Synthesis of heterocyclic geminal nitro azides*

D. V. Katorov, G. F. Rudakov, and V. F. Zhilin*

D. Mendeleyev University of Chemical Technology of Russia,
9 Miusskaya pl., 125047 Moscow, Russian Federation.
E-mail: KatorovDV@mail.ru

The oxidative azidation reactions of *C*-nitro-substituted saturated heterocyclic compounds, *viz.,* the nitro derivatives of oxetane, azetidine, 1,3-dioxane, tetrahydro-1,3-oxazine, and hexahydropyrimidine, were investigated. A novel representatives of the geminal nitro azides were prepared and their physicochemical properties were studied. The process of the formation of the geminal dinitro compounds upon oxidative azidation was analyzed.

Key words: oxidative azidation, nitration, geminal nitro azides.

Organic azides occupy a prominent place in the chemistry of energetic compounds. Thanks to the high heat content, they are important as active plasiticizers and highly energetic additives and also can serve as intermediates for the synthesis of various heterocyclic systems.[1—3]

At present, geminal azido nitro compounds are one of the less studied class of azido compounds. The list of the described α-nitro azides is limited and does not provide insight into the possibility of their synthesis in the series of heterocycles.[4—9]

The main method for the preparation of α-nitro azides consists of oxidative coupling of the azide anion with nitroalkane salts. The reaction is performed in an alkaline medium in the excess of azide under the conditions of electrochemical[4,6,9] and chemical oxidation.[5,7,8] In the latter case, ammonium persulfate or potassium ferricyanide are most widely used as oxidants.

Both primary and secondary (linear and cyclic) nitroalkanes undergo azidation. Depending on the structure of the hydrocarbon group and the method of oxidation, the yield of nitro azide varies over a wide range (16—89%).

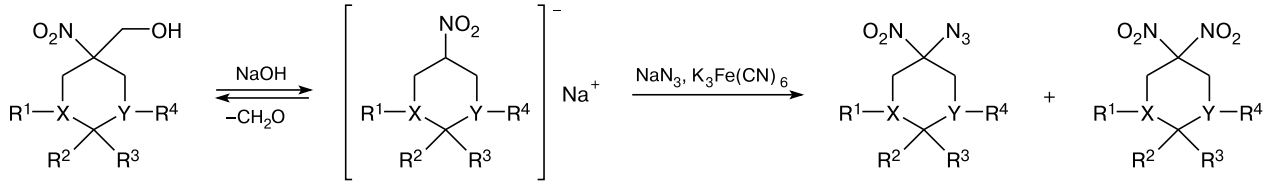
To reveal the influence of the structure of the heterocycle, the nature of the heteroatom and subsituents, we studied in the present work the oxidative azidation reaction by the example of nitro derivatives of 1,3-dioxane **1a—g**, 1,3-tetrahydrooxazine **1h,i**, hexahydropyrimidine **1j,k** (Scheme 1, Table 1), oxetane **4a**, and azetidine **4b** (Scheme 2, Table 2).

Table 1. The yields and physicochemical parameters of six-membered heterocyclic geminal nitro azides **2a—k**

2	X	Y	R^1	R^2	R^3	R^4	Yield (%)	M.p./°C (n_D^{20})
a	O	O	—	H	H	—	64	35—36
b	O	O	—	H	Me	—	66	25—26
c	O	O	—	Me	Me	—	71	39—40.5
d	O	O	—	Me	Et	—	70	(1.4699)
e	O	O	—	H	Ph	—	81	101.5—103
f	O	O	—	H	*m*-$NO_2C_6H_4$	—	62	80.5—83
g	O	O	—	—$(CH_2)_4$—		—	60	25—30
h	O	N	—	H	H	Bu^t	58	33—35
i	O	N	—	H	H	CH_2Ph	73	72.5—75
j	N	N	Pr^i	H	H	Pr^i	71	12 (1.4870)
k	N	N	Bu^t	H	H	Bu^t	53	57—58

* Dedicated to the memory of Corresponding Member of the Academy of Sciences of the USSR S. S. Novikov on the occasion of his 100th anniversary.

Scheme 1



1a—k **2a—k** **3a—c**

3a: $R^1X = R^4Y = O$, $R^2 = R^3 = Me$; **3b:** $R^1X = O$, $R^4Y = Bu^tN$, $R^2 = R^3 = H$; **3c:** $R^1X = R^4X = NBu^t$, $R^2 = R^3 = H$

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2240—2246, November, 2009.

1066-5285/09/5811-2311

Scheme 2

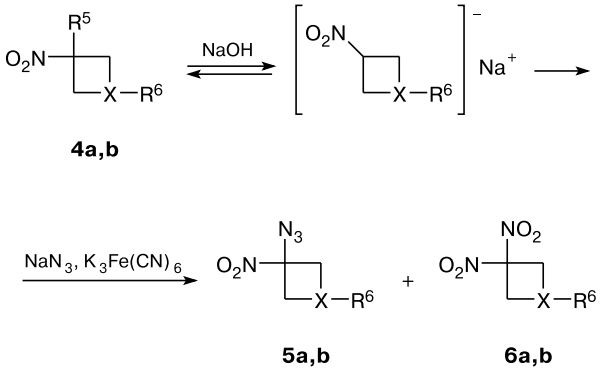


Table 2. The yields and physicochemical parameters of four-membered heterocyclic geminal nitro azides **5a,b**

5	X	R^5	R^6	Yield (%)	M.p./°C (n_D^{20})
a	O	H	—	26*	—
b	N	CH_2OH	Bu^t	60	3—5 (1.4360)

* According to the ^{1}H NMR spectral data.

Except for oxetane, the salts of the nitro-substituted heterocycles were prepared by the Henry retroreaction directly from hydroxymethyl derivatives **1** (see Schemes 1 and 2). Potassium ferricyanide was used as the oxidant.

It was shown that, regardless of the structure of the heterocyle, the main reaction product is *gem*-azido nitro compound **2a—k**, **5a,b** (see Scheme 1, 2, Tables 1, 2). The nature of the substituent in position 2 of 1,3-dioxane, as well as the passage to nitrogen heterocycles have no noticeable effect on the reaction pathway.

1-*tert*-Butyl-3-hydroxymethyl-3-nitroazetidine (**4b**), as in the case of the six-membered heterocyles, affords 3-azido-1-*tert*-butyl-3-nitroazetidine (**5b**) in a good yield (see Scheme 2, Table 2). The decrease in the yield was observed only in the case of 3-nitrooxetane (**4a**). This fact can be explained by the typical behavior of 3-nitrooxetane in the oxidative coupling reactions. For example, upon nitration under the same conditions,[10] the yield of 3,3-dinirooxetane was only 22%.

We observed the difference in the rates of azidation of the four- and six-membered rings (Figs 1, 2, Schemes 3, 4). Azidation of oxazine **1h** proceeds considerably faster than that of azetidine **4b**. The similar effect was observed by us in studies of oxidative nitration of compounds **1h** and **4b**. It should be noted that nitration proceeds 2—4-fold faster than azidation.

In contrast to 2-azido-2-nitropropane, the heterocyclic azido nitro compounds do not undergo subsequent nucleophilic subsitution reaction to form the *gem*-diazido derivative.[5] The major by-products are *gem*-dinitro

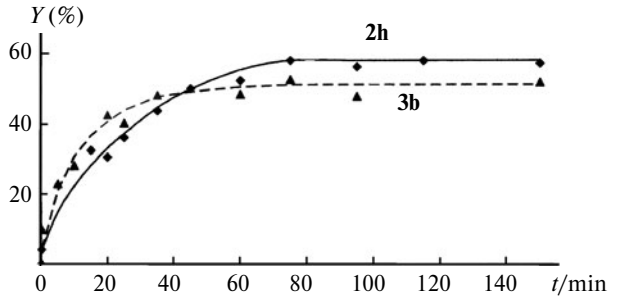
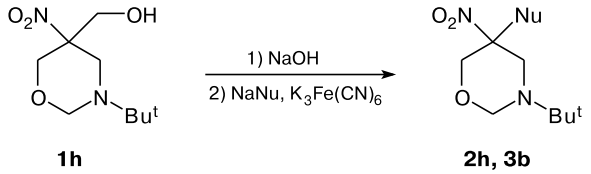


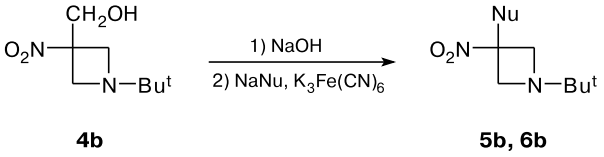
Fig. 1. Dependence of the yields (*Y*) of compounds **2h** and **3b** on the reaction time upon azidation (nitration) of 3-*tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine (**1h**) (see Scheme 3).

Scheme 3



Nu = N_3 (**2h**), NO_2 (**3b**)

Scheme 4



Nu = N_3 (**5b**), NO_2 (**6b**)

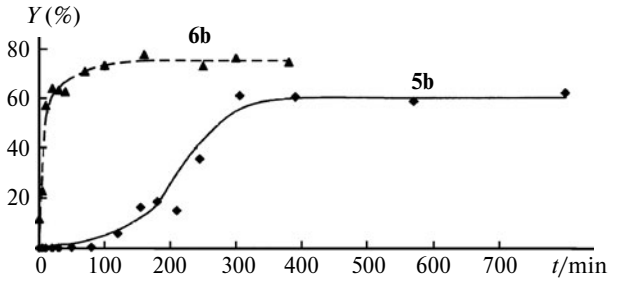
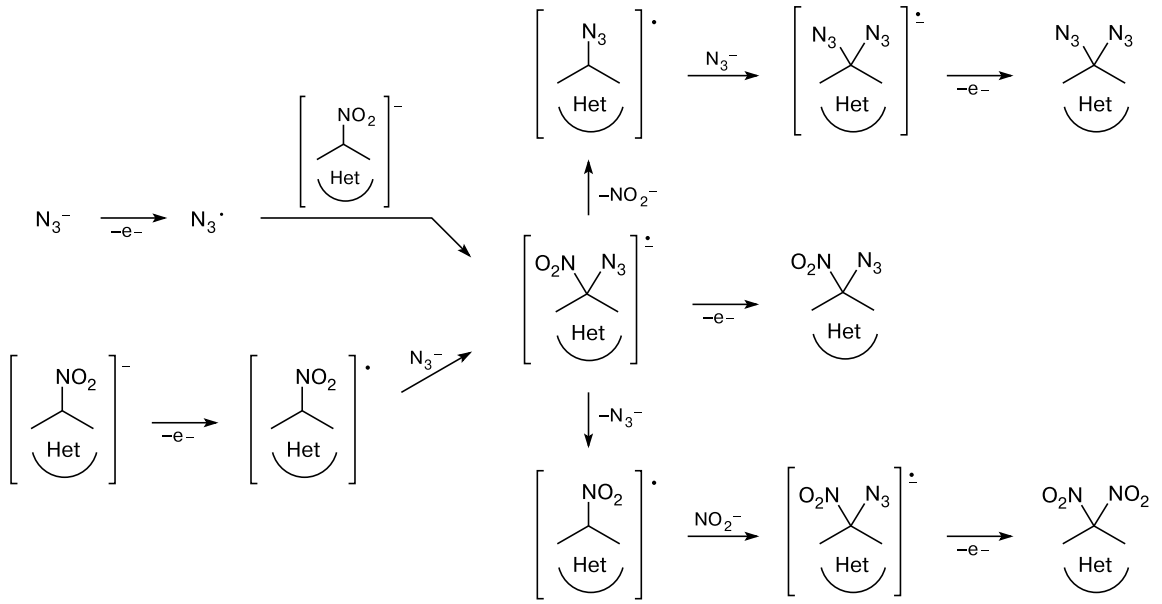


Fig. 2. Dependence of the yields (*Y*) of compounds **5b** and **6b** on the reaction time upon azidation (nitration) of 1-*tert*-butyl-3-hydroxymethyl-3-nitroazetidine (**4b**) (see Scheme 4).

derivatives **3** and **6** (see Schemes 1, 2). Their content was determined by ^{1}H NMR spectroscopy.

The formation of the *gem*-dinitro derivatives upon oxidative azidation also occured in the case of an analogous coupling reaction of nitroalkanes[5,8] with the nitrite anion. The nitrite anion can be formed upon decay of the

Scheme 5

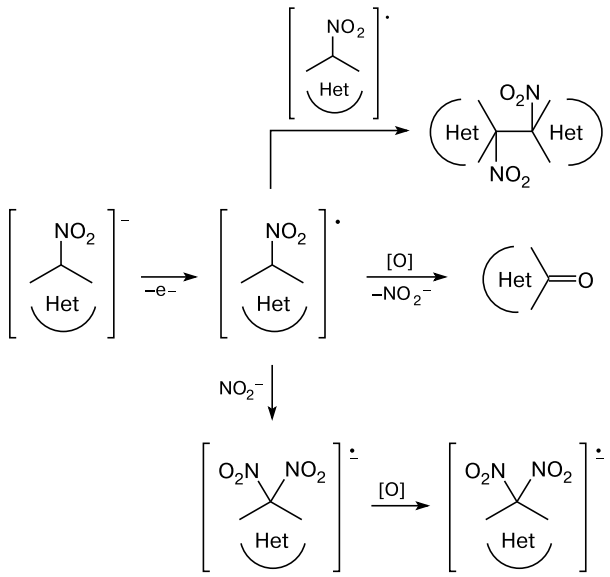


radical anions of the azido nitro compounds[5] (Scheme 5) or upon oxidation of the nitro compounds[11] (Scheme 6).

The former pathway implies the formation of the *gem*-diazido compounds that are not found among the azidation reaction products. The addition of nitrite at the different reaction steps leads to the proportional increase in the yield of the *gem*-dinitro derivative[12] in contrast to 2-nitropropane, for which the former pathway of the formation of the nitrite anion is typical.[5]

The analysis of the azidation products of 1-*tert*-butyl-3-hydroxymethyl-3-nitroazetidine (**4b**) showed that the yield of *gem*-dinitro product **6b** does not change upon increase in the reaction time (Table 3). It is seen from the kinetic curves (see Figs 1, 2) that, in spite of the great excess of the oxidant and sodium azide, nitro azide does not disappear from the reaction mixture. Consequently, the *gem*-dinitro compound is not produced from nitro azide.

Scheme 6



Oxidation of the starting nitro compounds **1c** and **4b** under the conditions similar to those of azidation affords *gem*-dinitro compounds **3a** and **6b** in yields of 8 and 15%, respectively, which suggests the formation of the nitrite anion by the latter pathway. Generation of the radicals of nitro compounds contemplates that the dimerization reaction proceeds and results in the vicinal dinitro compounds. The absence of the dimerization products is explained by the strong basicity of the reaction medium, wherein the vicinal dinitro compounds practically do not form.[11]

The structure of the heterocycle have an effect on the yield of the by-products. In the case of the more strained

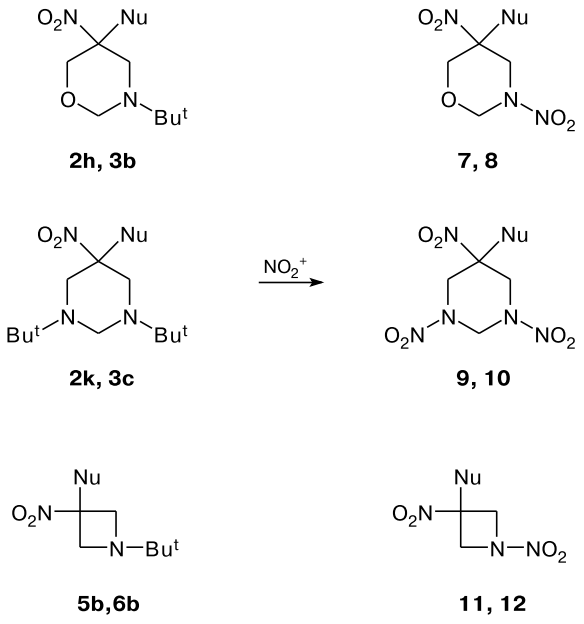
Table 3. The yields of nitro azides **2c,h**, **5a,b** and geminal dinitro compounds **3a,b**, **6a,b** upon oxidative azidation

Starting compound	*t*/h	m_{NaOH} /equiv.	Yield (%)	
			Nitro azide	*gem*-Dinitro compound
1c	24	5	69 (**2c**)	2 (**3a**)
1h	4.5	3	55 (**2h**)	3 (**3b**)
4a	4	1.5	26 (**5a**)	12 (**6a**)
4b	4.5	5	49 (**5b**)	11 (**6b**)
	24	5	50 (**5b**)	10 (**6b**)

four-membered rings, the content of the *gem*-dinitro compounds is significantly higher than in the case of the six-membered rings (see Table 3). This fact can be explained by the strain in the four-membered rings.

The nitro azides obtained are insufficiently stable under the conditions of acid nitration compared to the *gem*-dinitro analogs (Scheme 7, Table 4). The yields upon substitutive nitration of the *N*-*tert*-butyl-substituted nitro azides **2h,k**, **5b** are considerably lower than in the case of *gem*-dinitro analogs **3b,c**, **6b**. The best results were achieved when the system N_2O_5—MeCN was applied. Nitro azides, except for **2k**, and dinitro compounds are nitrated in this system in almost equal yields.

Scheme 7

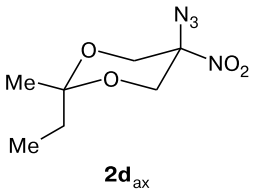


Nu = N_3 (**2**, **5**, **7**, **9**, **11**), NO_2 (**3**, **6**, **8**, **10**, **12**)

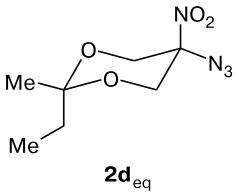
Nitration in media with higher acidity and the increase in temperature lead to the increase in the degree of destructive processes and the decrease in the yield of nitramines. The addition of NH_4Cl, which was successfully used in the nitration of the *gem*-dinitro analogs,[13] have no positive effect on the outcome of the reaction. Nitration of the derivatives of 1,3-dioxane affords the product whose IR spectrum contains the bands characteristic of both the nitrate and azido groups. However, we did not succeed in isolating it in a pure state because of its low chemical stability.

Studies of the obtained compounds by thermal gravimetry (TGA) and differential scanning calorimetry (DSC) showed that nitro azides decomposed at 150—160 °C. It was found that the structure of the heterocycle influences the stability of the α-nitro azide. Compounds **2h,j,k** and **5b** containing the strong electron-donating substituents (*tert*-butyl, isopropyl) are stable only at low temperatures (−20 °C) and decomposed at room temperature within 1 month to form a complex mixture of products, the IR spectrum of which does not contain the bands that are typical of antisymmetric stretching vibrations of the $-N_3$ and $-NO_2$ groups. The replacement of the *N*-alkyl group by the nitro group results in the stabilization of the structure. For example, compounds **7**, **9**, and **11** do not show the signs of light-induced decomposition at room temperature. The azido nitro derivatives of 1,3-dioxane, regardless of the structure and nature of the substituent, are stable at room temperature.

The α-nitro azides obtained are colorless solids and compound **5b** is a pale-yellow liquid. According to the data from ^{1}H NMR spectroscopy, compound **2d** was obtained as a 1 : 1 mixture of two isomers with the axial (**2d**$_{ax}$) and equatorial (**2d**$_{eq}$) positions of the azido group.



2d$_{ax}$



2d$_{eq}$

The structures of the obtained compounds were established by IR spectroscopy, as well as by ^{1}H and ^{13}C spec-

Table 4. The yields (%) of *N*-nitro compounds **7—12** depending on the nature of the nitration mixture (see Scheme 7)

Starting compound	Product	Nitration system (NO_2^+)					
		HNO_3	H_2SO_4—HNO_3	Ac_2O—HNO_3*	NH_4NO_3—Ac_2O**	NH_4NO_3—$(CF_3O)_2O$	N_2O_5—MeCN
2h	**7**	0	—	16	0	23	60
3b	**8**	23	—	37	45	60	66
2k	**9**	—	0	—	—	—	11
3c	**10**	—	81	44	—	22	54
5b	**11**	—	—	50	21	—	61
6b	**12**	—	—	61	82	—	64

* A 1 : 1 ratio.
** T = 70 °C.

Table 5. Spectral data for the nitro azides obtained

Compound	IR spectrum, ν/cm^{-1}			^{13}C NMR spectrum ($CDCl_3$)	
	N_3	NO_2 (as)	NO_2 (s)	Frequency/MHz	$C(NO_2)N_3$, δ
2a	2130	1560	1319	50	92.6
2b	2135	1561	1340	50	92.7
2c	2142	1558	1337	50	94.3
2d*	2125	1561	1337	50	93.9, 94.37
2e	2128	1566, 1552	1329	50	92.6
2f	2134	1559	1331	75	92.5
2g	2126	1559	1339	50	93.5
2h	2124	1560	1345	50	95.0
2i	2145	1556	1325	50	93.9
2j**	2119	1555	1341	75	97.1
2k	2126	1553	1348	50	97.7
4a***	2140	1590—1558	1336	—	—
4b	2128	1558	1353	50	92.1
7	2150, 2132	1561	1326, 1287	50	93.7
9**	2140	1566	1343, 1293	75	94.9
11	2135	1576, 1561	1352, 1342	75	89.0

* An isomeric mixture.
** The spectrum was recorded in DMSO-d_6.
*** In a mixture with 3,3-dinitrooxetane.

troscopy. In the IR spectra, the absorption bands are recorded in the region of the absorption of the azido group (2119—2142 cm^{-1}), the symmetrical (1325—1360 cm^{-1}) and antisymmetrical (1554—1566 cm^{-1}) vibrations of the nitro group (Table 5). In the ^{13}C NMR spectrum, the resonance signals for the carbon atom bearing the nitro and the azido groups are in the region of δ 89—98 (see Table 5).

The analysis of the IR spectra suggests the presence of the strong interaction between the azido group and the nitroamine fragment (see Table 5). The replacement of the *tert*-butyl by the nitro group results in the appreciable shift of the antisymmetrical vibration band of $-N_3$ to the high-frequency region, which is evidence of appearance of higher rigidity in the structure of the azido group. Introduction of the azido group also results in the shift of the antisymmetrical vibration band of NNO_2 to the high-frequency region, which can be explained by the formation of more planar configuration of the nitramine unit and, as a consequence, by certain decrease in the N—N bond length, which determines the higher stability of compounds **7**, **9**, and **11**.

Experimental

Attention! *The azido nitro compounds and by-products that can be formed in the preparation of the azido nitro compounds are toxic and explosive. Observe appropriate precautions during their handling!*

The ^{1}H and ^{13}C spectra were recorded on Bruker AC-200 (200 MHz), Bruker AM-300 (300 MHz) and Bruker AMX-400 (400 MHz) instruments in $CDCl_3$ and DMSO-d_6. The IR spectra were recorded on a Thermo Nicolet 360 FT IR spectrometer in KBr pellets (7 mm in diameter). The melting points were measured on a Boetius heating table at the heating rate 2 °C min^{-1}. DSC and TGA studies of the thermal stability were performed on a Mettler Toledo DSC 822^c instrument. The heating rate was 10 °C min^{-1} in the temperature range 20—250 °C. The course of the reaction was monitored by TLC using Sorbfil PTLC-AF-A-UV plates. The compounds obtained were purified by preparative chromatography on silica gel (Durasil H, 60—100 μ).

Compound **1a** was synthesized by the cyclization reaction of dimethoxymethane and nitroisobutylglycerol.[14] Compounds **1b—g** were prepared by the cyclization reaction of nitroisobutylglycerol with the corresponding ketones in the presence of $BF_3 \cdot Et_2O$ or *p*-toluenesulfonic acid.[15] Compounds **1h—k** were synthesized by the Mannich reaction from nitroisobutylglycerol, formaldehyde, and the corresponding amine.[16] Compounds **4a** and **4b** were synthesized according to the previously described procedures.[10,17]

Oxidative coupling of nitro compounds (general procedure). The starting nitro compound **1** or **4** (1 equiv.) was added with stirring at ~20 °C to a 20% aqueous solution of NaOH (5 equiv.) and the reaction mixture was kept for 10—15 min. To the resulting mixture, a saturated aqueous solution of NaN_3 ($NaNO_2$) (5 equiv.) was added and the mixture was poured with stirring into a saturated aqueous solution of $K_3Fe(CN)_6$ (5 equiv.). The reaction mixture was stirred for 2.5—4 h at ~20 °C and extracted with ethyl acetate. The extract was washed with brine, dried with magnesium sulfate, and concentrated on a rotary evaporator. If necessary, the obtained product was purified by preparative chromatography. ($CHCl_3$—CCl_4, 1 : 1 (v/v)).

5-Azido-5-nitro-1,3-dioxane (2a). IR, ν/cm^{-1}: 3006, 2947, 2875 (CH); 2130 (N_3); 1560, 1319 (NO_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 4.01 (d, 2 H, O—CH_2—C, J = 11.9 Hz); 4.52 (d, 2 H,

O—CH_2—C, J = 11.9 Hz); 4.85 (d, 1 H, O—CH_2—O, J = 6.2 Hz); 4.90 (d, 1 H, O—CH_2—O, J = 6.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 68.6 (O—$\underline{C}H_2$—C); 92.6 ($C(NO_2)N_3$); 93.6 (O—CH_2—O). Found (%): C, 27.63; H, 3.49; N, 32.15. $C_4H_6N_4O_4$. Calculated (%): C, 27.59; H, 3.47; N, 32.18.

5-Azido-2-methyl-5-nitro-1,3-dioxane (2b). IR, ν/cm^{-1}: 2873 (CH); 2135 (N_3); 1561, 1340 (NO_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.45 (d, 3 H, Me, J = 4.9 Hz); 4.27 (s, 4 H, CH_2); 4.81 (q, 1 H, CH, J = 5.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 19.9 (Me); 68.9 (CH_2); 92.7 ($C(NO_2)N_3$); 100.2 (CH). Found (%): C, 31.90; H, 4.21; N, 29.65. $C_5H_8N_4O_4$. Calculated (%): C, 31.92; H, 4.29; N, 29.78.

5-Azido-2,2-dimethyl-5-nitro-1,3-dioxane (2c). IR, ν/cm^{-1}: 3003, 2984, 2947 (CH); 2142 (N_3); 1558, 1337 (NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.45 (s, 3 H, Me); 1.46 (s, 3 H, Me); 4.00 (d, 2 H, CH_2, J = 12.8 Hz); 4.48 (d, 2 H, CH_2, J = 12.5 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 22.6 (Me); 23.2 (Me); 62.8 (CH_2); 94.3 ($C(NO_2)N_3$); 99.9 (C). Found (%): C, 35.69; H, 5.03; N, 27.68. $C_6H_{10}N_4O_4$. Calculated (%): C, 35.65; H, 4.99; N, 27.71.

5-Azido-2-ethyl-2-methyl-5-nitro-1,3-dioxane (2d), a 1 : 1 mixture of isomers (^{1}H NMR data). IR, ν/cm^{-1}: 2983, 2945 (CH); 2125 (N_3); 1561, 1337 (NO_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.91, 0.96 (both t, total 3 H, CH_2—C$\underline{H}_3$, J = 7.5 Hz); 1.42 (s, 3 H, Me); 1.72—1.81 (m, 2 H, C$\underline{H}_2$—CH_3); 4.00, 4.02 (both d, total 2 H, CH_2, J = 12.8); 4.48, 4.51 (both d, total 2 H, CH_2, J = 12.8). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 7.4, 7.6 (CH_2—$\underline{C}H_3$); 18.9, 19.3 (Me); 29.3, 29.9 ($\underline{C}H_2$Me); 62.4, 62.6 (CH_2); 93.9, 94.37 ($C(NO_2)N_3$); 101.5 (C). Found (%): C, 38.92; H, 5.63; N, 25.85. $C_7H_{12}N_4O_4$. Calculated (%): C, 38.89; H, 5.59; N, 25.92.

5-Azido-5-nitro-2-phenyl-1,3-dioxane (2e). IR, ν/cm^{-1}: 3096, 3064, 3043 (CH arom.); 2944, 2885, 2877 (CH); 2128, 2116 (N_3); 1566, 1552, 1329 (NO_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 4.44 (d, 2 H, CH_2, J = 11.5 Hz); 4.51 (d, 2 H, CH_2, J = 11.5 Hz); 5.64 (s, 1 H, CH); 7.44 (m, 3 H, Ph); 7.53 (m, 2 H, Ph). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 69.1 (CH_2); 92.6 ($C(NO_2)N_3$); 101.8 ($\underline{C}$—C_{ar}); 126.0 (C_o arom.); 128.4 (C_m arom.); 129.6 (C_p arom.); 135.6 ($\underline{C}_{ar}$—CO). Found (%): C, 48.08; H, 3.95; N, 22.28. $C_{10}H_{10}N_4O_4$. Calculated (%): C, 48.00; H, 4.03; N, 22.39.

5-Azido-5-nitro-2-(3-nitrophenyl)-1,3-dioxane (2f). IR, ν/cm^{-1}: 3102, 3087, 3051 (CH arom.); 2988, 2962 (CH); 2134 (N_3); 1534, 1352 (s, NO_2 arom.); 1559, 1331 (NO_2). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.44 (d, 2 H, CH_2, J = 11.7 Hz); 4.52 (d, 2 H, CH_2, J = 11.7 Hz); 5.70 (s, 1 H, CH); 7.59 (t, 1 H, Ph, J = 8.1 Hz); 7.83 (d, 1 H, Ph, J = 7.3 Hz); 8.25 (d, 1 H, Ph, J = 8.1 Hz); 8.36 (s, 1 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 69.2 (CH_2); 92.5 ($C(NO_2)N_3$); 100.1 ($\underline{C}$—C_{ar}); 121.5 (C_{ar}—$\underline{C}$H—CNO_2); 124.4 (CH—$\underline{C}$H—CNO_2); 129.5 (CH—$\underline{C}$H—CH); 132.2 (C_{ar}—$\underline{C}$H—CH); 137.5 ($\underline{C}_{ar}$—CO); 148.1 ($C_{ar}NO_2$)). Found (%): C, 40.58; H, 3.12; N, 23.68. $C_{10}H_9N_5O_6$. Calculated (%): C, 40.69; H, 3.07; N, 23.72.

8-Azido-8-nitro-6,10-dioxaspiro[4.5]decane (2g). IR, ν/cm^{-1}: 2974, 2945, 2878 (CH); 2126 (N_3); 1559, 1339 (NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.67 (s, 4 H, CH_2CH_2); 1.89 (s, 4 H, CH_2CH_2); 3.98 (d, 2 H, C—CH_2—O, J = 11.8 Hz); 4.46 (d, 2 H, C—CH_2—O, J = 11.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 23.2 (CH_2—$\underline{C}H_2$—$\underline{C}H_2$—CH_2); 34.1 (C—$\underline{C}H_2$—CH_2); 34.5 (C—$\underline{C}H_2$—CH_2); 64.1 ($C(NO_2)$—$\underline{C}H_2$—O); 93.5 ($C(NO_2)N_3$); 111.5 (O_2—$\underline{C}$—$(CH_2)_2$). Found (%): C, 42.11; H, 5.32; N, 24.53. $C_8H_{12}N_4O_4$. Calculated (%): C, 42.10; H, 5.30; N, 24.55.

5-Azido-3-*tert*-butyl-5-nitrotetrahydro-1,3-oxazine (2h). IR, ν/cm^{-1}: 2975, 2875, 2837 (CH); 2124 (N_3); 1560, 1345 (NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.10 (s, 9 H, Me); 3.14 (d, 1 H, C—CH_2—N, J = 12.1 Hz); 3.58 (d, 1 H, C—CH_2—N, J = 12.5 Hz); 3.73 (dd, 1 H, O—CH_2—C, J = 12.1 Hz, J = 1.0 Hz); 4.29 (m, 1 H, O—CH_2—C, 2 H, N—CH_2—O). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 26.6 (Me); 50.7 (C—$\underline{C}H_2$—N); 53.3 (N—$\underline{C}$Me); 69.1 (O—$\underline{C}H_2$—C); 81.0 (O—CH_2—N); 95.0 ($C(NO_2)N_3$). Found (%): C, 41.85; H, 6.63; N, 30.48. $C_8H_{15}N_5O_3$. Calculated (%): C, 41.92; H, 6.60; N, 30.55.

5-Azido-3-benzyl-5-nitrotetrahydro-1,3-oxazine (2i). IR, ν/cm^{-1}: 3087, 3061, 3036 (C—H arom.); 2934, 2866 (CH); 2145 (N_3); 1556, 1325 (NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 3.27 (d, 1 H, C—CH_2—N, J = 13.4 Hz); 3.76 (d, 1 H, C—CH_2—N, J = 13.4 Hz); 4.06 (m, 1 H, C—CH_2—O, 2 H, Ph—CH_2—N); 4.34 (m, 1 H C—CH_2—O, 2 H, N—CH_2—O); 7.35 (s, 5 H, Ph). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 54.0 (C_{ar}—$\underline{C}H_2$—N); 56.1 (N—$\underline{C}H_2$—C); 69.6 (C—$\underline{C}H_2$—O); 83.2 (O—CH_2—N); 93.9 ($C(NO_2)N_3$); 127.5 (C_p arom.); 128.4 (C_m arom.); 128.6 (C_o arom.); 137.0 (CH_2—$\underline{C}_{ar}$). Found (%): C, 50.15; H, 4.99; N, 26.50. $C_{11}H_{13}N_5O_3$. Calculated (%): C, 50.19; H, 4.98; N, 26.60.

5-Azido-1,3-diisopropyl-5-nitrohexahydropyrimidine (2j). IR, ν/cm^{-1}: 2968, 2932 (CH); 2119 (N_3); 1555, 1341 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.04 (d, 12 H, Me, J = 6.40 Hz); 2.92 (m, 2 H, C$\underline{H}$Me); 2.97 (d, 2 H, N—CH_2—C, J = 11.4 Hz); 3.23 (d, 2 H, N—CH_2—C, J = 11.9 Hz); 3.31 (d, 1 H, N—CH_2—N, J = 9.1 Hz); 3.46 (d, 1 H, N—CH_2—N, J = 9.1 Hz). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 18.5 (Me); 51.3 (N—$\underline{C}H_2$—C); 51.7 (CH); 67.9 (N—CH_2—N); 97.1 ($C(NO_2)N_3$). Found (%): C, 46.79; H, 7.90; N, 32.65. $C_{10}H_{20}N_6O_2$. Calculated (%): C, 46.86; H, 7.87; N, 32.79.

5-Azido-1,3-di-*tert*-butyl-5-nitrohexahydropyrimidine (2k). IR, ν/cm^{-1}: 2971 (Me); 2126 (N_3); 1553, 1348 (NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.09 (s, 18 H, Me); 2.99 (d, 2 H, N—CH_2—C, J = 11.8 Hz); 3.19 (d, 2 H, N—CH_2—C, J = 11.8 Hz); 3.26 (d, 1 H, N—CH_2—N, J = 9.1 Hz); 3.62 (d, 1 H, N—CH_2—N, J = 9.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 26.1 (Me); 51.1 (N—$\underline{C}H_2$—C); 53.8 ($\underline{C}$HMe); 63.6 (N—CH_2—N); 97.7 ($C(NO_2)N_3$). Found (%): C, 50.71; H, 8.58; N, 29.53. $C_{12}H_{24}N_6O_2$. Calculated (%): C, 50.69; H, 8.51; N, 29.55.

3-Azido-3-nitrooxetane (5a) was prepared as a mixture with 3,3-dinitrooxetane (**6a**)[10]. IR, ν/cm^{-1}: 2957, 2888 (CH); 2140 (N_3); 1590—1558, 1336 (NO_2). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.77 (d, 2 H, J = 8.1 Hz); 5.17 (d, 2 H, J = 8.1 Hz); 5.29* (s, **6a**).

3-Azido-1-*tert*-butyl-3-nitroazetidine (5b). IR, ν/cm^{-1}: 2968 (CH); 2128 (N_3); 1558, 1353 (NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.98 (s, 9 H, Me); 3.47 (dd, 2 H, CH_2, J = 8.3 Hz, J = 1.7 Hz); 3.91 (dd, 2 H, CH_2, J = 8.3 Hz, J = 1.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 23.8 (Me); 52.3 (N—$\underline{C}$Me);55.4 (CH_2); 92.1 ($C(NO_2)N_3$). Found (%): C, 42.11; H, 6.50; N, 35.06. $C_7H_{13}N_5O_2$. Calculated (%): C, 42.20; H, 6.58; N, 35.16.

3-*tert*-Butyl-5,5-dinitrotetrahydro-1,3-oxazine (3b).[18,19] The yield was 51%, m.p. 83—85 °C. IR, ν/cm^{-1}: 2985 (CH); 1572, 1366 (NO_2). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.11 (s, 9 H); 3.83 (s, 2 H); 4.37 (s, 2 H); 4.49 (s, 2 H).

1,3-Di-*tert*-butyl-5,5-dinitrohexahydropyrimidine (3c).[13,19] The yield was 48%, m.p. 75—76 °C. IR, ν/cm^{-1}: 2968 (CH); 1568, 1367 (NO_2).

* Signal of 3,3-dinitrooxetane.

1-*tert*-Butyl-3,3-dinitroazetidine (6b).[17] The yield was 75%, m.p. 20 °C. IR, ν/cm^{-1}: 2969 (CH); 1574, 1369 (NO_2). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.01 (s, 9 H, Me); 4.08 (s, 4 H, CH_2).

Study of kinetics of oxidative coupling. During azidation (nitration) of compounds **1h** or **4b**, aliquots of the reaction mixtures were withdrawn at definite intervals, extracted with ethyl acetate and the extract was concentrated. The residue was weighted, analyzed by HPLC and the yield of product **2h** or **5b** was determined. The chromatographic analysis was carried out on a Milichrom-4 instrument using a Silasorb CN chromatographic column, 2.0×120 mm, 5 μm. The rate of eluent feed (acetonitrile—water (1 : 1)) was 200 L min^{-1}. The retention times were 3.15 min for **2h**, 3.75 min for **3b**, 3.25 min for **5b**, and 4.35 min for **6b**.

Oxidation of nitro compounds. The starting nitro compound **1c** or **4b** (1 equiv.) was added with stirring at room temperature to a 20% aqueous solution of NaOH (5 equiv.) and kept for 10—15 min. Then the mixture was poured with stirring into a saturated aqueous solution of $K_3Fe(CN)_6$ (5 equiv.). The reaction mixture was stirred for 24 h at ~20 °C and extracted with ethyl acetate. The extract was washed with brine, dried with magnesium sulfate, and concentrated on a rotary evaporator. The residue was analyzed by ^{1}H NMR spectroscopy and the yield of *gem*-dinitro compound **3a** or **6b** was determined.

2,2-Dimethyl-5,5-dinitro-1,3-dioxane (3a).[19] ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.45 (s, 6 H, Me); 4.65 (s, 4 H, CH_2).

1-*tert*-Butyl-3,3-dinitroazetidine (6b).[17] ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.01 (s, 9 H, Me); 4.08 (s, 4 H, CH_2).

Nitration. To a cooled (0—5 °C) solution of the *N-tert*-butyl substituted derivative (**2h,k**, **3b,c, 5b, 6b**) in anhydrous acetonitrile, a solution of nitric anhydride (3 equiv. per Bu^t group) was slowly added, the temperature being maintained not above 5 °C. After completion of dosing, the mixture was kept for 1 h at 5 °C, then poured onto ice and extracted with ethyl acetate. The extract was washed with water until the neutral pH has been achieved, dried with Na_2SO_4, and concentrated *in vacuo* on a rotaty evaporator. The obtained product was purified by preparative chromatography, if necessary.

5-Azido-3,5-dinitrotetrahydro-1,3-oxazine (7). IR, ν/cm^{-1}: 2150, 2132 (N_3); 1561 (br, NO_2); 1326 (C—NO_2); 1287 (N—NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 4.17 (dd, 1 H, C—CH_2—O, J = 12.1 Hz, J = 2.1 Hz); 4.28 (d, 1 H, C—CH_2—O, J = 12.1 Hz); 4.44 (d, 1 H, N—CH_2—C, J = 15.3 Hz); 4.91 (d, 1 H, O—CH_2—N, J = 12.1 Hz); 4.94 (dt, 1 H, N—CH_2—C, J = 15.5 Hz, J = 2.0 Hz); 5.86 (dd, 1 H, O—CH_2—N, J = 12.1 Hz, J = 1.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 50.2 (N—$\underline{C}H_2$—C); 70.0 (C—$\underline{C}H_2$—O); 77.2 (O—CH_2—N); 93.7 ($C(NO_2)N_3$). Found (%): C, 22.11; H, 2.74; N, 38.49. $C_4H_6N_6O_5$. Calculated (%): C, 22.03; H, 2.77; N, 38.53.

5-Azido-1,3,5-trinitrohexahydropyrimidine (9). IR, ν/cm^{-1}: 2140 (N_3); 1566 (br, NO_2); 1343 (C—NO_2); 1293 (N—NO_2). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 4.28 (d, 2 H, N—CH_2—C, J = 15.0 Hz); 5.05 (d, 1 H, N—CH_2—N, J = 15.0 Hz); 5.07 (d, 2 H, N—CH_2—C, J = 15.0 Hz); 7.05 (d, 1 H, N—CH_2—N, J = 15.0). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 50.6 (N—$\underline{C}H_2$—C); 59.5 (N—CH_2—N); 94.9 ($C(NO_2)N_3$). Found (%): C, 18.28; H, 2.27; N, 42.65. $C_4H_6N_8O_6$. Calculated (%): C, 18.33; H, 2.31; N, 42.75.

3-Azido-1,3-dinitroazetidine (11). IR, ν/cm^{-1}: 2135 (N_3); 1576 (N—NO_2); 1561 (C—NO_2); 1352 (C—NO_2); 1342 (N—NO_2). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 4.6 (dd, 2 H, CH_2, J = 11.4 Hz, J = 1.4 Hz); 5.0 (dd, 2 H, CH_2, J = 11.4 Hz, J = 1.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 65.3 (CH_2); 89.0 ($C(NO_2)N_3$). Found (%): C, 19.06; H, 2.12; N, 44.60. $C_3H_4N_6O_4$. Calculated (%): C, 19.16; H, 2.14; N, 44.68.

3,5,5-Trinitrotetrahydro-1,3-oxazine (8).[19,20] IR, ν/cm^{-1}: 3078, 3020, 2968 (CH); 1581, 1560, 1307, 1288 (NO_2).

1,3,5,5-Terpanitrohexahydropyrimidine (10).[19,20] IR, ν/cm^{-1}: 3088, 3066, 3036 (CH); 1577, 1316, 1296 (NO_2). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 5.34 (s, 4 H); 6.11 (s, 2 H).

1,3,3-Trinitroazetidine (12).[17] IR, ν/cm^{-1}: 3038, 3022, 2975 (CH); 1601—1591, 1539, 1338, 1280 (NO_2). ^{1}H NMR (200 MHz, acetone-d_6), δ: 5.45 (s).

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Received March 25, 2009;
in revised form October 13, 2009