Nucleophilic Substitution of Dinitroolefins with 1,2-Difunctional Ethanes

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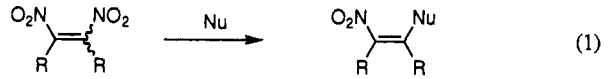
Reactions of α,β-dinitroolefins with 1,2-ethanedithiol form five-membered ring products. Similarly, reactions of α,β-dinitroolefins with 2-mercaptoethanol give five-membered ring products along with monosubstituted olefins and products disubstituted on one carbon. The formation of cyclic products from α,β-dinitroolefins and 1,2-difunctional nucleophiles is explained in terms of a stepwise addition–substitution mechanism in which a carbanion intermediate must be assumed. A Michael-type reaction seems to occur, and the addition intermediate loses a nitro group by intramolecular substitution. The reaction of 1,2-dinitrocyclohexene with 2-mercaptoethanol unexpectedly forms a β′-substituted α-nitroolefin by means of another reaction mechanism.

Introduction

Nucleophilic vinylic substitution reactions of α,β-dinitroolefins, such as (*E*)- and (*Z*)-2,3-dinitro-2-butene, with amine and thiocyanate yielded only (*Z*) isomers of vinylic-substituted nitroolefins (eq 1).[1-3] In contrast, nucleophilic vinylic substitution reactions of (*E*)- and (*Z*)-methyl α-bromo-β-nitrocinnamate and (*E*)-4-phenyl-4-nitro-3-bromo-3-buten-2-one with thiocyanate gave only (*E*) isomers of α,β-tandem disubstituted olefins (eq 2).[4]



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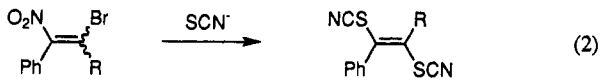


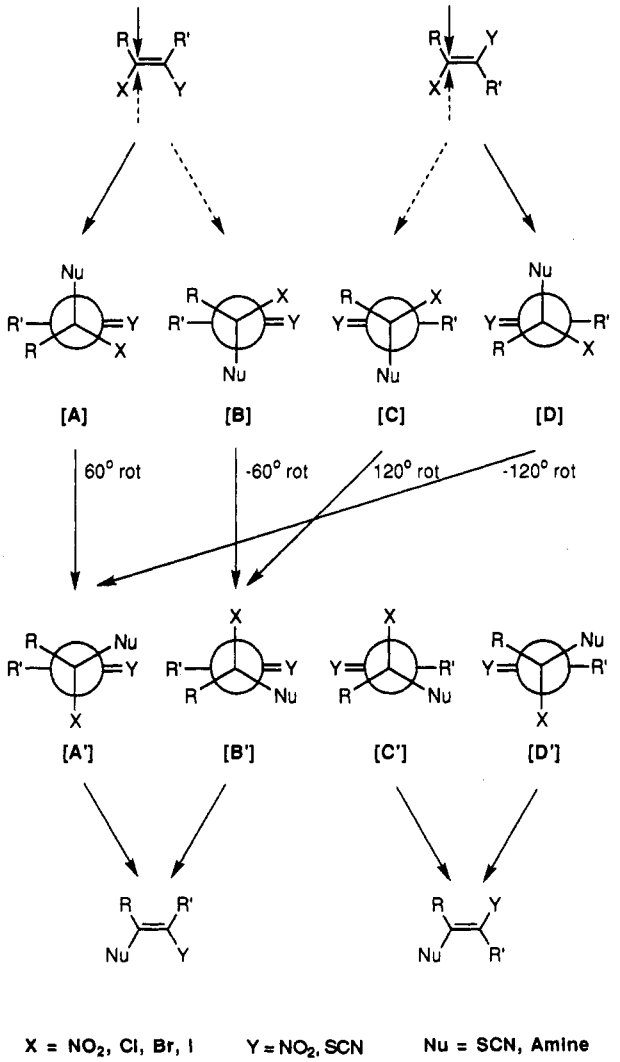
(2)

3 4

These stereospecific reactions were explained by an attractive or a repulsive interaction between the polar group (Y) and the appended nucleophile (Nu) in the conformation of the intermediate (see Scheme 1).

In our previous publications,[3,4] routes involving structures **[A]**, **[A′]**, **[D]**, and **[D′]** (see Scheme 1) were used for brevity at the time of publication. Professor Zvi Rappoport strongly suggested on a few occasions that this explanation was incomplete and needed more elaboration.[5] Thus, we forward the following more detailed explanation based on the same concept. Several assumptions were made. It was assumed that the nucleophiles approach was from above and below the plane of the double bond

Scheme 1



of (*E*)- and (*Z*)-α,β-dinitroolefins and that free rotation around the newly formed single bond occurs. Four conformations result from the two isomers of the α,β-dinitroolefins. If the nucleophile approaches from the top of the olefin, intermediate **[A]** will be formed, and epimer **[B]** will be formed through approach from the bottom. Intermediates **[C]** and **[D]** are formed in a similar manner.

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(1) For general references of nucleophilic vinylic substitution reaction, see (a) Patai, S.; Rappoport, Z. *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience: London, 1964; Chapter 8. (b) Shainyan, B. A. *Russ. Chem. Rev.* **1986**, *55*, 511. (c) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.

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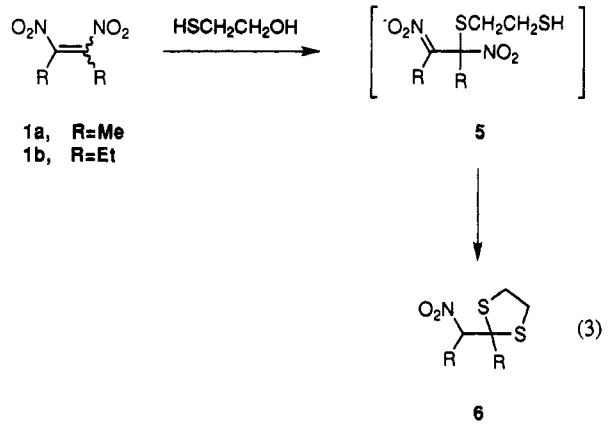
It is also assumed that the most favorable conformation for elimination is one in which the leaving group is parallel to the p orbital of the negatively charged sp^2 carbon. If this assumption is made, then, from these four conformers, only (*Z*) isomers will result if there is strong attractive interaction between Y and Nu (see conformers **[A']** and **[B']** in Scheme 1).[2,3] Exclusive formation of (*E*) isomers can be expected when a strong repulsive force exists between Y and Nu (see **[C']** and **[D']**).[4]

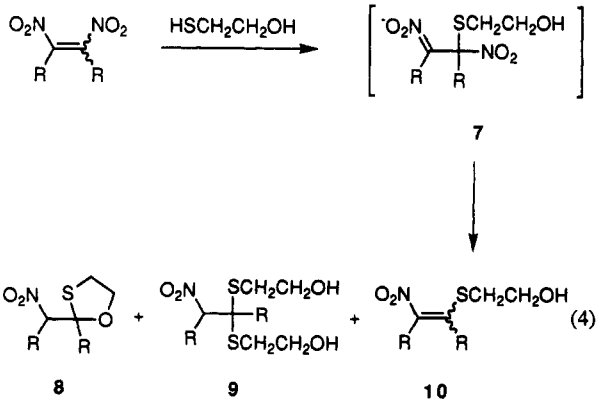
We also reported that tandem vinylic substitution of α-bromo-β-nitroolefins yields α,β-disubstituted olefins (eq 2). In contrast, reactions of α,β-dinitrolefins with 1,2-ethanedithiol and 2-mercaptoethanol afford products of α,α-tandem disubstitution.[6] Such α,α-disubstitution of α,β-dinitroolefins by 1,2-difunctional ethane introduces quite different stereochemical considerations.

Results and Discussion

When α,β-dinitroolefins are allowed to react with 1,2-ethanedithiol, one end of the double bond becomes doubly substituted, and only five-membered ring products **6** are obtained (eq 3).[7] With 2-mercaptoethanol, five-membered



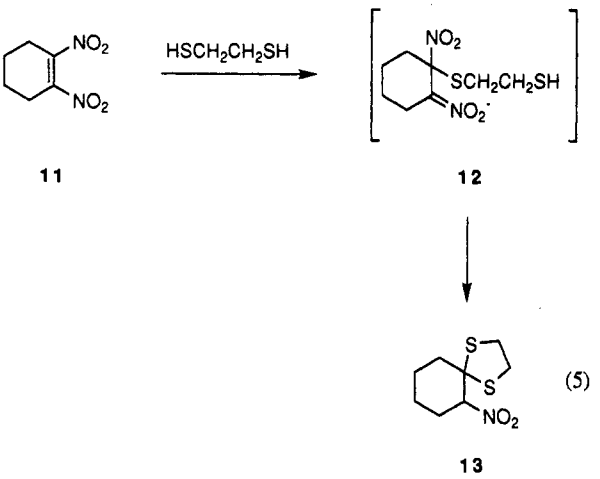
ring products **8**, α,α-disubstituted products **9**, and mono-substituted olefins **10** are the major products (eq 4). It seems that this wide range of products from reactions of α,β-dinitroolefins with 2-mercaptoethanol is due to the fact that addition intermediate **7** can follow several pathway (eq 4). It is possible that **8** is formed by



intramolecular 1,2-addition of **10** under basic conditions.[8]

Likewise, it can be assumed that **9** is formed by the 1,2-addition of another 2-mercaptoethanol to **10**.[9] However, the reaction of **10** with base does not lead to **8**, and the reaction of **10** with 2-mercaptoethanol does not lead to **8**. Consequently, the following reaction mechanism can be used to explain the formation of **8** or **9** from intermediate **7**. First, the α-nitro group of **7** may be substituted intramolecularly by the hydroxy group of the α-[(2-hydroxyethyl)thio] group to give oxathiolanes **8**, whose characterization will be discussed at the end of this section.[7] Second, the α-nitro group of **7** may be replaced by another molecule of 2-mercaptoethanol to produce **9**, after protonation of the β-carbon.[10] Lastly, addition intermediate **7** may lose a nitro group to form vinylic-substituted olefins (*E*)- and (*Z*)-**10**.[9,11]

When 1,2-dinitrocyclohexene is subjected to reaction with 1,2-ethanedithiol, only spiro compound **13** is obtained, via intermediate **12** (eq 5). The fact that the tertiary



hydrogen appears as a triplet in the ^1H NMR spectrm of **13** indicates the presence of two adjacent hydrogens with equal coupling constants (J = 4.9 Hz). This splitting pattern indicates that the final product probably exists in a chair conformation with the nitro group in an axial position. Otherwise, the tertiary hydrogen would appear as a set of two doublets because of the different dihedral angles (approximately 60° and 180°) between the tertiary hydrogens and the two adjacent hydrogens.[12] The product of ketalization of 2-nitrocyclohexanone with 1,2-ethanedithiol showed a similar ^1H NMR spectrum.[13]

With 2-mercaptoethanol, 1,2-dinitrocyclohexene does not yield a spiro compound; instead two different olefins are formed: the expected substitution product, 1-[(2'-

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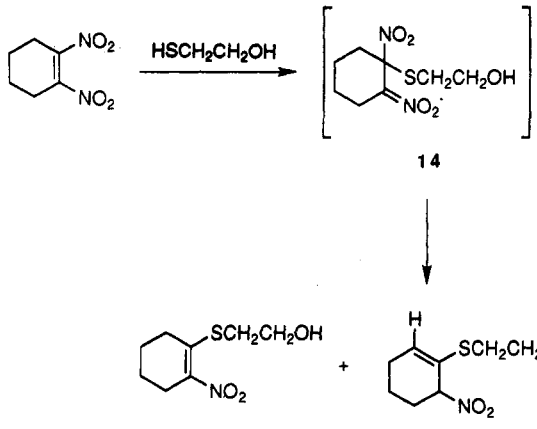
(13) Ethanediyl *S,S*-acetal was prepared from 2-nitrocyclohexanone by means of the reported procedure: Grobel, B. T.; Seebach, D. *Synthesis* **1977**, 357.

Table 1. Product Distribution for the Reactions of 2-Mercaptoethanol with α,β-Dinitroolefins

	products (%)				
dinitroolefins[a]	(R*,R*)-8	(R*,S*)-8	9	(E)-10	(Z)-10
(E)-1a	31.5	20.4	7.1	11.9	12.7
(Z)-1a	30.3	20.1	6.8	12.5	13.4
(E)-1b	25.2	17.1	8.2	9.1	10.9
(Z)-1b	26.7	17.0	7.8	9.8	10.8

[a] Reaction time: (Z)-1 = 3 h; (E)-1 = 4 h.

hydroxyethyl)thio]-2-nitrocyclohexene (15), and the unexpected 1-[(2′-hydroxyethyl)thio]-6-nitrocyclohexene (16) (eq 6). It is assumed that product 16 was formed from



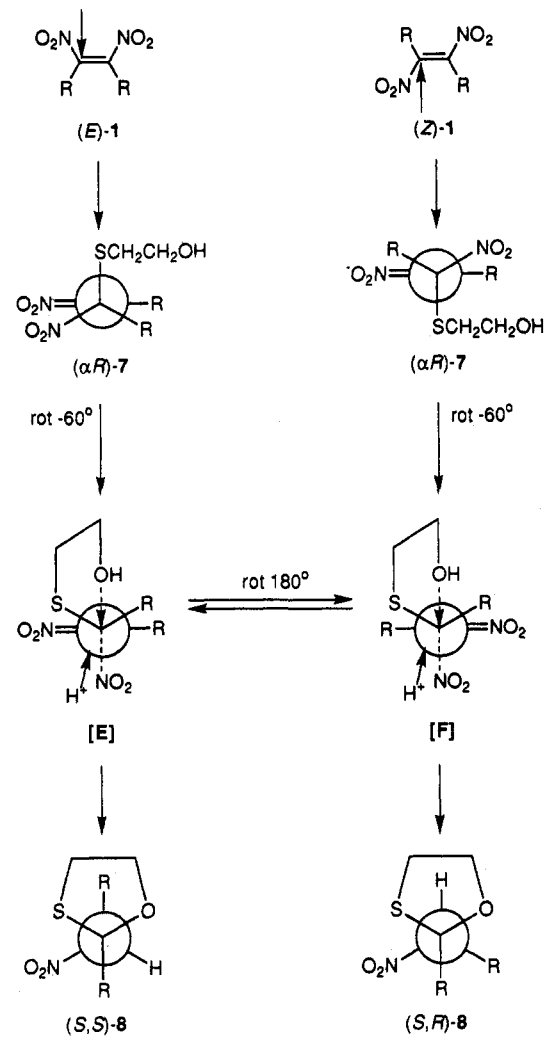
(6)

addition intermediate 14 by trans-elimination of HNO_2.

The reaction shown in eq 4 requires further elaboration. The reactions of (Z)-α,β-dinitroolefins with 2-mercaptoethanol are faster than those of the (E)-isomers by approximately 4:3 because of the extra driving force imparted by the release of steric strain in going from sp^2 to sp^3 hybridization. That the product distribution summarized in Table 1 indicates practically the same distribution for both isomers signifies common intermediates for both isomers.

In the case of α,α-cyclization, both the (R) and (S) configurations around the α-carbon of intermediate 7 are equally likely. Approach of the nucleophile from the top face of (Z)-1 as described in Scheme 2 will result in (αR)-7, approach from the bottom, (αS)-7. Intermediate (αR)-7 will also result from the approach of the nucleophile from the bottom face of (E)-1, and (αS)-7 will result from approach from the top face. In Scheme 2, only (αR)-7, with two conformations [E] and [F], is described. These four intermediates, two (αR)-7 and two (αS)-7, next cyclize by expulsion of the α-nitro group by the hydroxy group of the α-[(2-hydroxyethyl)thio] group, and protonation on the β-carbon occurs. Depending on how the hydroxy group approaches within the intermediate in relation to the β-carbon substituents and on how protonation follows, four products are possible: (αR,βR)-8; (αR,βS)-8; (αS,βR)-8, and (αS,βS)-8. If optical isomers are disregarded, only two products will result: (αR*,βR*)-8 and (αR*,βS*)-8.[14] In our previous paper,[3] we reported that substitution reactions between α,β-dinitroolefins and toluenethiol show a slight preference for conformation [E] over conformation [F]. A similar preference is expected for 1 and is confirmed

Scheme 2



by the slight excess of (Z)-10 over (E)-10. This preference is caused by the weak but attractive interaction of the sulfur atom and the nitro group. Since the product distribution indicates a slight preference for (R*,R*)-8 over (R*,S*)-8, protonation appears to occur in the fashion depicted in Scheme 2.

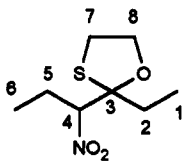
Assignment of Structure and Interpretation of ^1H NMR Spectra. For assignment of NMR peaks, particularly those of 1,3-oxathiolane derivatives (R*,R*)-8 and (R*,S*)-8 and their interpretation, we have to rely on some study of conformation. It is assumed that the conformation in which the nitro group is anti to the oxygen of the oxathiolane ring (as showned in Scheme 2) is the preferred conformer about the C_α–C_β bond of 8. It is also revealed at the same time that the two methylene hydrogens of both the ethyl and the propyl side chains in 8b are separated from each other in both the (R*,S*) and the (R*,R*) forms because of restriction of rotation on each ethyl moiety. By careful interpretation of these peaks, we were able to confidently assign the NMR spectra of the isomers (see Tables 2 and 3). More detailed spectral interpretation and other conformations will be discussed in a subsequent publication.

Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. ^1H NMR chemical shifts are given in ppm relative to internal TMS (0.00 ppm). All reagents were used as

(14) The IUPAC 1976 Recommendations: Rules for the Nomenclature of Organic Chemistry: Section E, Stereochemistry. *Pure Appl. Chem.* 1976, *45*, 11.

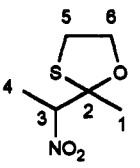
Table 2. Chemical Shifts (ppm) and Coupling Constants (Hz) for 2-(1′-Nitropropyl)-2-ethyl-1,3-oxathiolane in $CDCl_3$ at 300 MHz



compound	δ_1	δ_{2A}	δ_{2B}	δ_4	δ_{5A}	δ_{5B}	δ_6	δ_{7A}	δ_{7B}	δ_{8A}	δ_{8B}
(*R**,*R**)-**8b**	0.85	1.93	1.70	4.85	1.96	1.70	0.80	3.03	2.97	4.19	4.08
(*R**,*S**)-**8b**	0.88	1.75	1.74	4.77	1.97	1.87	0.79	2.95	2.88	4.12	3.99

compound	J_{12}	J_{2A2B}	J_{45A}	J_{45B}	J_{5A5B}	J_{56}	J_{7A7B}	J_{7A8A}	J_{7A8B}	J_{7B8A}	J_{7B8B}	J_{8A8B}
(*R**,*R**)-**8b**	7.2	14.7	11.5	2.5	14.5	7.2	10.5	4.8	5.4	6.3	7.4	9.3
(*R**,*S**)-**8b**	7.3	-	10.8	3.2	14.4	7.3	10.4	5.2	5.3	5.4	7.2	9.3

Table 3. Chemical Shifts (ppm) and Coupling Constants (Hz) for 2-(1′-Nitroethyl)-2-methyl-1,3-oxathiolane in $CDCl_3$ at 300 MHz



compound	δ_1	δ_3	δ_4	δ_{5A}	δ_{5B}	δ_{6A}	δ_{6B}	J_{34}	J_{5A5B}	J_{5A6A}	J_{5A6B}	J_{5B6A}	J_{5B6B}	J_{6A6B}
(*R**,*R**)-**8a**	1.69	4.82	1.67	3.10	3.04	4.33	4.12	6.8	10.4	3.9	5.3	5.5	8.2	9.4
(*R**,*S**)-**8a**	1.71	4.91	1.63	3.17	3.09	4.30	4.24	6.8	10.3	5.9	5.9	6.0	6.0	9.6

supplied without further purification unless specified. The silica gel used for column chromatography was Merck 200–230 mesh.

2,3-Dinitro-2-butene and 3,4-Dinitro-3-hexene (1). The (*E*) and (*Z*) isomers were prepared as previously described.[3]

1,2-Dinitrocyclohexene (11). Nitric acid (50 mL, 70%) was added to 1-nitro-1-cyclohexene (20 g, 15.7 mmol) at −5 °C, and the reaction mixture was stirred vigorously. Sodium nitrite (24 g, 34.8 mmol) was slowly added in small portions over a period of 30 min. After removal of the cooling bath, the reaction mixture was stirred at rt for 4 h. Then the reaction mixture was neutralized with a saturated $NaHCO_3$ solution, and the product was extracted with CH_2Cl_2. The organic layer was washed successively with water and brine, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel to give 8.99 g (33.2%) of 1,2-dinitrocyclohexene: ^1H NMR ($CDCl_3$, 60 MHz) δ 2.65–2.87 (m, 4H), 1.77–1.97 (m, 4H). Anal. Calcd for $C_6H_8N_2O_4$: C, 41.86; H, 4.68; N, 16.28. Found: C, 41.80; H, 4.59; N, 16.42.

General Procedure for the Reactions of 1,2-Ethandithiol with 1,2-Dinitroolefins. A mixture consisting of 1,2-dinitroolefin (2 mmol), $NaHCO_3$ (4.3 g), 1,2-ethanedithiol (1.7 mL), and ethanol (40 mL) was refluxed with stirring for 3 h. The reaction mixture was evaporated and extracted with CH_2Cl_2. The organic layer was washed successively with water and brine, dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. The concentrated residue was distilled to give the following products.

2-(1′-Nitroethyl)-2-methyl-1,3-dithiolane (6a): 89%; ^1H NMR ($CDCl_3$, 60 MHz) δ 4.85 (q, 1H), 3.39 (s, 4H), 2.91 (s, 3H), 2.76 (d, 3H); IR (KBr) 2982, 2928, 1551, 1449, 1381, 1354, 1283, 1080 cm^{-1}; MS *m/z* (%) 193 (M^+, 1.5), 163 (57), 147 (30), 132 (10), 119 (88), 104 (7), 87 (45), 85 (22), 77 (21), 71 (19), 61 (45), 59 (100). Anal. Calcd for $C_6H_{11}NO_2S_2$: C, 37.29; H, 5.74; N, 7.25. Found: C, 37.30; H, 5.77; N, 7.21.

2-(1′-Nitropropyl)-2-ethyl-1,3-dithiolane (6b): 84%; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.74 (d, $^1/_2$H), 4.69 (d, $^1/_2$H), 3.30 (s, 4H), 1.81–2.36 (m, 4H), 1.15 (t, 3H), 0.99 (t, 3H); IR (KBr) 2975, 2932, 2879, 1550, 1458, 1368, 1301, 1278, 1247, 1138, 1083, 860 cm^{-1}; MS *m/z* (%) 221 (M^+, 1.3), 191 (66), 175 (21), 146 (44), 133 (100), 131 (33), 115 (42), 105 (36), 85 (14), 81 (15), 77 (19), 73 (30), 61 (33), 59 (22). Anal. Calcd for $C_8H_{15}NO_2S_2$: C, 43.41; H, 6.83; N, 6.33. Found: C, 43.40; H, 6.84; N, 6.24.

6-Nitro-1,4-dithiaspiro[4.5]decane (12): 78%; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.77 (t, 1H), 3.20–3.35 (m, 4H), 2.66–2.74 (m, 1H), 2.17–2.32 (m, 2H), 2.04–2.11 (m, 1H), 1.73–1.80 (m, 1H), 1.47–1.68 (m, 3H). Anal. Calcd for $C_8H_{13}NO_2S_2$: C, 43.81; H, 5.97; N, 6.39. Found: C, 44.10; H, 5.95; N, 6.51.

General Procedure for the Reactions of 2-Mercaptoethanol with 1,2-Dinitroolefins. To a solution of 1,2-dinitroolefin (2 mmol) and $NaHCO_3$ (4.3 g) in ethanol (30 mL) was added dropwise 2-mercaptoethanol (1.7 mL) in ethanol (10 mL) over a period of 20 min with stirring. The reaction mixture was stirred for 3–4 h at reflux, and ethanol was removed by evaporation. The residue was dissolved in CH_2Cl_2, washed successively with water and brine, and dried over anhyd $MgSO_4$. Removal of the solvent was followed by isolation by silica gel chromatography. The following compounds were obtained:

(*R,*R**)-2-(1′-Nitroethyl)-2-methyl-1,3-oxathiolane ((*R**,*R**)-8a):** ^1H NMR ($CDCl_3$, 300 MHz) δ 4.82 (q, 1H), 4.30–4.36 (m, 1H), 4.08–4.16 (m, 1H), 3.00–3.14 (m, 2H), 1.69 (s, 3H), 1.67 (d, 3H); MS *m/z* (%) 177 (M^+, 1), 162 (1), 147 (12), 131 (22), 116 (11), 103 (76), 88 (6), 87 (10), 77 (67), 71 (30), 61 (28), 60 (100), 59 (44). Anal. Calcd for $C_6H_{11}NO_3S$: C, 40.67; H, 6.26; N, 7.90. Found: C, 40.50; H, 6.32; N, 8.14.

(*R,*S**)-2-(1′-Nitroethyl)-2-methyl-1,3-oxathiolane ((*R**,*S**)-8a):** ^1H NMR ($CDCl_3$, 300 MHz) δ 4.91 (q, 1H), 4.21–4.34 (m, 2H), 3.05–3.21 (m, 2H), 1.72 (s, 3H), 1.63 (d, 3H); MS *m/z* (%) 177 (M^+, 4.3), 162 (1), 147 (15), 131 (14), 116 (9), 103 (71), 88 (6), 87 (8), 77 (50), 71 (23), 61 (23), 60 (100), 59 (37). Anal. Calcd for $C_6H_{11}NO_3S$: C, 40.67; H, 6.26; N, 7.90. Found: C, 40.80; H, 6.43; N, 8.26.

2,2-Bis[(2′-hydroxyethyl)thio]-3-nitro-2-butane (9a): ^1H NMR ($CDCl_3$, 300 MHz) δ 4.84 (q, 1H), 3.91–4.03 (m, 2H), 3.72–3.83 (m, 4H), 2.85–2.95 (m, 4H), 1.74 (d, 3H), 1.69 (s, 3H); LC/MS, *m/z* = 255 (M^+). Anal. Calcd for $C_8H_{17}NO_4S_2$: C, 37.63; H, 6.71; N, 5.49. Found: C, 37.60; H, 6.74; N, 5.48.

(*E*)-2-[(2′-Hydroxyethyl)thio]-3-nitro-2-butene ((*E*)-10a): ^1H NMR ($CDCl_3$, 300 MHz) δ 3.83 (t, 2H), 3.09 (t, 2H), 2.35 (s, 6H), 2.31 (br, 1H), MS *m/z* (%) 177 (M^+, 3.1), 147 (21), 130 (45), 113 (34), 87 (49), 85 (58), 79 (32), 77 (61), 71 (64), 69 (28), 61 (73), 59 (50), 57 (25), 55 (69), 53 (100). Anal. Calcd for $C_6H_{11}NO_3S$: C, 40.67; H, 6.26; N, 7.90. Found: C, 40.80; H, 6.49; N, 8.08.

(*Z*)-2-[(2′-Hydroxyethyl)thio]-3-nitro-2-butene ((*Z*)-10a): ^1H NMR ($CDCl_3$, 300 MHz) δ 3.88 (t, 2H), 3.06 (t, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.98 (br, 1H); MS *m/z* (%) 177 (M^+, 2), 147 (12), 130 (15), 113 (20), 103 (13), 97 (12), 87 (36), 85 (42), 79 (30), 77 (47), 71 (57), 69 (24), 61 (66), 59 (44), 57 (21), 55 (65), 53 (100). Anal. Calcd for $C_6H_{11}NO_3S$: C, 40.67; H, 6.26; N, 7.90. Found: C, 40.90; H, 6.27; N, 7.87.

(R*,R*)-2-(1′-Nitropropyl)-2-ethyl-1,3-oxathiolane ((R*,R*)-8b): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.71 (d, $^1/_2$H), 4.65 (d, $^1/_2$H), 4.26–4.36 (m, 1H), 4.06–4.17 (m, 1H), 2.98–3.04 (m, 2H), 2.14–2.27 (m, 1H), 1.85–2.05 (m, 3H), 1.06 (t, 3H), 0.98 (t, 3H); IR (KBr) 2978, 2940, 2883, 1740, 1551, 1461, 1438, 1367, 1300, 1262, 1215, 1160, 1096, 1055, 1020, 957, 926, 898, 809 cm^{-1}; MS *m/z* (%) 205 (M^+, 0.2), 176 (12), 175 (9), 159 (16), 130 (44), 117 (100), 115 (32), 99 (23), 77 (7), 71 (6), 60 (11), 57 (18). Anal. Calcd for $C_8H_{15}NO_3S$: C, 46.81; H, 7.37; N, 6.83. Found: C, 47.20; H, 7.44; N, 7.08.

(R′,S*)-2-(1′-Nitropropyl)-2-ethyl-1,3-oxathiolane ((R*,S*)-8b): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.82 (d, $^1/_2$H), 4.76 (d, $^1/_2$H), 4.15–4.37 (m, 2H), 3.05–3.11 (m, 2H), 2.07–2.25 (m, 2H), 1.72–1.87 (m, 2H), 1.01 (t, 3H), 0.97 (t, 3H); IR (KBr) 2977, 2941, 2883, 1740, 1552, 1462, 1439, 1366, 1308, 1268, 1214, 1159, 1118, 1051, 1024, 958, 900, 810 cm^{-1}; MS *m/z* (%) 205 (M^+, 0.4), 176 (6), 175 (4), 159 (14), 130 (34), 117 (100), 115 (36), 99 (24), 77 (12), 71 (14), 60 (32), 57 (55). Anal. Calcd for $C_8H_{15}NO_3S$: C, 46.81; H, 7.37; N, 6.83. Found: C, 47.10; H, 7.45; N, 6.82.

3,3-Bis[(2′-hydroxyethyl)thio]-4-nitro-3-hexane (9b): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.68 (d, $^1/_2$H), 4.63 (d, $^1/_2$H), 3.75–3.82 (m, 6H), 2.87–2.96 (m, 4H), 1.93–2.40 (m, 4H), 1.13 (t, 3H), 0.96 (t, 3H); IR (KBr) 3396, 2977, 2940, 2881, 1739, 1658, 1553, 1461, 1366, 1312, 1287, 1137, 1048, 1012, 944, 806, 737, 638 cm^{-1}; LC/MS, *m/z* = 283 (M^+). Anal. Calcd for $C_{10}H_{21}NO_4S_2$: C, 42.38; H, 7.47; N, 4.94. Found: C, 42.30; H, 7.44; N, 5.16.

(E)-3-[(2′-Hydroxyethyl)thio]-4-nitro-3-hexene ((E)-10b): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.79 (t, 2H), 2.98 (t, 2H), 2.81 (q, 2H), 2.79 (br, 1H), 2.48 (q, 2H), 1.19 (t, 3H), 1.10 (t, 3H); IR (KBr) 3388, 2977, 2937, 2878, 1715, 1553, 1521, 1461, 1312, 1174, 1048, 1013, 959, 928, 809, 759 cm^{-1}; MS *m/z* (%) 205 (M^+, 2), 175 (12), 159 (11), 144 (4), 141 (4), 131 (5), 115 (10), 113 (14), 99 (20), 85 (29), 83 (23), 81 (100), 79 (80), 77 (45), 73 (22), 71 (16), 67 (16), 65 (12), 61 (17), 59 (10), 57 (21). Anal. Calcd for $C_8H_{15}NO_3S$: C, 46.81; H, 7.37; N, 6.83. Found: C, 47.10; H, 7.41; N, 6.72.

(Z)-3-[(2′-Hydroxyethyl)thio]-4-nitro-3-hexene ((Z)-10b): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.64 (t, 2H), 3.01 (t, H), 3.27 (br, 1H), 2.47–2.82 (m, 4H), 1.23 (t, 3H), 1.15 (t, 3H); IR (KBr) 3434, 2976, 2937, 2878, 1728, 1556, 1475, 1377, 1294, 1110, 1048, 1019, 928, 872, 810, 765 cm^{-1}; MS *m/z* (%) 205 (M^+, 0.4), 175 (1), 160 (4), 144 (7), 130 (7), 117 (10), 115 (11), 113 (11), 99 (23), 95 (11), 85 (35), 82 (21), 81 (80), 79 (100), 73 (17), 71 (15), 69 (13), 67 (21), 65 (15), 63 (13), 61 (19), 59 (17), 57 (43). Anal. Calcd for $C_8H_{15}NO_3S$: C, 46.8; H, 7.37; N, 6.82. Found: C, 47.10; H, 7.45; N, 6.84.

1-[(2′-Hydroxyethyl)thio]-2-nitrocyclohexene (15): 32%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.88 (t, 2H), 3.07 (t, 2H), 3.00 (br, 1H), 2.65–2.71 (m, 4H), 1.72–1.78 (m, 4H); IR (KBr) 3382, 2941, 2875, 2834, 1627, 1550, 1448, 1372, 1282, 1164, 1049, 1015, 955, 921, 853, 792, 756 cm^{-1}. Anal. Calcd for $C_8H_{13}NO_3S$: C, 47.27; H, 6.45; N, 6.89. Found: C, 47.30; H, 6.48; N, 6.95.

1-[(2′-Hydroxyethyl)thio]-6-nitrocyclohexene (14): 27%; mp 79.5–80 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.43 (d, $^1/_2$H), 6.41 (d, $^1/_2$H), 5.07–5.12 (m, 1H), 3.71–3.77 (m, 2H), 2.74–3.03 (m, 2H), 2.07–2.44 (m, 4H), 1.69–1.80 (m, 2H); IR (KBr) 3381, 2939, 2868, 1577, 1461, 1430, 1294, 1056, 1001 cm^{-1}. Anal. Calcd for $C_8H_{13}NO_3S$: C, 47.27; H, 6.45; N, 6.89. Found: C, 47.10; H, 6.42; N, 7.01.