1,3-Dipolar Cycloaddition of Unstabilized *N*-Methyl Azomethine Ylide to Nitrobenzene Annelated with Azoles

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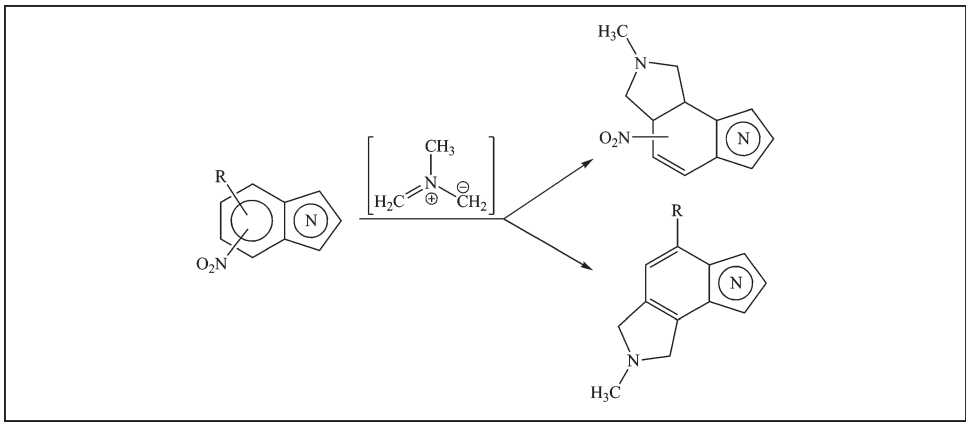

The 1,3-dipolar cycloaddition of unstabilized *N*-methyl azomethine ylide to mononitro benzazoles was studied. Depending on the nature of substituents and annelated azoles, the reaction affords previously unknown isoindole fused heterocyclic systems. The reactivity of the cycloadducts was examined.

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INTRODUCTION

1,3-Dipolar cycloaddition (1,3-DC) of azomethine ylides to alkenes is widely used in modern organic synthesis being one of the simplest methods for the construction of pyrrolidine, pyrroline, and pyrrole rings [1]. A wide variety of nitrogen heterocyclic, polycyclic, and natural compounds was recently synthesized by means of this methodology [2]. The use of chiral catalysts allows obtaining the target products with high stereoselectivity [3].

Recently [4], we reported on the first example of 1,3-DC reactions of azomethine ylides and nitroarenes. As a result of double cycloaddition of unstabilized *N*-methyl azomethine ylide **1** to meta-dinitrobenzene fused with nitrogen aromatic heterocycles, the derivatives of decahydropyrrolo[3,4-*e*]isoindole series **3a–e** were synthesized in good yields (Scheme 1). Thus, both of the fragments C—C—NO_2 of the starting bicyclic systems **2a–e** acted as dipolarophiles similar to conjugated nitro alkenes which readily give adducts with azomethine ylides [3c,d,5].

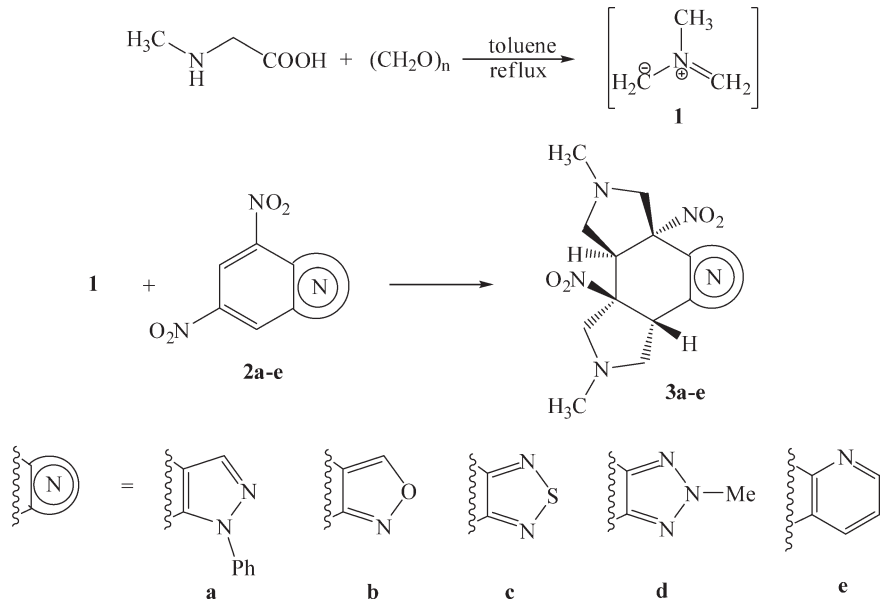
RESULTS AND DISCUSSION

In continuation of our research, we studied 1,3-DC reactions of unstabilized *N*-methyl azomethineylide with mononitro benzazoles. The π-deficient benzoheterocycles with sp^2-nitrogen atom of azole fragment adjacent to the benzene ring—mononitro derivatives of benzofurazan, benzothiadiazole, and benzo[*c*]isoxazole (**4a–e**) [6]—were used as dipolarophiles. Azomethine ylide **1** was generated *in situ* by refluxing sarcosine and paraformaldehyde in toluene [5a] in the presence of nitro compounds **4a–e** (Scheme 2).

In all cases, cycloaddition afforded previously unknown tricyclic heterosystems—fused tetrahydroisoindoles **5a–e** (Scheme 2, Table 1). Interestingly, the resulting cycloadducts did not undergo neither further aromatization with the loss of HNO_2 nor consequent addition of another molecule of azomethine ylide **1** to C—C double bond that became nonaromatic.

In case of less π-deficient 6-nitro-1-phenylindazole (Scheme 3, R = R_1 = H, X = NC_6H_5), no cycloadduct was detected during 48 h (TLC); the starting compound remained intact although 4,6-dinitro-1-phenylindazole (**2a**, Scheme 1) readily underwent double cycloaddition under the action of azomethine ylide **1**. Therefore, the influence of the substituents in benzene ring of mononitro indazoles was studied. It was found that the replacement of 4-NO_2 in compound **2a** with electron-releasing groups, such as OPh, OMe, SPh (see for example ref.

Scheme 1



7), does not favor the 1,3-DC reactions with **1**—no formation of products was observed (Scheme 3). The same results were obtained using 6-nitrobenzo[d]isoxazoles as dipolarophiles (Scheme 3, X = O). Moreover, introduction of the cyano group in position 3 of indazole or benzo[*d*]isoxazole system (The synthesis was described in ref. 8a,c) did not promote the cycloaddition (Scheme 3, $R = SC_6H_5$, $R_1 = CN$).

In contrast, the introduction of electron-withdrawing groups in position 4 of the heterocyclic system (*e.g.*, alkyl- and arylsulfonyl) afforded the corresponding cycloadducts. Sulfonyl compounds **6** (Table 2) were synthesized starting from 4,6-dinitrobenzoannelated heterocycles via selective substitution of 4-NO_2 with thiols and further oxidation according to the procedures described before (Scheme 4) [8].

Reactions of sulfones **6a–h** with *N*-methyl azomethine ylide **1** generated *in situ* afforded isoindolines **8a–h** fused with corresponding azoles in moderate yields (Scheme 5). In contrast to 4,6-dinitroindazole **2a** that formed bis-adducts (Scheme 1), in case of sulfonyl compounds **6**, the cycloaddition takes place exclusively at C=C—NO_2 fragment. Besides, the intermediate cycloadducts **7a–h** could not be isolated due to the rapid rearomatization with elimination of HNO_2 (Scheme 5, Table 2).

Such a behavior of compounds **7a–h** differs from all other cases of cycloaddition we studied (Schemes 1 and 2). However, a number of examples of base-catalyzed rearomatization of the carbocyclic rings with loss of HNO_2 was described (ref. 9 and references therein). We suppose that cycloadduct **7** itself could play the role of a base in rearomatization process.

Unexpected result was obtained on interaction of *peri*-annelated tricyclic compound **9** [10] with *N*-methyl azomethine ylide in standard conditions—the cycloaddition takes place even without other electron-withdrawing substituents in benzene ring apart from the nitro group (Scheme 6). In this case, the aromatization was not observed.

Oxidation of isoindolines **8** was supposed to be a route to isoindole derivatives fused with azoles. Indeed, compound **8f** was oxidized with excess of activated MnO_2 in refluxing THF to give isoindole **11**. However, oxidation of **8a** in the same conditions gave dioxo compound **12** (Scheme 7). Thus, the direction of the oxidation seems to be dependent on the nature of azole annelated to the isoindoline moiety.

On interaction of compound **8a** with excess of CH_3I in chloroform at room temperature, the quaternary ammonium salt **13** was obtained in good yield (Scheme 8):

In summary, a general method for the synthesis of 2,3,3a,7a-tetrahydro-1*H*-isoindoles and isoindolines fused with azoles was developed on the basis of 1,3-dipolar cycloaddition reactions of nitro benzoazoles with unstabilized *N*-methyl azomethine ylide. It was found

Scheme 2

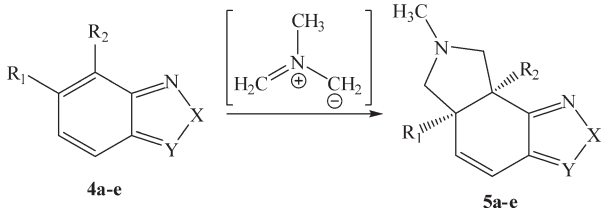


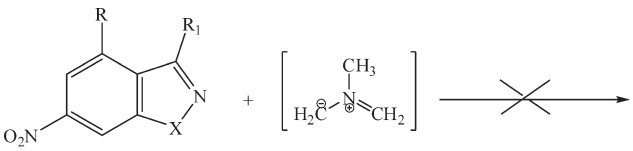
Table 1

1,3-Dipolar cycloaddition of *N*-methyl azomethine ylide to mono nitro benzoannaleted heterocycles.[a]

Entry	Nitro compound	X	Y	R_1	R_2	Product	Reaction time (h)	% Isolated yield
1	**4a**	O	N	H	NO_2	**5a**	0.2	75
2	**4b**	S	N	H	NO_2	**5b**	12	42
3	**4c**	O	CH	NO_2	H	**5c**	2	40
4	**4d**	O	N	NO_2	H	**5d**	0.2	98
5	**4e**	S	N	NO_2	H	**5e**	1	64

[a] Reaction conditions: Compound **4** (1.0 mmol), *N*-Methyl glycine (4.5 mmol), paraformaldehyde (6.0 mmol), and toluene (15 mL), reflux.

Scheme 3



R = H, OCH_3, OC_6H_5, SC_6H_5
R_1 = H, CN X = NC_6H_5, O

that electron withdrawing groups in the benzene ring of benzoazoles facilitate the cycloaddition.

EXPERIMENTAL

Melting points were measured on a Boetius apparatus and are uncorrected. NMR spectra were recorded on a Bruker DRX-500 spectrometer in $CDCl_3$ as a solvent. Chemical shifts are reported in ppm downfield from TMS using the δ-scale. All reactions were monitored by TLC using Silufol UV-254 plates which were visualized with UV light. For all new compounds, satisfactory microanalyses were obtained. Compounds **4a–e** were prepared according to the procedures described in ref. 6. Commercially available (Aldrich) activated MnO_2 (~85%, <5 μm) was used for the oxidations.

Compounds 5a–e, 8a–h, and 10; general procedure. A mixture of compound **4, 6**, or **9** (1 mmol), *N*-methylglycine (5 mmol), paraformaldehyde (0.18 g, 6 mmol), and toluene (15 mL) was heated under reflux for the time indicated in Tables 1 and 2. After the starting material disappeared (TLC), the mixture was cooled to r.t. and filtered. The solvent was evaporated under reduced pressure, and the residue was dissolved in THF (5 mL). On pouring in hexane (50 mL), the precipitate formed was filtered off and dried in air to give pure (NMR) product. In case of liquid products (**5a,d,e**), the residue was purified by column chromatography (Silica gel/$CHCl_3$).

7-Methyl-8a-nitro-6,7,8,8a-tetrahydro-5a*H*-[1,2,5]oxadiazolo[3,4-*e*]isoindole (5a). Light yellow oil; ^{1}H NMR: δ 2.27 (t, 1 H, J = 9.3 Hz), 2.39 (s, 3 H), 2.93 (d, 1 H, J = 11.1 Hz), 3.42 (t, 1 H, J = 8.6 Hz), 4.04 (m, 1 H), 4.25 (d, 1 H, J = 11.5 Hz), 6.43 (dd, 1 H, J = 10.2, 4.6 Hz), 6.89 (dd, 1 H, J = 10.2, 1.8 Hz); ^{13}C nmr: δ 40.88, 47.79, 61.90, 66.04, 87.92, 112.90, 136.37, 147.88, 148.43; Anal. Calcd. for $C_9H_{10}N_4O_3$: C, 48.65; H, 4.54; N, 25.21 Found: C, 48.36; H, 4.78; N, 25.51.

7-Methyl-8a-nitro-6,7,8,8a-tetrahydro-5a*H*-[1,2,5]thiadiazolo[3,4-*e*]isoindole (5b). Pale yellow crystals; mp 61–62°C; ^{1}H NMR: δ 2.19 (t, 1 H, J = 9.2 Hz), 2.38 (s, 3 H), 2.83 (d, 1 H, J = 11.6 Hz), 3.43 (t, 1 H, J = 8.5 Hz), 4.0 (m, 1 H), 4.33 (d, 1 H, J = 11.6 Hz), 6.38 (dd, 1 H, J = 10.2, 4.6 Hz), 6.89 (dd, 1 H, J = 11.0, 1.7 Hz); Anal. Calcd. for $C_9H_{10}N_4O_2S$: C, 45.37; H, 4.23; N, 23.51. Found: C, 45.58; H, 4.18; N, 23.17.

7-Methyl-5a-nitro-6,7,8,8a-tetrahydro-5a*H*-isoxazolo[3,4-*e*]isoindole (5c). White solid; mp 83–85°C; ^{1}H NMR: δ 2.34 (s, 3 H), 2.48 (t, 1 H, J = 8.7 Hz), 2.64 (t, 1 H, J = 12.5 Hz), 3.58 (t, 1 H, J = 8.8 Hz), 3.87 (d, 1 H, J = 11.1 Hz), 4.68 (t, 1 H, J = 8.2 Hz), 6.04 (d, 1 H, J = 9.9 Hz), 6.69 (d, 1 H, J = 10.1 Hz), 8.34 (s, 1 H); Anal. Calcd. for $C_{10}H_{11}N_3O_3$: C, 54.29; H, 5.01; N, 19.00. Found: C, 54.41; H, 5.08; N, 18.71.

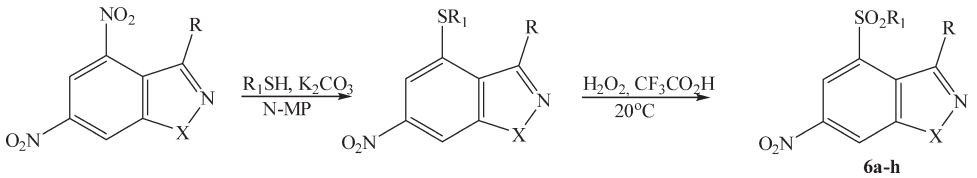
7-Methyl-5a-nitro-6,7,8,8a-tetrahydro-5a*H*-[1,2,5]oxadiazolo[3,4-*e*]isoindole (5d). Yellow oil; ^{1}H NMR: δ 2.36 (s, 3 H), 2.54 (t, 1 H, J = 8.9 Hz), 2.71 (d, 1 H, J = 11.4 Hz), 3.61 (t, 1 H, J = 8.9 Hz), 3.84 (d, 1 H, J = 11.1 Hz), 4.81 (t, 1 H, J = 7.9 Hz), 6.56 (d, 1 H, J = 10.1 Hz), 7.05 (d, 1 H, J = 10.1 Hz); ^{13}C NMR: δ 37.94, 40.57, 61.93, 67.62, 95.32, 117.47, 132.53, 143.46, 150.43; Anal. Calcd. for $C_9H_{10}N_4O_3$:

Table 2

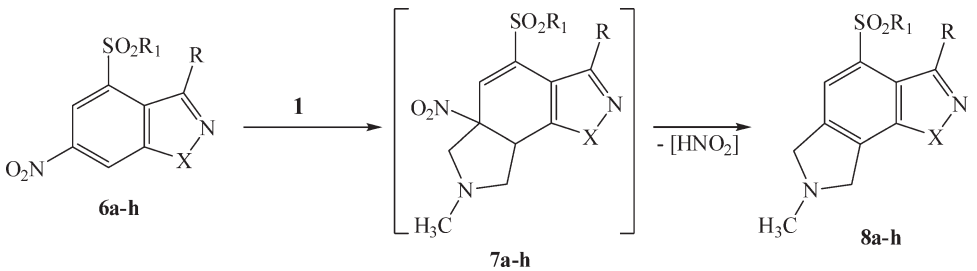
1,3-Dipolar cycloaddition of *N*-methyl azomethine ylide to nitro sulfones **6a–h**.

Entry	Sulfone	X	R	R_1	Reaction time (h)	% Isolated yield of **8**
1	**6a**	NC_6H_5	H	C_6H_5	6	30
2	**6b**	NC_6H_5	H	$CH_2C_6H_5$	11	32
3	**6c**	NC_6H_5	$CO_2C_2H_5$	$CH_2C_6H_5$	16	54
4	**6d**	NC_6H_5	$CONHC_6H_4OCH_3$-4	$CH_2C_6H_5$	12	61
5	**6e**	O	1,3-dioxolan-2-yl	$CH_2C_6H_5$	24	30
6	**6f**	O	1,3-dioxolan-2-yl	C_6H_5	4	39
7	**6g**	O	1,3-dioxolan-2-yl	c-C_6H_{11}	16	64
8	**6h**	O	1,3-dioxolan-2-yl	$(CH_2)_2CO_2CH_3$	24	40

Scheme 4



Scheme 5



C, 48.65; H, 4.54; N, 25.21 Found: C, 48.82; H, 4.43; N, 25.39.

7-Methyl-5a-nitro-6,7,8,8a-tetrahydro-5a*H*-[1,2,5]thiadiazolo[3,4-*e*]isoindole (5e). Yellow oil; ^{1}H NMR: δ 2.27 (s, 3 H), 2.43 (t, 1 H, J = 9.0 Hz), 2.65 (d, 1 H, J = 11.2 Hz), 3.55 (t, 1 H, J = 8.9 Hz), 3.79 (d, 1 H, J = 11.2 Hz), 4.74 (t, 1 H, J = 8.0 Hz), 6.41 (d, 1 H, J = 10.1 Hz), 6.95 (d, 1 H, J = 10.0 Hz); ^{13}C NMR: δ 40.58, 44.34, 62.29, 68.14, 96.11, 124.15, 129.76, 152.05, 157.74; Anal. Calcd. for $C_9H_{10}N_4O_2S$: C, 45.37; H, 4.23; N, 23.51. Found: C, 45.60; H, 4.33; N, 23.18.

7-Methyl-1-phenyl-4-(phenylsulfonyl)-1,6,7,8-tetrahydropyrrolo[3,4-*g*]indazole (8a). Melting point 166–168°C; ^{1}H NMR: δ 2.54(s, 3H, CH_3), 3.75 (s, 2H), 4.06 (s, 2H), 7.40–7.63 (m, 8H, Ph), 7.83 (s, 1H), 8.05 (d, 2H, J = 7.0 Hz), 8.65 (s, 1H); Anal. Calcd. for $C_{22}H_{19}N_3O_2S$: C, 67.84; H, 4.92; N, 10.79. Found: C, 67.59; H, 5.28; N, 10.61.

4-(Benzylsulfonyl)-7-methyl-1-phenyl-1,6,7,8-tetrahydropyrrolo[3,4-*g*]indazole(8b). Melting point 192–195°C; ^{1}H NMR: δ 2.55 (s, 3H, CH_3), 3.76 (s, 2H), 3.99 (s, 2H), 4.44 (s, 2H), 7.07(d, 2H J = 7.2 Hz), 7.21–7.33 (m, 3H), 7.44–7.59 (m, 6H), 8.26 (s, 1H). Anal. Calcd. for $C_{23}H_{21}N_3O_2S$ C, 67.50; H, 5.41; N, 10.73. Found C, 67.46; H, 5.38; N, 10.57.

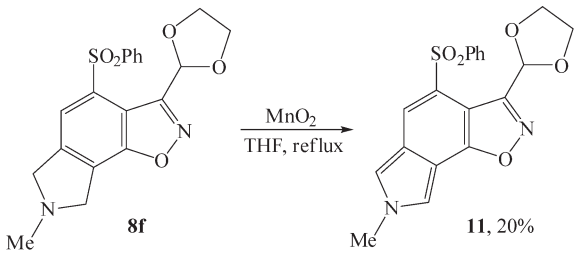
Ethyl 4-(benzylsulfonyl)-7-methyl-1-phenyl-1,6,7,8-tetrahydropyrrolo[3,4-*g*]indazole-3-carboxylate (8c). Melting point 185–187°C; ^{1}H NMR: δ 1.51 (t, 3H, J = 7.1 Hz) 2.51 (s, 3H, CH_3), 3.71 (s, 2H), 3.96 (s, 2H), 4.61 (dd, 2H, J = 14.8, 7.1 Hz), 4.91 (s, 2H), 7.32–7.38 (m, 5H), 7.49–7.58 (m, 6H); IR (potassium bromide): 700, 1100, 1132, 1224, 1316, 1456, 1504, 1720 (CO) cm^{-1}; ms: m/z 472 (M^+); Anal. Calcd. for $C_{26}H_{25}N_3O_4S$ C, 65.67; H, 5.30; N, 8.84. Found C, 65.81; H, 5.30; N, 9.24.

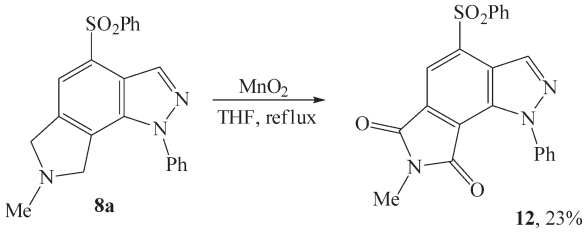
4-(Benzylsulfonyl)-*N*-(4-methoxyphenyl)-7-methyl-1-phenyl-1,6,7,8-tetrahydropyrrolo[3,4-*g*]indazole-3-carboxamide (8d). Melting point 218–221°C; ^{1}H NMR: δ 2.50 (s, 3H), 3.70 (s, 2H), 3.64 (s, 3H), 3.94 (s, 2H), 5.09 (s, 2H), 6.92 (d, 2H, J = 8.2 Hz), 7.27–7.41 (m, 6H), 7.51–7.62 (m, 7H), 8.69 (s, 1H); Anal. Calcd. for $C_{31}H_{28}N_4O_4S$: C, 67.37; H, 5.11; N, 10.14. Found: C, 67.53; H, 5.24; N, 9.96.

4-(Benzylsulfonyl)-3-(1,3-dioxolan-2-yl)-7-methyl-7,8-dihydro-6*H*-isoxazolo[5,4-*e*]isoindole (8e). Melting point 181–184°C; ^{1}H NMR: δ 2.65 (s, 3H), 4.00 (s, 2H), 4.26–4.29 (m, 6H), 4.78 (s, 2H), 7.19–7.35 (m, 6H), 7.54 (s, 1H); Anal. Calcd. for $C_{20}H_{20}N_2O_5S$: C, 59.99; H, 5.03; N, 7.00. Found: C, 60.18; H, 4.88; N, 6.86.

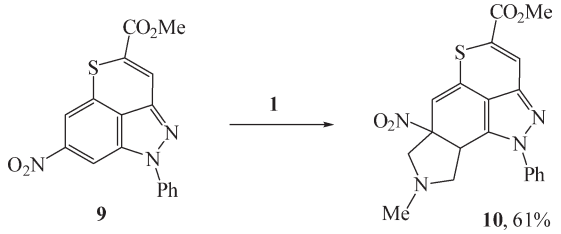
3-(1,3-Dioxolan-2-yl)-7-methyl-4-(phenylsulfonyl)-7,8-dihydro-6*H*-isoxazolo[5,4-*e*]isoindole (8f). Melting point 175–177°C; ^{1}H NMR: δ 2.66 (s, 3H), 4.04–4.12 (m, 6H), 4.27 (s, 2H), 7.47–7.58 (m, 3H), 7.94–7.99 (m, 3H); ms: m/z 386

Scheme 7

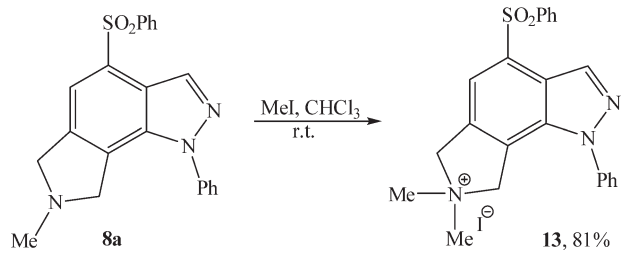




Scheme 6



Scheme 8



(M^+). Anal. Calcd. for $C_{19}H_{18}N_2O_5S$ C, 58.75; H, 5.00; N, 8.25. Found C, 58.75; H, 4.75; N, 8.19.

4-(Cyclohexylsulfonyl)-3-(1,3-dioxolan-2-yl)-7-methyl-7,8-dihydro-6*H*-isoxazolo[5,4-*e*]isoindole (8g). Melting point 220–222°C; ^{1}H NMR: δ 1.19–1.23 (m, 3H), 1.57–1.67 (m, 3H), 1.85–1.99 (m, 4H), 2.67 (s, 3H), 3.61–3.74 (m, 1H), 4.12–4.23 (m, 6H), 4.29 (s, 2H), 7.07 (s, 1H), 7.85 (s, 1H); Anal. Calcd. for $C_{19}H_{24}N_2O_5S$: C, 58.15; H, 6.16; N, 7.14. Found: C, 58.41; H, 6.02; N, 7.01.

Methyl 3-{[3-(1,3-dioxolan-2-yl)-7-methyl-7,8-dihydro-6*H*-isoxazolo[5,4-*e*]isoindol-4-yl]sulfonyl}propanoate (8h). Melting point 192–194°C; ^{1}H NMR: δ 2.68 (s, 3H), 2.82 (t, 2H, J = 7.7 Hz), 3.66 (s, 3H), 3.85 (t, 2H, J = 7.7 Hz), 4.17 (m, 6H), 4.27 (s, 2H), 7.04 (s, 1H), 7.92 (s, 1H); Anal. Calcd. for $C_{17}H_{20}N_2O_7S$: C, 51.51; H, 5.09; N, 7.07. Found: C, 51.73; H, 4.93; N, 7.32.

Methyl 8-methyl-6a-nitro-1-phenyl-1,6a,7,8,9,9a-hexahydropyrrolo[3,4-*g*]thiopyrano[4,3,2-*cd*]indazole-4-carboxylate (10). Melting point 110–113°C; ^{1}H NMR: δ 2.53 (s, 3H, NCH_3), 3.08–3.14 (m, 2H), 3.47 (t, 1H, J = 8.9 Hz), 3.69 (s, 3H, OCH_3), 3.72 (d, 1H, J = 11.8 Hz), 4.36 (t, 1H, J = 8.6 Hz), 7.45 (t, 1H, J = 7.5 Hz), 7.60 (t, 2H, J = 7.5 Hz), 7.75 (d, 2H, J = 7.8 Hz), 7.87 (s, 1H), 8.39 (s, 1H); ms: m/z 410 (M^+); Anal. Calcd. for $C_{20}H_{18}N_4O_4S$: C, 58.53; H, 4.42; N, 13.65. Found: C, 58.37; H, 4.84; N, 13.80.

Oxidation of compounds 8a and 8f (general procedure). A mixture of compound **8a** or **8f** (0.5 mmol), MnO_2 (435 mg, 5 mmol), and THF (10 mL) was heated under reflux for 6 h. The mixture was cooled to r.t. and filtered. The solvent was evaporated under reduced pressure, and the residue was recrystallized from EtOH to give pure (NMR) compounds **11** or **12**.

3-(1,3-Dioxolan-2-yl)-7-methyl-4-(phenylsulfonyl)-7*H*-isoxazolo[5,4-*e*]isoindole (11). Melting point 214–216°C; ^{1}H NMR: δ 3.98–4.16 (m, 7H, N-CH_3, $2CH_2$), 7.00 (s, 1H), 7.43–7.61 (m, 5H), 7.91 (d, 2H, J = 7.7), 8.35 (s, 1H); ms: m/z 384 (M^+); Anal. Calcd. for $C_{19}H_{16}N_2O_5S$: C, 59.37; H, 4.20; N, 7.29. Found: C, 59.58; H, 4.08; N, 7.44.

7-Methyl-1-phenyl-4-(phenylsulfonyl)pyrrolo[3,4-*g*]indazole-6,8(1*H*,7*H*)-dione (12). Yellow solid, mp 294–296°C; ^{1}H NMR: δ 2.95 (s, 3H, CH_3), 7.54–7.74 (m, 8H), 8.19–8.26 (m, 3H), 8.96 (s, 1H); ms: m/z 417 (M^+); IR (potassium bromide): 623, 668, 704, 720, 736, 760, 928, 996, 1156, 1324, 1376, 1436, 1504, 1716 (CO), 1772 cm^{-1}; Anal. Calcd. for $C_{22}H_{15}N_3O_4S$ C, 63.30; H, 3.62; N, 10.07. Found C, 63.25; H, 3.78; N, 10.03.

7,7-Dimethyl-1-phenyl-4-(phenylsulfonyl)-1,6,7,8-tetrahydropyrrolo[3,4-*g*]indazol-7-ium iodide (13). To a solution of compound **8a** (100 mg, 0.26 mmol) in $CHCl_3$ (5 mL), CH_3I (0.4 mL) was added. The mixture was stirred for 12 h at r.t. and then poured in 30 mL of hexane. The precipitate formed was filtered off and dried in air to give 110 mg (81%) of compound **13**. mp 166–168°C; ^{1}H NMR: δ 3.28 (s, 6H, $2CH_3$), 4.75 (s, 2H, CH_2), 5.04 (s, 2H, CH_2), 7.60–7.72 (m, 8H), 8.15–8.18 (m, 3H), 8.80 (s, 1H); Anal. Calcd. for $C_{23}H_{20}IN_3O_2S$: C, 52.18; H, 3.81; N, 7.94. Found: C, 52.47; H, 3.58; N, 7.72.

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