Synthesis of 3-R-2-aryl-4,6-dinitroindoles and specific features of their reactions with anionic nucleophiles*

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Reaction of different anionic S-nucleophiles with 3-R-2-aryl-4,6-dinitroindoles led to a regiospecific nucleophilic substitution of the nitro group in position 4 with 6-NO_2 group remaining intact. The representatives of some *peri*-annulated polycyclic systems were synthesized on the basis of the substitution products.

Key words: nitro compounds, indoles, nucleophilic substitution, nitro group.

The interest of researchers to the chemistry of indoles, to the elaboration of new methods for the synthesis of its derivatives and their functionalization is connected first of all with a large number of compounds of indole series found in the nature. Many of indole derivatives both of the natural and man-made origin have various biological activities. Such compounds are of interest from the point of view of preparation of their synthetic analogs as the potential chemiotherapeutic medicines. A considerable part of data on the synthesis and reactivity of indole derivatives is summarized in monograph.[1]

Earlier, a preparative method for the synthesis of a new type of substituted indoles, *viz.*, 2-aryl-4,6-dinitroindoles, has been developed on the basis of 2,4,6-trinitrotoluene (TNT).[2] The present research work deals with functionalization of this type of indoles through the substitution of nitro group upon treatment with nucleophiles and possible subsequent annulation of the other heterocyclic fragments. Such an approach would have allowed us to use 2-aryl-4,6-dinitroindoles as the basis for the creation of new indole derivatives with potential useful biological activity.

Earlier, we have reported the regiospecific nucleophilic substitution of 4-NO_2 groups in various 4,6-dinitrobenzo-annulated heterocycles (3-R-4,6-dinitrobenzo[*d*]isoxazoles,[3] 3-R-1-aryl-4,6-dinitro-1*H*-indazoles,[4] 4,6-dinitrobenzo[*b*]thiophenes,[5] *etc.*). During this, the nitro group in position 6 remained intact both when the excess of nucleophile was used and when the reaction conditions were made increasingly drastic. However, in case of highly electrophilic 3-R-4,6-dinitrobenzo[*d*]isoxazoles (R = CN and CH=NOMe), 6-NO_2 group can also be substituted upon treatment with thiols.[6] As to 2-aryl-4,6-dinitroindoles, to date, there is no information on substitution of the nitro group in these compounds.

We found that 2-aryl-1-methyl-4,6-dinitroindoles **1** without substituents in position 3 do not react with anionic nucleophiles even under drastic conditions. We believe that this results from the low electrophilicity of these compounds. To increase the electrophilicity of the heterocyclic system, it was reasonable to introduce electron-withdrawing substituents, such as CHO, CN, *etc.*, in position 3 of the indole ring.

Indoles are well known to undergo the formylation at position 3 under the Vilsmeier reaction conditions. The isolated examples of such transformations for 4,6-dinitroindoles were described earlier.[7] We used a modified procedure for the introduction of a formyl group to the dinitroindole core, which enabled us to obtain 2-aryl-3-formyl-4,6-dinitroindoles **2** in high yields (Scheme 1). Treatment of aldehydes **2** with hydroxylamine hydrochloride in acetic (in case of **2a**) or formic (in case of **2b**) acid led to the formation of the earlier unknown 3-cyano derivatives **3**. When the reaction was carried out with $NH_2OH \cdot HCl$ in ethanol, oximes **4** were obtained, whereas treatment of aldehydes **2** with arylhydrazines led to the corresponding hydrazones **5**. The yield of compounds **2—5** varied from 67 to 83%.

The study on interaction of 3-R-4,6-dinitroindoles **2** and **3** with anionic S-nucleophiles was carried out on their model reaction with aromatic and aliphatic thiols. Thus compounds **2** and **3** react with thiophenol, benzylmercaptane, 1-thioglycerol, and methyl thioglycolate in the presence of K_2CO_3 in *N*-methylpyrrolidone (*N*-MP) already at room temperature (Scheme 2), giving rise to the products of substitution of the nitro group in position 4 **(6a—g)** in high yields (61—88%). In all cases, de-

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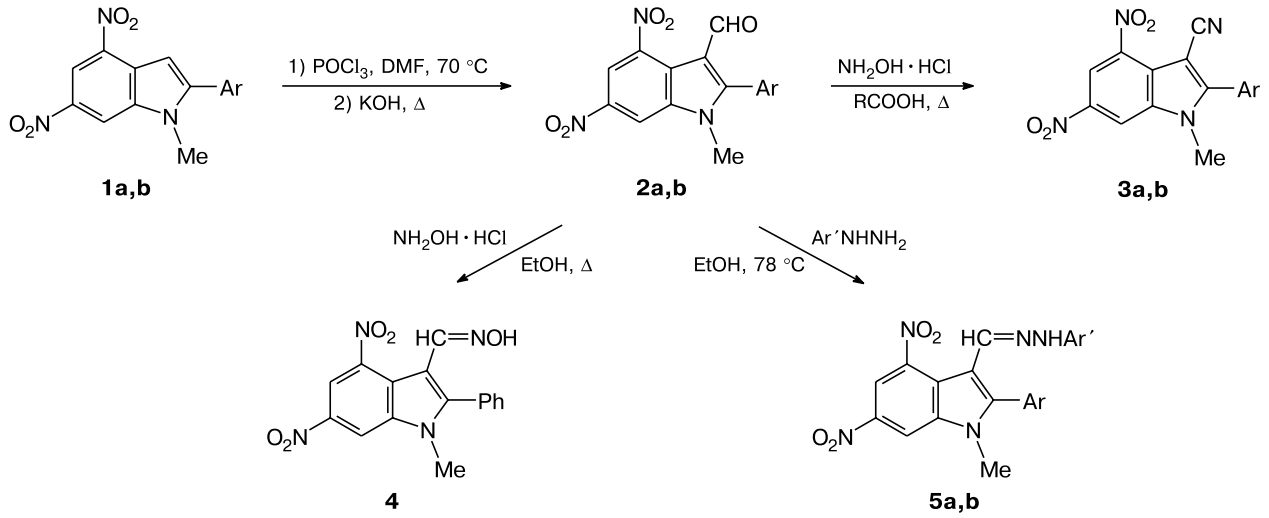
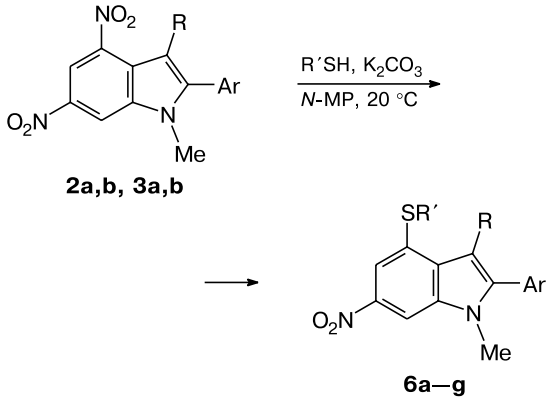
Scheme 1



Ar = Ph (**2a, 3a, 5a,b**);4-ClC_6H_4 (**2b, 3b**); Ar′ = Ph (**5a**), 4-MeC_6H_4 (**5b**)

spite of the use of nucleophilic reagent in excess, no products of substitution of 6-NO_2 group were observed according to the ^{1}H NMR spectra of the crude reaction product.

Scheme 2

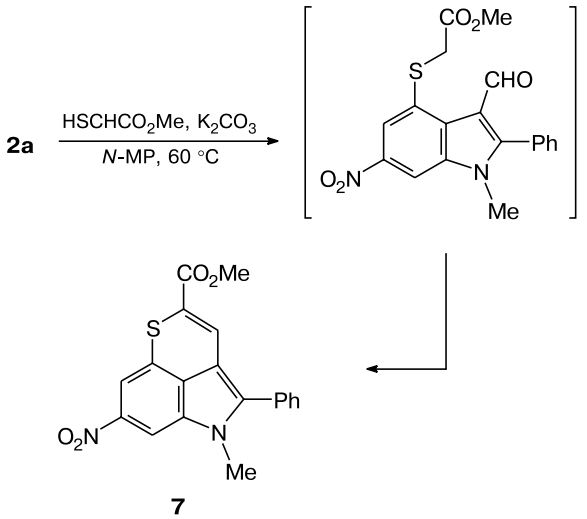


Compound	Ar	R	R′
6a	Ph	CHO	Bn
6b	Ph	CHO	Ph
6c	Ph	CHO	$CH_2CH(OH)CH_2OH$
6d	4-ClC_6H_4	CHO	$CH_2CH(OH)CH_2OH$
6e	Ph	CN	Bn
6f	Ph	CN	CH_2CO_2Me
6g	4-ClC_6H_4	CN	CH_2CO_2Me

The direction of substitution of the nitro group was established by ^{1}H NMR spectroscopy (2D NOESY). For compounds **6a,b,e**, the interactions between hydrogen atoms of the *N*-methyl group of indole and H(7) (8.4—8.5 ppm), as well as between H(5) (7.9—8.1 ppm) and the methylene hydrogen atoms of SCH_2Ph substituent (for **6a** and **6e**) or *ortho*-protons of SPh substituent (for **6b**) were observed. These facts allowed us to make an unambiguous conclusion about the substitution of the very nitro groups in position 4. For the other sulfides **6**, the evidence of substitution of 4-NO_2 group was obtained by chemical methods (see below).

In the reaction of dinitroindole **2a** with methyl thioglycolate, the intermediately formed product of substitution of 4-NO_2 group under the reaction conditions undergoes cyclization through the addition of the active methylene unit in SCH_2CO_2Me substituent at the formyl group (Scheme 3) to form a representative of the

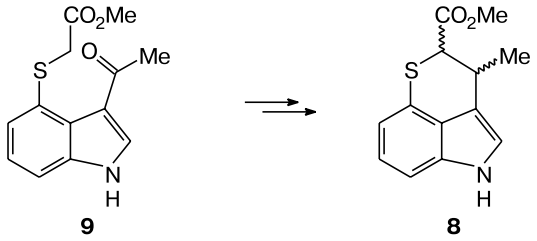
Scheme 3



peri-annulated tricyclic heteroaromatic compounds **7** of thiopyrano[4,3,2-*cd*]indole series.

The fact of formation of such a tricyclic system is a chemical evidence of substitution of the 4-NO_2 group. Compound **7** is a structural analog of the natural antibiotic chuansinmycin **8**, which has been synthesized[8] by the similar scheme, starting from methyl (3-acetylindol-4-yl)thioacetate (**9**) (Scheme 4).

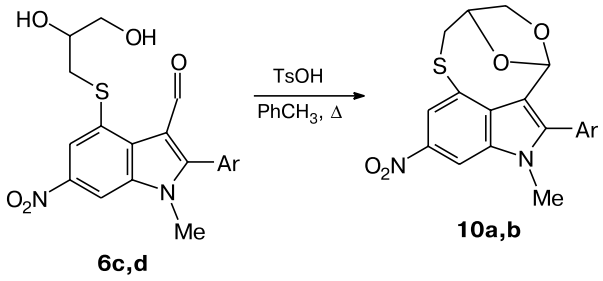
Scheme 4



It shows activity toward a number of gram-positive and gram-negative bacteria.[8]

The products of substitution of the nitro group in dinitrophenylindoles by the residue of 1-thioglycerol (**6c,d**) form cyclic acetals **10a,b** upon treatment with catalytic amounts of TsOH (Scheme 5), which is another evidence of the regiospecific substitution of the nitro groups in position 4.

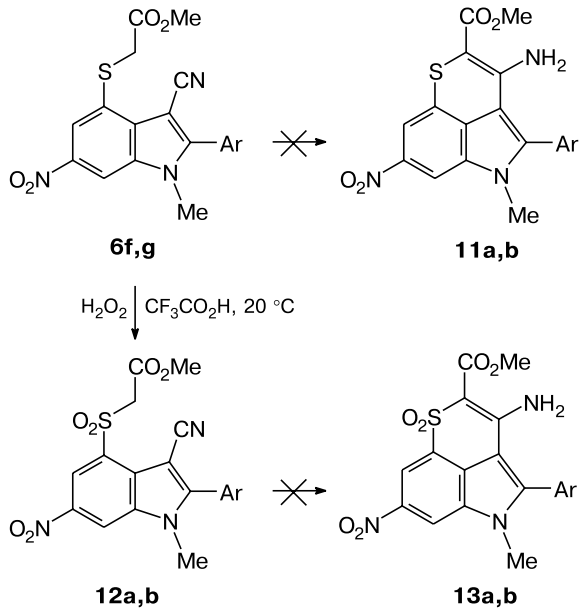
Scheme 5



It should be noted that dinitro derivatives **2** and **3** do not react with other anionic nucleophiles, such as NaN_3, as well as with phenol in dipolar aprotic solvents in the presence of K_2CO_3: the increasingly drastic reaction conditions (100 °C) only cause resinification.

Attempted cyclization of sulfides **6f,g** through the addition of the methylene unit of SCH_2CO_2Me substituent at the CN bond to form tricyclic compounds **11a,b** similarly to cyclization of indazole[4b] and benzo[*d*]isoxazole[6] derivatives failed. In order to obtain compounds with the more active methylene fragment, sulfides **6f,g** were oxidized to the corresponding sulfones **12a,b** (Scheme 6). However, treatment of the latter with K_2CO_3 in *N*-MP at 80—90 °C gave no *peri*-annulated tricyclic derivatives **13a,b**, too, resulting only in decomposition of the starting sulfones.

Scheme 6



In conclusion, a series of 3-R-2-aryl-4,6-dinitroindoles were synthesized; a study of their reactions with anionic nucleophiles showed that the nitro group in position 4 is regiospecifically substituted upon treatment with various S-nucleophiles, leaving the 6-NO_2 group intact. The representatives of some *peri*-annulated heterocyclic systems were synthesized on the basis of the products of substitution of the 4-NO_2 group in 3-R-4,6-dinitro-2-arylindoles.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer, ^{13}C NMR spectra, on a Bruker AM-300 spectrometer. Chemical shifts (δ) are given from Me_4Si. All the samples for NMR spectroscopy were prepared in DMSO-d_6. IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets. Mass spectra were recorded on a Kratos MS-30 (EI, 70 eV). The reaction progress and the purity of compounds were monitored by TLC on Silufol UV-254 plates. Dry DMF was used for the reactions. The other solvents were used without additional drying. Compounds **1a,b** were synthesized according to the procedure described earlier.[7]

Synthesis of aldehydes 2a,b (general procedure). Dinitroindole **1a** or **1b** (5.75 mmol) was added to a mixture of DMF (20 mL) and $POCl_3$ (5.3 mL, 57.5 mmol). The mixture was heated for 15 h at 70—75 °C. Then, the cooled mixture was poured on ice (100 g) and treated with 58% aq. HNO_3 (15 mL). The precipitate thus formed was filtered off, the filtrate was kept

for 16 h. The precipitate formed from the filtrate was filtered off and added to 20% aq. NaOH (200 mL). The mixture was refluxed for 1 h, cooled, the precipitate was filtered off and dried in air.

1-Methyl-4,6-dinitro-2-phenyl-1*H*-indole-3-carbaldehyde (2a). The yield was 1.44 g (77%), m.p. 224—226 °C (*cf.* Ref. 7: m.p. 225—228 °C). ^{1}H NMR, δ: 3.91 (s, 3 H, Me); 7.52—7.89 (m, 5 H, Ph); 8.60 (s, 1 H, H(5)); 9.03 (s, 1 H, H(7)); 10.65 (s, 1 H, CHO).

2-(4-Chlorophenyl)-1-methyl-4,6-dinitro-1*H*-indole-3-carbaldehyde (2b). The yield was 1.6 g (82%), m.p. 244—246 °C. Found (%): C, 53.31; H, 2.99; N, 11.84; $C_{16}H_{10}ClN_3O_5$. Calculated (%): C, 53.42; H, 2.80; N, 11.68. ^{1}H NMR, δ: 3.89 (s, 3 H, Me); 7.65—7.85 (m, 4 H, 4-ClC_6H_4); 8.65 (s, 1 H, H(5)); 9.05 (s, 1 H, H(7)); 10.63 (s, 1 H, CHO).

1-Methyl-4,6-dinitro-2-phenyl-1*H*-indole-3-carbonitrile (3a). A solution of aldehyde **1a** (1.3 g, 4 mmol) and $NH_2OH \cdot HCl$ (0.42 g, 6 mmol) in AcOH (7 mL) was refluxed for 6 h, cooled and poured in water (50 mL). The precipitate formed was filtered off and dried in air to obtain compound **3a** (1.0 g, 77%), m.p. 255—259 °C. Found (%): C, 59.37; H, 3.23; N, 17.49. $C_{16}H_{10}N_4O_4$. Calculated (%): C, 59.63; H, 3.13; N, 17.38. ^{1}H NMR, δ: 3.95 (s, 3 H, Me); 7.65—7.80 (m, 5 H, Ph); 8.85 (s, 1 H, H(5)); 9.20 (s, 1 H, H(7)). IR, ν/cm^{-1}: 2300, 1664, 1552, 1536, 1516, 1408, 1368, 1296, 1232, 1140, 1020, 968, 928, 876, 824, 788, 756, 688.

2-(4-Chlorophenyl)-1-methyl-4,6-dinitro-1*H*-indole-3-carbonitrile (3b). A solution of aldehyde **2b** (0.54 g, 1.5 mmol) and $NH_2OH \cdot HCl$ (0.16 g, 2.25 mmol) in 95—98% aq. HCOOH (7 mL) was refluxed for 6 h, cooled and poured in water (50 mL)). The precipitate formed was filtered off and refluxed in Ac_2O (5 mL) for 4 h. The solvent was evaporated, the residue was washed with water and dried in air to obtain compound **3b** (0.2 g, 67%), m.p. 231—236 °C. Found (%): C, 54.06; H, 2.32; N, 15.39. $C_{16}H_9ClN_4O_4$. Calculated (%): C, 53.87; H, 2.54; N, 15.71. ^{1}H NMR, δ: 4.03 (s, 3 H, Me); 7.71—7.89 (m, 4 H, 4-ClC_6H_4); 8.80 (s, 1 H, H(5)); 9.2 (s, 1 H, H(7)). IR, ν/cm^{-1}: 2232, 1508, 1428, 1296, 1060, 828, 716.

1-Methyl-4,6-dinitro-2-phenyl-1*H*-indole-3-carbaldehyde oxime (4). A mixture of aldehyde **2a** (0.325 g, 1 mmol), $NH_2OH \cdot HCl$ (0.07 g, 1 mmol), and EtOH (10 mL) was refluxed for 30 min, then cooled, the precipitate was filtered off to obtain compound **4** (0.24 g, 71%), m.p. 225—228 °C. Found (%): C, 56.19; H, 3.38; N, 16.79. $C_{16}H_{12}N_4O_5$. Calculated (%): C, 56.47; H, 3.55; N, 16.46. ^{1}H NMR, δ: 3.89 (s, 3 H, Me); 7.52—7.54 (m, 5 H, Ph); 8.0 (s, 1 H, CH); 8.59 (s, 1 H, H(5)); 9.0 (s, 1 H, H(7)); 11.01 (s, 1 H, OH).

Synthesis of hydrazones 5a,b (general procedure). A mixture of aldehyde **2a** (0.49 g, 1.5 mmol), the corresponding arylhydrazine hydrochloride (1.5 mmol) and EtOH (10 mL) was refluxed for 30 min. Then it was cooled, the precipitate formed was filtered off and dried in air.

1-Methyl-4,6-dinitro-2-phenyl-1*H*-indole-3-carbaldehyde *N*-phenylhydrazone (5a). The yield was 0.52 g (83%), m.p. 220—225 °C. Found (%): C, 63.37; H, 4.28; N, 17.09. $C_{22}H_{17}N_5O_4$. Calculated (%): C, 63.61; H, 4.12; N, 16.86. ^{1}H NMR, δ: 3.85 (s, 3 H, Me); 6.65 (t, 1 H, Ph, $^3J_{H-H}$ = 8.8 Hz); 6.80 (d, 2 H, Ph, $^3J_{H-H}$ = 8.9 Hz); 7.23 (t, 2 H, Ph, $^3J_{H-H}$ = 8.8 Hz); 7.62—7.70 (m, 5 H, Ph); 7.79, 8.50, 8.95 (all s, 1 H each); 10.05 (s, 1 H, NH).

1-Methyl-4,6-dinitro-2-phenyl-1*H*-indole-3-carbaldehyde *N*-(4-methylphenyl)hydrazone (5b). The yield was 0.55 g (82%), m.p. 230—233 °C. Found (%): C, 64.59; H, 4.72; N, 16.03. $C_{23}H_{19}N_5O_4$ Calculated (%): C, 64.33; H, 4.46; N, 16.31. ^{1}H NMR, δ: 2.85 (s, 3 H, CMe); 3.85 (s, 3 H, NMe); 6.70 (d, 2 H, 4-MeC_6H_4, $^3J_{H-H}$ = 10 Hz); 6.95 (d, 2 H, 4-MeC_6H_4, $^3J_{H-H}$ = 10 Hz); 7.60—7.70 (m, 5 H, Ph); 7.80, 8.50, 8.95 (all s, 1 H each); 9.95 (s, 1 H, NH).

Synthesis of sulfides 6a—g (general procedure). Potassium carbonate (3 mmol) and the corresponding thiol (3 mmol) (in case of 1-thioglycerol, thiol (4.5 mmol) and K_2CO_3 (4.5 mol)) were added to a solution of compounds **2a,b** or **3a,b** (1.5 mmol) in *N*-MP (7 mL). The reaction mixture was stirred for 24 h at 20 °C, poured in water (50 mL), acidified with conc. HCl to pH = 3, the precipitate formed was filtered off, dried in air, and washed with hot EtOH; in case of oily products, they were extracted with ethyl acetate (2×50 mL), dried with Na_2SO_4, and the solvent was evaporated.

4-Benzylsulfanyl-1-methyl-6-nitro-2-phenyl-1*H*-indole-3-carbaldehyde (6a). The yield was 0.47 g (79%), m.p. 185—190 °C. Found (%): C, 68.87; H, 4.65; N, 6.80. $C_{23}H_{18}N_2O_3S$. Calculated (%): C, 68,64; H, 4,51; N, 6,96. ^{1}H NMR, δ: 3.70 (s, 3 H, Me); 4.50 (s, 2 H, CH_2); 7.20—7.50 (m, 5 H, Ph); 8.12 (s, 1 H, H(5)); 8.48 (s, 1 H, H(7)); 10.31 (s, 1 H, CHO).

1-Methyl-6-nitro-2-phenyl-4-phenylsulfanyl-1*H*-indole-3-carbaldehyde (6b). The yield was 0.46 g (81%), m.p. 198—201 °C. Found (%): C, 68.24; H, 4.18; N, 7.31. $C_{22}H_{16}N_2O_3S$. Calculated (%): C, 68.02; H, 4.15; N, 7.21. ^{1}H NMR, δ: 3.70 (s, 3 H, Me); 7.58 (m, 3 H, Ph); 7.64 (m, 2 H, Ph); 7.80 (s, 1 H, H(5)); 8.50 (s, 1 H, H(7)); 10.30 (s, 1 H, CHO).

4-(2,3-Dihydroxypropylsulfanyl)-1-methyl-6-nitro-2-phenyl-1*H*-indole-3-carbaldehyde (6c). The yield was 0.45 g (79%), m.p. 98—102 °C. Found (%): C, 59.37; H, 4.49; N, 7.01. $C_{19}H_{18}N_2O_5S$. Calculated (%): C, 59.06; H, 4.70; N, 7.25. ^{1}H NMR, δ: 3.10, 3.50 (both m, 2 H each); 3.70 (s, 3 H, Me); 4.80, 5.20 (both br.s, 1 H each, OH); 7.60—7.80 (m, 5 H, Ph); 8.10 (s, 1 H, H(5)); 8.40 (s, 1 H, H(7)). IR, ν/cm^{-1}: 2924, 2872, 1508, 1452, 1392, 1356, 1328, 1156, 1092, 952, 880, 760, 748, 708.

2-(4-Chlorophenyl)-4-(2,3-dihydroxypropylsulfanyl)-1-methyl-6-nitro-1*H*-indole-3-carbaldehyde (6d). The yield was 0.45 g (71%), m.p. 100—105 °C. Found (%): C, 54.50; H, 3.89; N, 6.87. $C_{19}H_{17}ClN_2O_5S$. Calculated (%): C, 54.22; H, 4.07; N, 6.66. ^{1}H NMR, δ: 3.10, 3.50 (both m, 2 H each); 3.70 (s, 3 H, Me); 4.80, 5.20 (both br.s, 1 H each, OH); 7.50—7.80 (m, 4 H, 4-ClC_6H_4); 8.10 (s, 1 H, H(5)); 8.50 (s, 1 H, H(7)).

4-Benzylsulfanyl-1-methyl-6-nitro-2-phenyl-1*H*-indole-3-carbonitrile (6e). The yield was 0.44 g (75%), m.p. 187—190 °C. Found (%): C, 68.91; H, 4.49; N, 10.80. $C_{23}H_{17}N_3O_2S$. Calculated (%): C, 69.15; H, 4.29; N, 10.52. ^{1}H NMR, δ: 3.85 (s, 3 H, Me); 4.50 (s, 2 H, CH_2); 7.20—7.50, 7.60—7.80 (both m, 5 H each, Ph); 8.10 (s, 1 H, H(5)); 8.50 (s, 1 H, H(7)).

Methyl 2-[(3-cyano-1-methyl-6-nitro-2-phenyl-1*H*-indole-4-yl)sulfanyl]acetate (6f). The yield was 0.47 g (88%), m.p. 205—206 °C. Found (%): C, 59.55; H, 3.79; N, 11.27. $C_{19}H_{15}N_3O_4S$. Calculated (%): C, 59.83; H, 3.96; N, 11.02. ^{1}H NMR, δ: 3.70, 3.90 (both s, 3 H each, Me); 4.20 (s, 2 H, CH_2); 7.60—7.80 (m, 5 H, Ph); 8.00 (s, 1 H, H(5)); 8.60 (s, 1 H, H(7)).

Methyl 2-[2-(4-chlorophenyl)-3-cyano-1-methyl-6-nitro-1*H*-indole-4-yl)sulfanyl]acetate (6g). The yield was 0.42 g (61%), m.p. 215—216 °C. Found (%): C, 55.12; H, 3.07; N, 10.31. $C_{19}H_{14}ClN_3O_4S$. Calculated (%): C, 54.88; H, 3.39; N, 10.10. ^{1}H NMR, δ: 3.65, 3.90 (both s, 3 H each, Me); 4.20 (s, 2 H, CH_2); 7.70—7.80 (m, 4 H, 4-ClC_6H_4); 8.00 (s, 1 H, H(5)); 8.60 (s, 1 H, H(7)).

Methyl 5-methyl-7-nitro-4-phenyl-5*H*-thiopyrano[4.3.2-*cd*]indole-2-carboxylate (7). A mixture of aldehyde **2a** (0.395 g, 1.2 mmol), methyl thioglycolate (0.17 mL, 3.6 mmol), K_2CO_3 (0.5 g, 3.6 mmol), and *N*-MP (10 mL) was stirred for 24 h at 60 °C under argon atmosphere. The reaction mixture was poured in water and acidified to pH = 2. The precipitate was filtered off, dried and chromatographed on a column (SiO_2 with $CHCl_3$ as the eluent). The yield was 0.25 g (56%), m.p. 205—211 °C. Found (%): C, 62.16; H, 4.49; N, 7.95. $C_{19}H_{16}N_2O_4S$. Calculated (%): C, 61.94; H, 4.38; N, 7.60. ^{1}H NMR, δ: 3.65, 3.70 (both s, 3 H each, Me); 7.20 (s, 1 H, CH); 7.40 (s, 1 H, H(5)); 7.50—7.70 (m, 5 H, Ph); 8.00 (s, 1 H, H(7)). IR, ν/cm^{-1}: 1676, 1568, 1476, 1332, 1308, 1220, 1188, 1080, 1004, 836, 744, 716, 676, 1348, 1264, 1136, 1092, 1028, 988, 948, 904, 884, 856, 800, 764, 744.

Synthesis of compounds 10a,b (general procedure). A solution of the corresponding sulfide (1 mmol) and TsOH (50 mg) in toluene (35 mL) was refluxed with the Dean-Stark trap for 14 h. The precipitate formed after cooling was filtered off. The filtrate was concentrated, the residue was chromatographed on a column (SiO_2 with $CHCl_3$ as the eluent).

13-Methyl-10-nitro-14-phenyl-3,16-dioxa-7-thia-13-azatetracyclo[6.6.1.1^{2,5}.0^{12,15}]hexadeca-1(14),8(15),9,11-tetraene (10a). The yield was 0.2 g (50%), m.p. 250—260 °C. Found (%): C, 62.22; H, 4.70; N, 7.89. $C_{19}H_{16}N_2O_4S$. Calculated (%): C, 61.94; H, 4.38; N, 7.60. ^{1}H NMR, δ: 3.10 (m, 2 H, CH_2); 3.70 (s, 3 H, Me); 3.90 (m, 1 H); 4.45 (d, 1 H, J = 9.8 Hz); 4.60 (br.s, 1 H); 5.80 (s, 1 H); 7.45—7.70 (m, 5 H, Ph); 8.15 (s, 1 H, H(5)); 8.55 (s, 1 H, H(7)).

14-(4-Chlorophenyl)-13-methyl-10-nitro-3,16-dioxa-7-thia-13-azatetracyclo[6.6.1.1^{2,5}.0^{12,15}]hexadeca-1(14),8(15),9,11-tetraene (10b). The yield was 0.2 g (47%), m.p. 252—256 °C. Found (%): C, 56.37; H, 3.52; N, 7.19. $C_{19}H_{15}ClN_2O_4S$. Calculated (%): C, 56.65; H, 3.75; N, 6.95. ^{1}H NMR, δ: 3.10 (m, 2 H, CH_2); 3.70 (s, 3 H, Me); 3.90 (m, 1 H); 4.40 (d, 1 H, J = 9.7 Hz); 4.60 (br.s, 1 H); 5.80 (s, 1 H); 7.55, 7.70 (both d, 4 H, 4-ClC_6H_4, J = 9.6 Hz); 8.15 (s, 1 H, H(5)); 8.50 (s, 1 H, H(7)).

Synthesis of sulfones 12a,b (general procedure). A 30% solution of H_2O_2 (1.0 mL) was added dropwise to a solution of the corresponding sulfide (1.3 mmol) in CF_3CO_2H (10 mL). The mxture was stirred for 15 h at 20 °C, then poured in water (50 mL). The precipitate formed was filtered off, washed with hot EtOH (5 mL) and dried in air.

Methyl 2-[(3-cyano-1-methyl-6-nitro-2-phenyl-1*H*-indole-4-yl)sulfonyl]acetate (12a). The yield was 0.12 g (20%), m.p. 232—236 °C. Found (%): C, 57.97; H, 4.17; N, 7.02. $C_{20}H_{16}N_2O_6S$. Calculated (%): C, 58.25; H, 3.91; N, 6.79. ^{1}H NMR, δ: 3.60, 4.00 (both s, 3 H each, Me); 4.90 (s, 2 H, CH_2); 7.65—7.80 (m, 5 H, Ph); 8.60 (s, 1 H, H(5)); 9.15 (s, 1 H, H(7)).

Methyl 2-[2-(4-chlorophenyl)-3-cyano-1-methyl-6-nitro-1*H*-indole-4-yl]sulfonylacetate (12b). The yield was 0.34 g (58%), m.p. 173—177 °C. Found (%): C, 54.11; H, 3.74; N, 6.61. $C_{20}H_{15}ClN_2O_6S$. Calculated (%): C, 53.76; H, 3.38; N, 6.27. ^{1}H NMR, δ: 3.60, 4.00 (both s, 3 H each, Me); 4.90 (s, 2 H, CH_2); 7.70—7.90 (m, 4 H, 4-ClC_6H_4); 8.60 (s, 1 H, H(5)); 9.15 (s, 1 H, H(7)).

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