Chemistry of Heterocyclic Compounds, Vol. 39, No. 8, 2003

$S_{RN}1$ REACTIONS IN THE NITRO-BENZO[1,3]DIOXOLE SERIES

J. Meuche-Albeny, P. Rathelot, M. P. Crozet, and P. Vanelle

5-Chloromethyl-6-nitrobenzo[1,3]dioxole has been shown to react with 2-nitropropane anion to give C-alkylation by an $S_{RN}1$ mechanism. The reaction was extended to various aliphatic, cyclic, and heterocyclic nitronate anions, leading to a new series of nitrobenzo[1,3]dioxole derivatives.

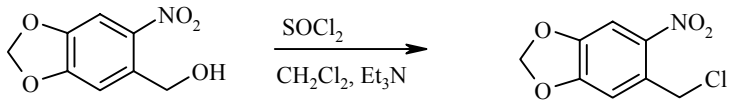
Keywords: nitrobenzo[1,3]dioxole, nitronate anion, C-alkylation, $S_{RN}1$ reaction.

$S_{RN}1$ reactions have been studied extensively on aza- and thiaheterocycles [1-7]. Works relating the reactivity with such a mechanism on O-heterocycles are rarer. In the nitrofuran series, while the C-alkylation of 2-chloromethyl-5-nitrofuran has been well known since 1951 [8], it was only proved to succeed *via* an $S_{RN}1$ mechanism in 1980 [9]. Then, Beadle and Bowman published a complete study on the reactivity of the 2-nitropropane anion with various 2-substituted 5-nitrofuran derivatives [10].

This work presents the reactivity of 5-chloromethyl-6-nitrobenzo[1,3]dioxole (**1**) with various nitronate anions.

The target compound **1** was easily prepared in one step from the 6-nitropiperonyl alcohol.

Scheme 1



1 96%

In order to study the reactivity of **1** with 2-nitropropane anion (**2a**), various operating conditions were used as shown in Table 1. The reaction led to several compounds in yields which depended on experimental conditions.

The C-alkylation of **1** was sensitive to the solvent, and the yields of C-alkylated products **3a** and **4a** were higher when an aprotic solvent was used (DMF, DMSO). These results were in complete agreement with the works of Bowman [11] and Russell [12]. The best yields were observed with DMSO as solvent (entries 6-11) in Kornblum conditions [13]. Most of the published works have reported that an anion excess led to higher yields in C-alkylated compounds [5, 14]. In this series, an anion excess enhanced yields of **3a** + **4a** either in DMF (entry 2 versus entry 1) or DMSO (entry 7 versus entry 6) up to more than 90% excess for 3 equivalents of anion **2a** (entries 7 and 8). Above such an excess, the yields decreased (entries 9-11). The ethylenic compound **4a** was formed *via* the C-alkylated product **3a** by base-promoted nitrous acid elimination. Even if such an elimination reaction can occur spontaneously in the reaction mixture, in the benzo[1,3]dioxole series it only occurred after a 120 h reaction time (entry 8).

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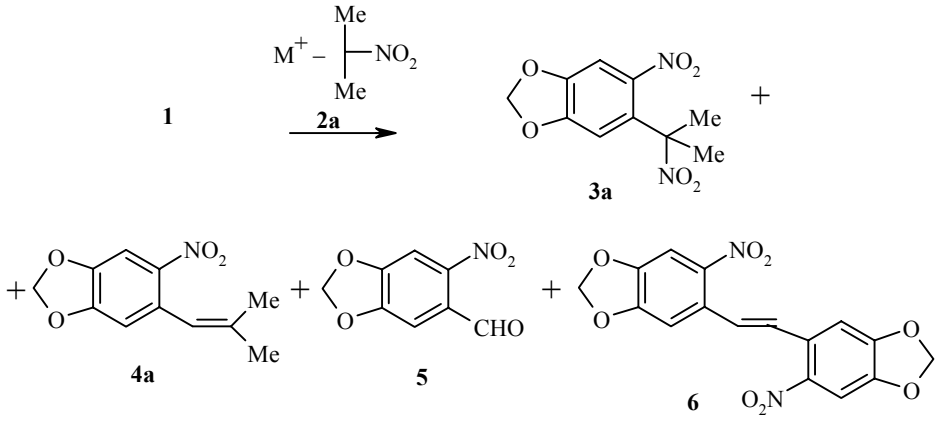
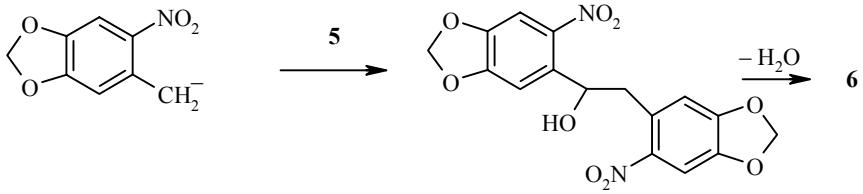
0009-3122/03/3908-0989$25.00

Scheme 2



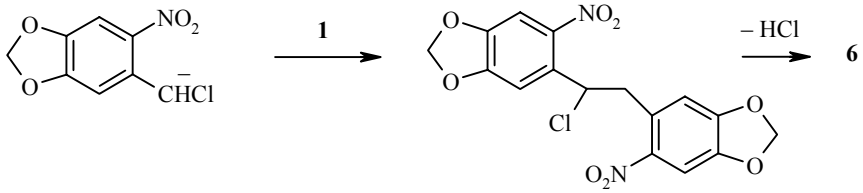
Investigation of the mechanism of the reaction requires the use of classical inhibitors [15]. The best operating conditions (entry 7) were used to perform the inhibition experiments (entries 12-20). The results reported in Table 1 show that the C-alkylation rate strongly decreased while the formation of 6-nitropiperonal **5**, the product of the competitive O-alkylation reaction due to the ambident character of **2a**, was increased. The formation of a side product, the 1,2-bis[(6-nitrobenzo[1,3]dioxol-5-yl)ethylene] (**6**), was observed (entries 16 and 17). A similar compound was observed in nitrothiophene [16] and in the nitrothiazole [17] series. Two possible mechanisms were suggested to explain the formation of **6**. In the first one, the carbanion obtained by reduction of the intermediate radical could react with the 6-nitropiperonal **5**; the resulting alcohol may be dehydrated into the alkene **6**.

Scheme 3



In the second one, the carbanion resulting from attack of the anion **2a** (as a base) on the chloride **1** could react with **1** leading to **6** after dehydrohalogenation of the intermediate condensation product.

Scheme 4



Thus, using the same operating conditions except to replace **2a** by a stronger base, we obtained **6** in 60% yield and 6-nitropiperonylalcohol (**7**) simultaneously.

TABLE 1. Influence of Experimental Conditions in the Reaction of Compound **1** with **2a***

Entry	**2a**, mol. eq.	Solvent	Scavenger, mol. eq.	Yields, %				
				1	C-alkylation		**5**	**6**
					3a	**4a**		
1	2	DMF	—	22	30	—	—	—
2	3	DMF	—	—	54	—	—	—
3	3	CH_3OH	—	—	42	—	12	—
4	3	CH_2Cl_2/H_2O	—	—	Traces	—	—	—
5	3	$C_6H_5CH_3/H_2O$	—	—	Traces	—	—	—
6	2	DMSO	—	—	80	—	—	—
7	3	DMSO	—	—	88	4	5	—
8*[2]	3	DMSO	—	—	63	29	5	—
9	4	DMSO	—	—	82	—	—	—
10	5	DMSO	—	—	80	—	—	—
11	6	DMSO	—	—	73	—	—	—
12	3	DMSO	Dark	—	45	—	11	—
13	3	DMSO	O_2 bubbling	—	45	—	52	—
14	3	DMSO	O_2 bubbling + Dark	—	21	—	52	—
15	3	DMSO	$CuCl_2$ (0.1 eq.)	—	45	—	17	—
16	3	DMSO	$CuCl_2$ (1 eq.)	3	25	—	45	10
17	3	DMSO	*p*-DNB (0.1 eq.)	5	36	—	29	5
18	3	DMSO	*p*-DNB (1 eq.)	15	10	—	45	—
19	3	DMSO	TEMPO (0.1 eq.)	14	20	—	45	—
20	3	DMSO	TEMPO (1 eq.)	5	5	—	53	—

* All the reactions were performed under nitrogen and irradiation with two 60-W fluorescent tungsten lamps for 24 h.
*[2] The reaction was performed for 120 h.

TABLE 2. C-Alkylated Compounds Synthesized *via* the $S_{RN}1$ Reaction of **1** with **2b-g***

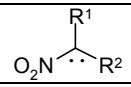
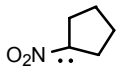
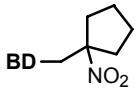
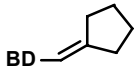
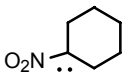
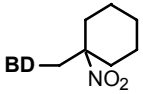
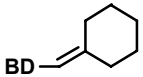
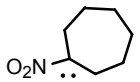
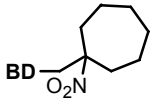
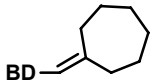
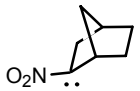
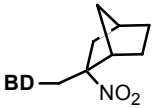
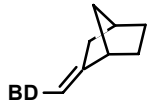
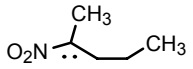
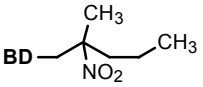
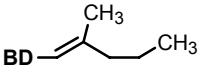
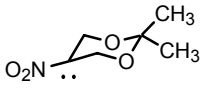
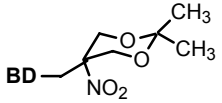
Anion		Reaction time, h	Compound	Formula*[2]	Yield, %	*E*/*Z* ratio
1	2	3	4	5	6	7
2b		24	**3b**		62	—
			4b		19	—
2c		60	**3c**		48	—
			4c		20	—

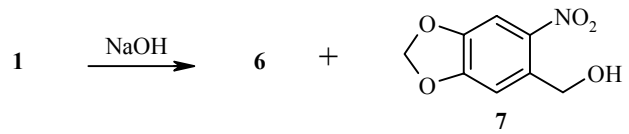
TABLE 2 (continued)

1	2	3	4	5	6	7
2d		48	**3d**		40	—
			4d		14	—
2e		48	**3e**		16	—
			4e		42	90/10
2f		24	**3f**		59	—
			4f		13	70/30
2g		48	**3g**		69	—

* All the reactions were performed under nitrogen and irradiation with two 60-W fluorescent tungsten lamps for 24 h, using 3 eq of anion.

*[2] BD for nitrobenzo[1,3]dioxole.

Scheme 5



Such a result was consistent with the second hypothesis for the formation of compound **6**.

The results of the inhibition experiments reported in Table 1 were in complete agreement with an $S_{RN}1$ mechanism [18] for the C-alkylation of **1**.

Electron-transfer reactions might provide a versatile access to new benzo[1,3]dioxole derivatives. Therefore, we have synthesized various nitronate anions obtained from commercially available nitroalkanes or from oxidation of the corresponding amines with *m*-chloroperoxybenzoic acid [19]. As observed for the reaction of **1** with **2a**, the reactions led to a mixture of C-alkylated product and its ethylenic derivative. When the latter was unsymmetrical, the *E*-isomer was the main product (Table 2).

Thus, in this series, the $S_{RN}1$ mechanism appears to be a convenient pathway for the formation of a C–C bond under mild operating conditions.

EXPERIMENTAL

Melting points were determined on a Büchi B-540 apparatus and are uncorrected. ^{1}H NMR spectra were determined on a Bruker ARX 200 spectrometer. The ^{1}H chemical shifts were reported as ppm downfield from Me_4Si. Column chromatography was performed using silica gel 60 (Merck, particle size 0.063-0.200 mm, 70-230 mesh ASTM) as adsorbent. Microanalyses for C, H, N were performed by the Microanalytical Section of St-Jerome Faculty, Aix-Marseille III University, France.

5-Chloromethyl-6-nitrobenzo[1,3]dioxole (**1**). Triethylamine (0.61 g) was added to a solution of 6-nitropiperonyl alcohol (0.99 g, 5 mmol) in dichloromethane (40 ml). After cooling at 0°C, cool anhydrous thionyl chloride (0.44 ml, 6 mmol) was added dropwise. The reaction mixture was stirred for 1 h at 0°C and 2 h at room temperature. Then it was poured over crushed ice and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The crude oil was purified by chromatography on a silica gel column, eluting with dichloromethane, to give **1** in 96% yield (1.03 g). Yellow solid; mp 76°C (ethanol–chloroform, 1:1) (78-80°C [20]). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 4.90 (2H, s, CH_2Cl); 6.10 (2H, s, $H_{(2)}$); 7.05 (1H, s, $H_{(4)}$); 7.56 (1H, s, $H_{(7)}$). Found, %: C 44.30; H 2.70; N 6.43. $C_8H_6ClNO_4$. Calculated, %: C 44.57; H 2.81; N 6.50.

2-Nitropropane Lithium Salt (2a) was prepared from 2-nitropropane as previously described [21].

General Procedure for $S_{RN}1$ Reactions

A. Kornblum Conditions. Chloride **1** (200 mg, 0.92 mmol) was added to a solution of **2a** (1.8 or 2.7 mmol) in 30 ml of dry DMF (entries 1-2, Table 1) or to a solution of **2a** (1.8 to 5.4 mmol) in 30 ml of dry DMSO (entries 6-11, Table 1) under nitrogen and anhydrous conditions. The reaction mixture was then irradiated with two 60-W fluorescent lamps. After stirring at room temperature for 24 h (except for entry 8: 120 h) under nitrogen, it was poured into water and extracted with toluene (3 × 50 ml) and ether (1 × 50 ml). The organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. Purification by chromatography on a silica gel column, eluting with dichloromethane, gave 5-(2-methyl-2-nitropropyl)-6-nitrobenzo[1,3]dioxole (**3a**) and 5-(2-methylpropenyl)-6-nitrobenzo[1,3]dioxole (**4a**) in various yields depending on reaction time and anion excess (see Table 1).

5-(2-Methyl-2-nitropropyl)-6-nitrobenzo[1,3]dioxole (3a). Yellow solid; mp 105°C (ethanol–water, 1:1). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.61 (6H, s, $2CH_3$); 3.75 (2H, s, CH_2); 6.18 (2H, s, $H_{(2)}$); 6.55 (1H, s, $H_{(4)}$); 7.49 (1H, s, $H_{(7)}$). Found, %: C 49.77; H 4.54; N 10.39. $C_{11}H_{12}N_2O_6$. Calculated, %: C 49.66; H 4.51; N 10.44.

5-(2-Methylpropenyl)-6-nitrobenzo[1,3]dioxole (4a). Yellow solid; mp 73°C (ethanol–water, 1:1). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.72 (3H, s, CH_3); 1.95 (3H, s, CH_3); 6.14 (2H, s, $H_{(2)}$); 6.49 (1H, s, ethylenic H); 6.72 (1H, s, $H_{(4)}$); 7.56 (1H, s, $H_{(7)}$). Found, %: C 59.70; H 4.88; N 6.30. $C_{11}H_{11}NO_4$. Calculated, %: C 59.73; H 5.01; N 6.33.

B. **Norris Conditions**. Under nitrogen atmosphere, a solution of 2-nitropropane (245 mg, 2.76 mmol) in 40% tetrabutylammonium hydroxide in water (1.8 ml, 2.76 mmol) was stirred at room temperature for 1 h. Then a solution of **1** (200 mg, 0.92 mmol) in 30 ml of dichloromethane (entry 4) or toluene (entry 5) was added. The mixture was stirred for 24 h at room temperature under nitrogen and irradiated with two 60-W fluorescent lamps. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 30 ml). The combined organic layers were evaporated under reduced pressure. The crude residue was dissolved in 40 ml of benzene, washed with water, dried over anhydrous $MgSO_4$, and evaporated. The NMR data of the crude residue showed only trace amounts of **3a**.

C. **Experiment Performed in Methanol**. Entry 3 was performed in the Kornblum operating conditions but using methanol as solvent and gave **3a** and **5** in 42 and 12% yields, respectively.

6-Nitropiperonal (5): mp 93°C (Acros Organics mp 93-94°C).

D. **Inhibition Experiments (Entries 12-20).** These experiments were performed with the operating conditions of entry 7 and carried out in the dark, bubbling dioxygen in the reaction mixture, or adding the required amount of cupric chloride, *p*-dinitrobenzene (*p*-DNB), or 2,2,6,6-tetramethyl-1-piperidinyl oxyl (TEMPO). Yields of **3a**, **4a** and **5** are reported in Table 1.

Using 1 eq. of $CuCl_2$ (entry 16) or 0.1 eq. of *p*-DNB (entry 17), a side product, 1,2-bis[(6-nitrobenzo[1,3]dioxol-5-yl)-ethylene] (**6**), was isolated in 10 and 5% yields, respectively. Yellow solid; mp 81°C (ethanol). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 4.48 (2H, s, CH=CH); 6.19 (4H, s, $2H_{(2)}$); 7.16 (2H, s, $2H_{(4)}$); 7.72 (2H, s, $2H_{(7)}$). Found, %: C 53.79; H 2.67; N 7.77. $C_{16}H_{10}N_2O_8$. Calculated, %: C 53.64; H 2.81; N 7.82.

Preparation of the Nitroalkanes and Their Lithium Salts. The nitrolkanes were commercially available or prepared from the secondary amines by oxidation with *m*-chloroperoxybenzoic acid [19, 22] in refluxed 1,2-dichloroethane for 3 h (**2b-f**). 2,2-Dimethyl-5-nitro-1,3-dioxane (**2g**) was obtained as previously described [23].

A lithium methoxide solution was prepared by careful addition of lithium (175 mg, 0.025 at. g) to methanol (15 ml). After the solution had become clear, the nitroalkane (25 mmol) was added. The solution was stirred at room temperature for 2 h and concentrated under vacuum. When the solution became viscous, about 300 ml of ether was added to cause precipitation. The lithium salt was filtered off, washed with ether, and kept under oil-pump vacuum for 24 h.

***S_{RN}*1 Reactions with Various Lithium Salts.** All the reactions were performed with the Kornblum conditions of entry 7, using (200 mg, 0.92 mmol) of the chloride **1** and 3 eq. of the lithium salt **2b-g**. The crude residues were treated like those of entry 7 to give the required compounds. The silica gel column was eluted by chloroform for the reactions performed with anions **2c-e**,**g** and was eluted by chloroform–cyclohexane, 3:2, for the anions **2b** and **2f**.

5-Nitro-6-(1-nitrocyclopentylmethyl)benzo[1,3]dioxole (3b). Yellow solid, yield 62%; mp 84°C (*i*-PrOH). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.60-1.70 (4H, m, $2CH_2$); 1.71-1.79 (4H, m, $2CH_2$); 3.69 (2H, s, allylic CH_2); 6.01 (2H, s, $H_{(2)}$); 6.45 (1H, s, $H_{(4)}$); 7.36 (1H, s, $H_{(7)}$). Found, %: C 53.06; H 4.72; N 9.43. $C_{13}H_{14}N_2O_6$. Calculated, %: C 53.06; H 4.80; N 9.52.

5-Cyclopentylidenemethyl-6-nitrobenzo[1,3]dioxole (4b). Oil, yield 19%. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.70-1.73 (4H, m, $2CH_2$); 2.26 (2H, t, *J* = 5.3, allylic CH_2); 2.41 (2H, t, *J* = 5.3, allylic CH_2); 6.01 (2H, s, $H_{(2)}$); 6.54 (1H, s, ethylenic H); 6.77 (1H, s, $H_{(4)}$); 7.39 (1H, s, $H_{(7)}$). Found, %: C 62.95; H 5.36; N 5.64. $C_{13}H_{13}NO_4$. Calculated, %: C 63.15; H 5.30; N 5.67.

5-Nitro-6-(1-nitrocyclohexylmethyl)benzo[1,3]dioxole (3c). Yellow solid, yield 48%; mp 105°C (ethanol). ^{1}H NMR ($CDCl_3$),δ, ppm (*J*, Hz): 1.12-1.22 (2H, m, CH_2); 1.41-1.53 (6H, m, $3CH_2$); 2.30-2.37 (2H, m, CH_2); 3.48 (2H, s, allylic CH_2); 6.01 (2H, s, $H_{(2)}$); 6.36 (1H, s, $H_{(4)}$); 7.35 (1H, s, $H_{(7)}$). Found, %: C 54.50; H 5.21; N 9.05. $C_{14}H_{16}N_2O_6$. Calculated, %: C 54.54; H 5.23; N 9.09.

5-Cyclohexylidenemethyl-6-nitrobenzo[1,3]dioxole (4c). Oil, yield 20%. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.40-1.59 (6H, m, $3CH_2$); 2.02 (2H, t, *J* = 5.6, allylic CH_2); 2.18 (2H, t, *J* = 5.6, allylic CH_2); 6.12 (2H, s, $H_{(2)}$); 6.31 (1H, s, ethylenic H); 6.55 (1H, s, $H_{(4)}$); 7.43 (1H, s, $H_{(7)}$). Found, %: C 64.39; H 5.68; N 5.46. $C_{14}H_{15}NO_4$. Calculated, %: C 64.36; H 5.79; N 5.36.

5-Nitro-6-(1-nitrocycloheptylmethyl)benzo[1,3]dioxole (3d). Yellow solid, yield 40%; mp 115°C (ethanol). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.47-1.53 (8H, m, $4CH_2$); 1.72 (2H, dd, *J* = 11.0, *J* = 5.0, β-$H_{(3')}$ and β-$H_{(8')}$); 2.24 (2H, dd *J* = 11.0, *J* = 5.0, α-$H_{(3')}$ and α-$H_{(8')}$); 3.60 (2H, s, allylic CH_2); 6.00 (2H, s, $H_{(2)}$); 6.36 (1H, s, $H_{(4)}$); 7.35 (1H, s, $H_{(7)}$). Found, %: C 55.93; H 5.54; N 8.65. $C_{15}H_{18}N_2O_6$. Calculated, %: C 55.90; H 5.63; N 8.69.

5-Cycloheptylidenemethyl-6-nitrobenzo[1,3]dioxole (4d). Oil, yield 14%. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.43-1.60 (8H, m, $4CH_2$); 2.12 (2H, t, *J* = 5.1, allylic CH_2); 2.31 (2H, t, *J* = 5.1, allylic CH_2); 6.02 (2H, s, $H_{(2)}$); 6.34 (1H, s, ethylenic H); 6.60 (1H, s, $H_{(4)}$); 7.43 (1H, s, $H_{(7)}$). Found, %: C 65.41; H 6.15; N 5.03. $C_{15}H_{17}NO_4$. Calculated, %: C 65.44; H 6.22; N 5.09.

5-Nitro-6-(2-nitrobicyclo[2.2.1]hept-2-ylmethyl)benzo[1,3]dioxole (3e). Yellow solid, yield 16%; mp 102°C (ethanol–water, 1:1). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.09-1.22 (2H, m, CH_2); 1.35-1.55 (4H, m, $2CH_2$); 1.75-1.76 (1H, m, $H_{(3')}$ *exo*); 2.19-2.21 (1H, m, $H_{(4')}$); 2.29-2.30 (1H, m, $H_{(3')}$ *endo*); 2.57-2.58 (1H, m, $H_{(7')}$); 3.63 (1H, d, *J* = 15.7, α-$H_{(1')}$); 3.81 (1H, d, *J* = 15.7, β-$H_{(1')}$); 6.01 (2H, s, $H_{(2)}$); 6.37 (1H, s, $H_{(4)}$); 7.38 (1H, s, $H_{(7)}$). Found, %: C 56.19; H 4.90; N 8.75. $C_{15}H_{16}N_2O_6$. Calculated, %: C 56.25; H 5.04; N 8.75.

5-Bicyclo[2.2.1]hept-2-ylidenemethyl-6-nitrobenzo[1,3]dioxole (4e). Oil, yield 42%. *E*-isomer: ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.16-1.39 (6H, m, $3CH_2$); 1.96-2.16 (2H, m, allylic CH_2); 2.34 (1H, br. s, CH); 2.77 (1H, br. s, allylic CH); 5.98 (2H, s, $H_{(2)}$); 6.52 (1H, s, ethylenic H); 6.78 (1H, s, $H_{(4)}$); 7.34 (1H, s, $H_{(7)}$). *Z*-isomer: ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.51-1.66 (6H, m, $3CH_2$); 1.96-2.16 (2H, m, allylic CH_2); 2.25 (1H, br. s, CH); 2.78 (1H, br. s, allylic CH); 5.98 (2H, s, $H_{(2)}$); 6.51 (1H, s, ethylenic H); 6.78 (1H, s, $H_{(4)}$); 7.34 (1H, s, $H_{(7)}$). Found, %: C 65.88; H 5.49; N 5.11. $C_{15}H_{15}NO_4$. Calculated, %: C 65.92; H 5.53; N 5.13.

5-(2-Methyl-2-nitropentyl)-6-nitrobenzo[1,3]dioxole (3f). Yellow solid, yield 59%; mp 101°C (ethanol). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 0.96 (3H, t, *J* = 6.7, $CH_2C\underline{H}_3$); 1.21-125 (2H, m, $C\underline{H}_2CH_3$); 1.40 (3H, s, CCH_3); 1.83-1.85 (1H, m, α-$H_{(3')}$); 2.12-2.13 (1H, m, β-$H_{(3')}$); 3.55 (1H, d, *J* = 14.6, α-$H_{(1')}$); 3.90 (1H, d, *J* = 14.6, β-$H_{(1')}$); 6.12 (2H, s, $H_{(2)}$); 6.54 (1H, s, $H_{(4)}$); 7.52 (1H, s, $H_{(7)}$). Found, %: C 52.55; H 5.38; N 9.41. $C_{13}H_{16}N_2O_6$. Calculated, %: C 52.70; H 5.44; N 9.46.

5-(2-Methylpent-1-enyl)-6-nitrobenzo[1,3]dioxole (4f). Oil, yield 13%. *E*-isomer: ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 0.71 (3H, t, *J* = 7.3, $CH_2C\underline{H}_3$); 1.34 (2H, sextuplet, *J* = 7.3, $C\underline{H}_2CH_3$); 1.78 (3H, d, *J* = 1.3, CCH_3); 1.90 (2H, t, *J* = 7.3, allylic CH_2); 6.01 (2H, s, $H_{(2)}$); 6.35 (1H, br. s, ethylenic H); 6.56 (1H, s, $H_{(4)}$); 7.43 (1H, s, $H_{(7)}$). *Z*-isomer: ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 0.87 (3H, t, *J* = 7.3, $CH_2C\underline{H}_3$); 1.51 (2H, sextuplet, *J* = 7.3, $C\underline{H}_2CH_3$); 1.57 (3H, d, *J* = 1.2, CCH_3); 2.07 (2H, t, *J* = 7.3, allylic CH_2); 6.01 (2H, s, $H_{(2)}$); 6.35 (1H, br. s, ethylenic H); 6.60 (1H, s, $H_{(4)}$); 7.43 (1H, s, $H_{(7)}$). Found, %: C 62.59; H 6.14; N 5.63. $C_{13}H_{15}NO_4$. Calculated, %: C 62.64; H 6.07; N 5.62.

5-(5,5-Dimethyl-2-nitro-1,3-dioxan-2-ylmethyl)-6-nitrobenzo[1,3]dioxole (3g). Yellow solid, yield 69%; mp 173°C (ethanol–water, 1:1). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 1.38 (3H, s, CH_3); 1.50 (3H, s, CH_3); 3.58 (2H, s, CH_2); 4.37 (2H, d, *J* = 12.7, CH_2O); 4.90 (2H, d, *J* = 12.7, CH_2O); 6.15 (2H, s, $H_{(2)}$); 6.56 (1H, s, $H_{(4)}$); 7.53 (1H, s, $H_{(7)}$). Found, %: C 49.31; H 4.67; N 8.15. $C_{14}H_{16}N_2O_8$. Calculated, %: C 49.41; H 4.74; N 8.23.

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