 3.98 s (3H, NCO_2**Me**), 7.64 d (7-H, J = 8.0 Hz), 8.01 d (6-H, J = 8.0 Hz), 8.31 s (4-H), 8.54 br.s (1H, NH), 9.69 s and 10.32 s (1H, OH). Found, %: C 56.11; H 4.99; N 13.02. $C_{15}H_{17}N_3O_5$. Calculated, %: C 56.43; H 5.33; N 13.17.

Methyl 4-hydroxyimino-6-(methoxycarbonylamino)-2,2-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (IIb) was synthesized in a similar way by reaction of 0.5 g (1.45 mmol) of tetrahydrocarbazole **Ib** and 0.1 g (1.45 mmol) of hydroxylamine hydrochloride. Yield 0.37 g (71%), Colorless crystals, mp 202–203°C (from EtOH). IR spectrum, ν, cm^{-1}: 3360 (NH, OH); 1725 (C=O); 1640 (C=N); 1615, 1595, 1540 (C=C, C=C_{arom}). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 29.50 and 30.72 (Me), 35.01 and 35.25 (C^{11}), 37.14 and 37.23 (C^{10}), 39.51 and 42.81 (C^{12}, $\Delta\delta_C$ = 3.30), 52.75 ($NHCO_2$**C**H_3), 53.42 (NCO_2**C**H_3), 108.41 and 123.21 (C^3, $\Delta\delta_C$ = 14.80), 115.23 and 116.01 (C^7), 118.51 and 119.02 (C^6), 120.15 and 120.21 (C^4), 125.65 and 126.07 (C^8), 131.62 and 131.65 (C^9), 131.72 and 132.58 (C^5), 145.14 and 145.27 (C^2), 146.65 and 147.55 (C^{13}), 149.01 (N**C**O_2Me), 153.43 (NH**C**O_2Me). Found, %: C 59.96; H 5.92; N 11.58. $C_{18}H_{21}N_3O_5$. Calculated, %: C 60.17; H 5.85; N 11.70.

Methyl 3-(1-hydroxyethyl)-2-methyl-1*H*-indol-5-ylcarbamate (IIIa). Several drops of a 10% aqueous solution of sodium hydroxide was added to a mixture of 12 ml of ethanol and 6 ml of water, 0.2 g (5.4 mmol) of sodium tetrahydridoborate was added, the mixture was heated to 60–70°C, and 1.1 g (3.62 mmol) of compound **Ia** was added in portions under stirring. The mixture was stirred for 1 h at that temperature, diluted with water (30 ml), and extracted with diethyl ether (3×25 ml), the extracts were combined, washed with water (50 ml), dried over sodium sulfate, and evaporated, and the residue was recrystallized from ethyl acetate–petroleum ether (1:3 by volume). Yield 0.88 g (79%), colorless crystals, mp 165–166°C. IR spectrum, ν, cm^{-1}: 3470–3320 (NH, OH); 1710 (C=O); 1620, 1595, 1555 (C=C, C=C_{arom}). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.50 m (3H, CHC**H**$_3$), 2.75 s (3H, 2-CH_3), 3.55 s (1H, OH), 3.71 s (3H, $NHCO_2$C**H**$_3$), 4.63 m (1H, C**H**CH_3), 6.05 br.s (1H, NH), 7.30 d (1H, 6-H, J = 8.0 Hz), 7.42 d (1H, 7-H, J = 8.0 Hz), 7.92 s (1H, 4-H), 8.45 br.s (1H, NH). Found, %: C 63.14; H 6.19; N 11.25. $C_{13}H_{16}N_2O_3$. Calculated, %: C 62.90; H 6.45; N 11.29.

Methyl 4-hydroxy-2,2-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazol-6-ylcarbamate (IIIb) was synthesized in a similar way by reduction of 1 g (2.9 mmol) of compound **Ib** with 0.17 g (4.33 mmol) of sodium tetrahydridoborate. The product was extracted into methylene chloride (3×20 ml). Yield 0.8 g (82%), colorless crystals, mp 266–268°C (from chloroform). IR spectrum, ν, cm^{-1}: 3375–3300 (NH, OH); 1710 (C=O); 1635, 1575, 1545 (C=C, C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.05 s (6H, Me), 2.30 s (2H, CH_2), 2.82 s (2H, CH_2), 3.65 s (4H, $NHCO_2$C**H**$_3$, OH), 5.50 t (1H, C**H**OH, J = 2.3 Hz), 5.75 s (1H, NH), 7.25 q (2H, H_{arom}, J = 7.1 Hz), 8.05 s (1H, 4-H), 9.35 br.s (1H, NH). Found, %: C 66.50; H 7.03; N 9.41. $C_{16}H_{20}N_2O_3$. Calculated, %: C 66.67; H 6.94; N 9.72.

Methyl 3-[hydroxy(phenyl)methyl]-2-methyl-1*H*-indol-5-ylcarbamate (IIIc) was synthesized in a similar way by reduction of 1.32 g (3.61 mmol) of indole **Ic** with 0.2 g (5.4 mmol) of sodium tetrahydridoborate. Yield 0.96 g (71%), colorless crystals, mp 130–133°C (from ethyl acetate–petroleum ether, 1:3 by volume). IR spectrum, ν, cm^{-1}: 3410–3300 (NH, OH); 1715 (C=O); 1635, 1600, 1555 (C=C, C=C_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 s (3H, Me), 3.50 d (1H, OH), 3.72 s (3H, $NHCO_2$C**H**$_3$),

5.90 s (1H, C**H**OH), 6.25 br.s (1H, NH), 7.00–7.25 m (5H, H_{arom}), 7.30 d (1H, 6-H, J = 8.0 Hz), 7.48 d (1H, 7-H, J = 8.0 Hz), 7.72 s (1H, 4-H), 8.45 br.s (1H, NH). Found, %: C 69.41; H 5.58; N 9.17. $C_{18}H_{18}N_2O_3$. Calculated, %: C 69.68; H 5.81; N 9.03.

Methyl 3-acetyl-5-(methoxycarbonylamino)-2-methyl-4-nitro-1*H*-indole-1-carboxylate (IVa). A mixture of 1.7 g (5.59 mmol) of indole **Ia**, 0.99 g (3.35 mmol) of copper(II) nitrate hexahydrate, 10 ml of glacial acetic acid, and 3 ml of acetic anhydride was heated for 1 h at 70°C. The mixture was cooled and poured into 100 ml of ice water, and the precipitate was filtered off, washed on a filter with water (50 ml), dried in air, and recrystallized from glacial acetic acid. Yield 1.3 g (58%), light yellow crystals, mp 173–175°C. IR spectrum, ν, cm^{-1}: 3360 (NH); 1760, 1690 (C=O); 1620, 1590, 1550 (C=C, C=C_{arom}); 1520, 1330 (NO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, COMe), 3.02 s (3H, 2-Me), 3.75 s (3H, $NHCO_2C\mathbf{H}_3$), 4.10 s (3H, NCO_2CH_3), 7.55 d (1H, 7-H, J = 10.0 Hz), 8.25 d (1H, 6-H, J = 10.0 Hz), 9.20 br.s (1H, NH). Found, %: C 51.22; H 3.98; N 12.31. $C_{15}H_{15}N_3O_7$. Calculated, %: C 51.58; H 4.30; N 12.03.

Methyl 3-benzoyl-5-(methoxycarbonylamino)-2-methyl-4-nitro-1*H*-indole-1-carboxylate (IVc) was synthesized in a similar way by reaction of 2 g (5.59 mmol) of indole **Ic** with 0.99 g (3.35 mmol) of copper(II) nitrate hexahydrate. Yield 1.35 g (60%), yellow crystals, mp 214–215°C (from glacial acetic acid). IR spectrum, ν, cm^{-1}: 3360 (NH); 1770, 1670 (C=O); 1620, 1570, 1550 (C=C, C=C_{arom}); 1510, 1350 (NO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.43 s (3H, Me), 3.70 s (3H, $NHCO_2C\mathbf{H}_3$), 4.10 s (3H, NCO_2CH_3), 7.45 t (2H, H_{arom}, J = 6.0 Hz), 7.60 t (1H, H_{arom}, J = 6.0 Hz), 7.75 d (3H, H_{arom}, J = 8.5 Hz), 8.38 d (1H, H_{arom}, J = 8.5 Hz), 9.10 br.s (1H, NH). Found, %: C 58.51; H 4.02; N 10.56. $C_{20}H_{17}N_3O_7$. Calculated, %: C 58.39; H 4.14; N 10.22.

Dimethyl {2-[1,3-dioxo-1-(pyridin-3-yl)butan-2-yl]benzene-1,4-diyl}biscarbamate (VII). Dimethyl cyclohexa-2,5-diene-1,4-diylidenebiscarbamate (**V**), 0.99 g (4.5 mmol), was dissolved in 10 ml of anhydrous dioxane, 0.75 g (4.6 mmol) of 1-(pyridin-3-yl)-butane-1,3-dione (**VI**) and 0.04 g of sodium methoxide were added, and the mixture was kept for 8 h (until complete conversion of **V**). The mixture was poured into 50 ml of ice water, 2 drops of glacial acetic acid were added, and the precipitate was filtered off, dried in air, and recrystallized from chloroform–petroleum ether (1:2 by volume). Yield 1.4 g (84%), colorless crystals, mp 159–160°C. IR spectrum, ν, cm^{-1}: 3340 (NH); 1725, 1670 (C=O); 1620, 1570, 1550 (C=C, C=C_{arom}). Found, %: C 58.98; H 4.72; N 10.81. $C_{19}H_{19}N_3O_6$. Calculated, %: C 59.22; H 4.94; N 10.91.

Methyl 5-(methoxycarbonylamino)-2-methyl-3-(pyridin-3-ylcarbonyl)-1*H*-indole-1-carboxylate (VIII). A mixture of 1 g of compound **VII** and 10 ml of 22% hydrochloric acid was heated for 3 h at the boiling point. The mixture was cooled, 25% aqueous ammonia was added dropwise until neutral reaction, and the precipitate was filtered off, washed on a filter with water, dried in air, and recrystallized from ethanol. Yield 0.9 g (94%), colorless crystals, mp 185–187°C. IR spectrum, ν, cm^{-1}: 3330 (NH); 1715 (C=O); 1635, 1600, 1555 (C=C, C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.64 s (3H, Me), 3.73 s (3H, $NHCO_2C\mathbf{H}_3$), 3.96 s (3H, NCO_2CH_3), 8.08–8.19 m (4H, H_{arom}), 8.48 s (1H, 4-H), 8.58 d (1H, 4′-H, J = 5.2 Hz), 8.65 br.s (1H, NH), 8.85 s (1H, 2′-H). Found, %: C 62.24; H 4.36; N 11.14. $C_{19}H_{17}N_3O_5$. Calculated, %: C 62.13; H 4.63; N 11.44.

Methyl 5-(methoxycarbonylamino)-3-(4-methyl-1,2,5-oxadiazol-3-ylcarbonyl)-1*H*-indole-1-carboxylate (XI). Compound **V**, 0.6 g (2.7 mmol), was dissolved in 10 ml of methylene chloride, 0.5 g (2.7 mmol) of 3-dimethylamino-1-(4-methyl-1,2,5-oxadiazol-3-yl)prop-2-en-1-one (**X**) and two drops of boron trifluoride–ether complex were added, and the mixture was kept for 30 min at room temperature. The crystalline solid was filtered off, washed on a filter with diethyl ether (10 ml), and recrystallized from glacial acetic acid. Yield 0.74 g (77%), colorless crystals, mp 233–235°C. IR spectrum (KBr), ν, cm^{-1}: 3360 (NH); 3168, 3135, 2961 (C–H_{aliph}); 1733 (C=O); 1595, 1541, 1487 (C=C, C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.50 s (3H, Me), 3.71 s (3H, $NHCO_2C\mathbf{H}_3$), 4.07 s (3H, NCO_2CH_3), 7.55 d.d (1H, 6-H, J = 2.1, 9.0 Hz), 8.06 d (1H, 7-H, J = 9.0 Hz), 8.57 s (1H, 2-H), 8.72 s (1H, 4-H), 9.76 br.s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 359 $[M + 1]^+$ (23), 358 $[M]^+$ (100), 326 (7.7), 317 (11), 275 (69), 268 (38.5), 243 (23.1), 216 (38.5), 199 (46.2), 184 (38.4), 171 (30.8), 157 (61.5), 143 15.4), 129 (23.1), 116 (12.3), 102 (21.5), 79 (12.3). Found, %: C 53.38; H 4.02; N 15.45. $C_{16}H_{14}N_4O_6$. Calculated, %: C 53.63; H 3.91; N 15.64.

***N*-[3-(4-Methyl-1,2,5-oxadiazol-3-ylcarbonyl)-1-phenylsulfonyl-1*H*-indol-5-yl]benzenesulfonamide (XII).** *p*-Quinone diimine **IX**, 1.0 g (2.59 mmol), was dissolved in 10 ml of glacial acetic acid, 0.5 g

(2.59 mmol) of compound **X** and two drops of boron trifluoride–ether complex were added, and the mixture was stirred for 10 h and poured into ice water (100 ml). The precipitate was filtered off, dried in air, and recrystallized from dioxane. Yield 1.15 g (85%), colorless crystals, mp 256–258°C. IR spectrum (KBr), ν, cm^{-1}: 3246 (NH); 3142 (C–H_{aliph}); 1651 (C=O); 1618, 1600, 1531 (C=C, C=C_{arom}); 1335, 1159 (SO_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.50 s (3H, Me), 7.25 d (1H, H_{arom}, J = Hz), 7.47–7.53 m (3H, H_{arom}, 2-H), 7.55–7.57 m (1H, H_{arom}), 7.63 t (2H, H_{arom}, J = 8.3 Hz), 7.72–7.80 m (3H, H_{arom}), 7.93 d (1H, H_{arom}, J = 9.0 Hz), 8.14 d (2H, H_{arom}, J = 9.0 Hz), 8.81 s (1H, H_{arom}), 10.45 br.s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 522 $[M]^+$ (2.6), 381 (46), 157 (77), 141 (100), 77 (98). Found, %: C 54.83; H 3.22; N 10.56. $C_{24}H_{18}N_4O_6S_2$. Calculated, %: C 55.11; H 3.44; N 10.72.

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