Chemistry of polyhalogenated nitrobutadienes, 4: reactions of mono-, bis-, and tris(4-tolylthio) derivatives of 2-nitroperchloro-1,3-butadiene with α,β-bifunctional nucleophiles

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Abstract

The reaction of 1-(4-tolylthio)-, 1,1-bis(4-tolylthio)-, or 1,1,3-tris(4-tolylthio)perchloro-2-nitro-1,3-butadiene with α,β-bifunctionalized ethanes such as *N*,*N*-, *N*,*O*,-, *N*,*S*-, *O*,*S*-, *S*,*S*-, or *O*,*O*-bisnucleophiles leads to both, highly functionalized 2-(1-nitroallylidene) derivatives of imidazolidine, oxazolidine, thiazolidine, [1,3]oxathiolane, or [1,3]dithiolane, respectively, and to the open chain, next higher thiolated buta-1,3-diene. The product distribution is highly sensitive to modifications of the reaction conditions: apart from changes of molar ratios of substrates and reagents the reaction temperature plays an important role. Thus, increase of the reaction temperature favours formation of the 1,3-heterocyclic ring. In all cases, extensive spectroscopic investigations have been performed and, in the case of the [1,3]oxathiolane also an X-ray analysis.

Keywords: 2-Nitro-perchloro-1,3-butadiene, imidazolidine, thiol, vinylic substitution, nmr spectroscopy, X-ray structure

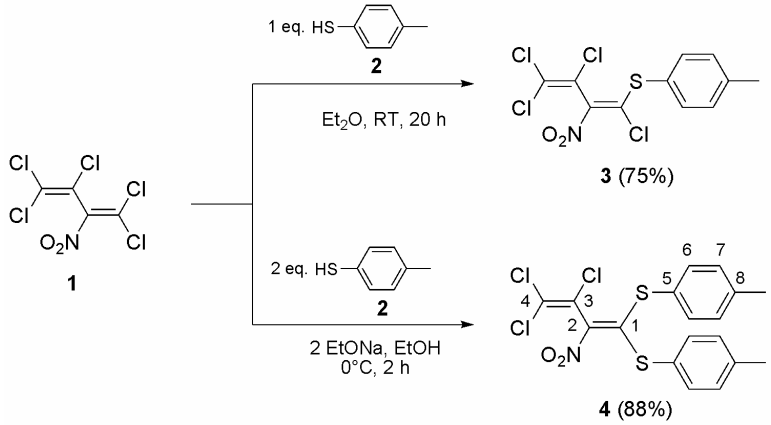
Introduction

Due to their stepped reactivity in S_N reactions, nitro-substituted polyhalogeno-1,3-butadienes have proven to be valuable synthetic precursors for a variety of polyfunctionalized bioactive heterocycles.[1,2] Often times, the building block of choice is 2-nitroperchloro-1,3-butadiene (**1**) which is easily accessible by the introduction of an activating and directing nitro group into 2*H*-pentachloro-1,3-butadiene. Synthetic use of **1** opens access to a quite diverse chemistry, the documentation of which has been started by our group recently.[1] The preferred primary reaction center of **1** is the activated terminal carbon atom C-1 of the nitrodichlorovinyl moiety. This

carbon atom allows for an attack by different nucleophiles in S_NVin processes. Under harsher conditions the internal carbon atom, C-3, is additionally open to the attack of nucleophiles. Therefore, in this fourth paper of our series we present the results of various reactions of 1-(4-tolylthio)-1,3,4,4-tetrachloro-, 1,1-bis(4-tolylthio)-3,4,4-trichloro-, and also 1,1,3-tris(4-tolylthio)-4,4-dichloro-2-nitro-1,3-butadiene with aliphatic *N*,*N*-, *N*,*O*,-, *N*,*S*-, *O*,*S*-, *S*,*S*-, or *O*,*O*-bisnucleophiles as well as some additional conversions of the resulting compounds.

Results and Discussion

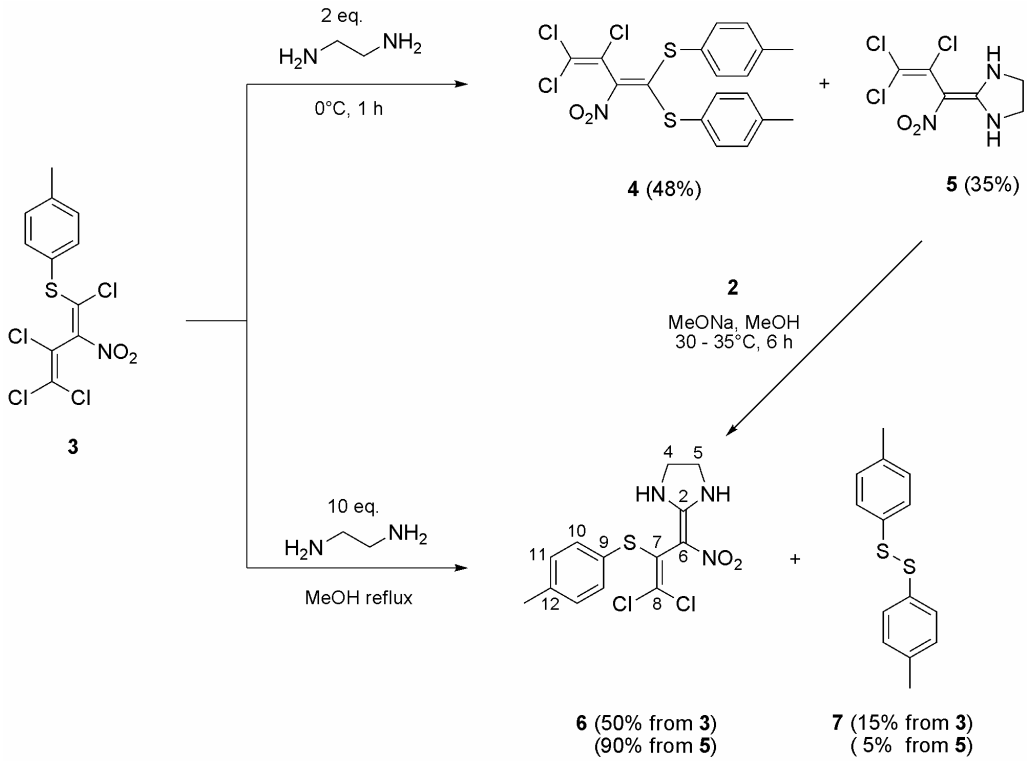
The reaction of pentachloro-2-nitro-1,3-butadiene (**1**) with one molar equivalent of 4-tolylthiol (**2**) in diethyl ether at room temperature furnishes (*Z*)-1,3,4,4-tetrachloro-2-nitro-1-(4-tolylthio)-1,3-butadiene (**3**) as a single isomer (75% yield).[2b] Use of two equivalents of thiol **2** in the presence of sodium ethoxide in ethanol at 0°C (diene:thiol:EtONa = 1:2:2) provides the dithio-substituted trichloronitrobutadiene **4** in 88% yield (Scheme 1).



Scheme 1

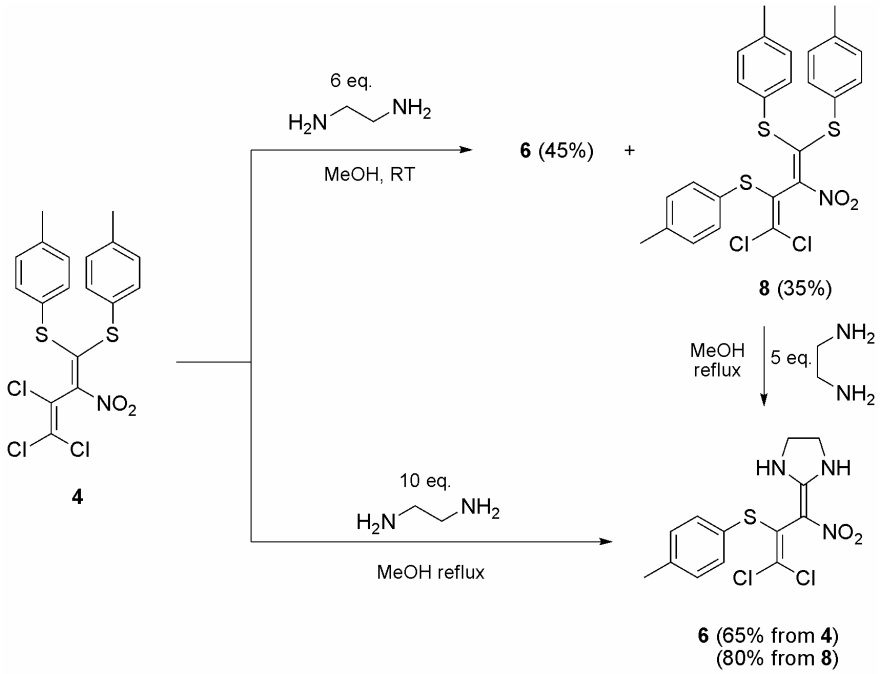
The subsequent vinylic substitution of the monothio compound **3** by means of 1,2-ethylenediamine (MeOH, 0°C,1 h; **3**:amine = 1:2) gives dithio compound **4** (48%) as well as 2-(2,3,3-trichloro-1-nitroallylidene)imidazolidine (**5**) (35% yield). The latter reaction can be classified as a nucleophilic exchange reaction which, starting from the monothio derivative **3**, leads to the 1,1-dithio compound **4** and, in addition, the sulfur-free imidazolidine **5**. Arylthiols are known to be both good nucleophiles as well as good leaving groups. Successive, regioselective reaction of imidazolidine **5** with thiol **2** (MeONa, MeOH, 30-35°C, 6 h) provides the C-3 thio-substituted imidazolidine **6** in very good yield (90%). As a side-product, di(4-tolyl)disulfide (**7**) was obtained (5%) also. This oxidative coupling in the presence of air is quite common for thermal conversions or nucleophilic vinylic substitutions with aryl thiols.[3] At higher temperatures (*e.g.* methanol reflux) and with an excess of ethylenediamine, the direct conversion

of the mononitrodiene **3** into the imidazolidine **6** was feasible, but the yield dropped down to 50% and, unfortunately, the undesired disulfide **7** then was produced in 15% yield (Scheme 2). The first mentioned imidazolidine **5** is speculated to be a reaction intermediate, the trichlorovinyl group of which is attacked by an *in situ* formed arenethiolate anion. Apparently, this pathway ends up with the release of a chloride anion, which for its part forms the corresponding hydrochloride with excess ethylenediamine.



Scheme 2

Moreover, reacting the bis-tolylthiodiene **4** with a six-fold excess of ethylenediamine at room temperature (MeOH, 10 h) gave the imidazolidine **6** in 45% yield accompanied by 10% of the disulfide **7** and 35% of 1,1,3-tris(4-tolylthio)-4,4-dichloro-2-nitro-1,3-butadiene (**8**). Turning to methanol reflux conditions (7 h) afforded the imidazolidine **6** in higher yield (65%), which apparently was due to the *in situ* reaction of the initially generated tris-arylthio compound **8**. This assumption was verified by the conversion of independently synthesized tris(arylthio)nitrodiene **8**, which also gave **6** in 80% yield (Scheme 3). It should be mentioned that the released 4-tolylthiolate anion again formed the disulfide **7**, which was isolated in 15% yield.



Scheme 3

In contrast to expectations by analogy to the nucleophilic exchange reaction described above, no 1,1,3,4-tetrakis(4-tolylthio) derivative was observed, potentially due to steric hindrance at the α-tolylthio and β,β-dichlorovinyl positions. Similar substitution reactions had been published starting from 1,1-bis(methylsulfanyl)-2-nitroethylene and α,ω–diaminoalkanes, which led to the corresponding 1,3-diamino heterocyclic compounds.[4] However, the conversion of imidazolidine **6** with sodium 4-tolylthiolate in ethanol (reflux, 10 h), as well as the reaction with a fivefold excess of 1,2-ethylenediamine (EtOH reflux, 5 h) failed, perhaps due to the decreased electrophilicity of the terminal carbon atom of the β,β–dichloro-α–(4-tolyl)thio-vinyl group (in contrast to the same carbon within the α,β,β–trichlorovinyl moiety, *i.e.* lacking the thio substitutent).

Discussion of the NMR and IR data for compounds 1, 3, 4 and 8

First of all, it is worthy of note that our spectroscopic data are in accordance with those reported by Ibis et al.[2a] but, apparently, the reported tris(4-tolylthio)dichloronitro-1,3-butadiene is not a 1,1,4-substituted, but a 1,1,3-tris(4-tolylthio) regioisomer instead. This indication was proven by X-ray analysis and, in addition, by an independent synthesis of imidazolidine **6** starting from the tris(thio)nitrodiene **8**.

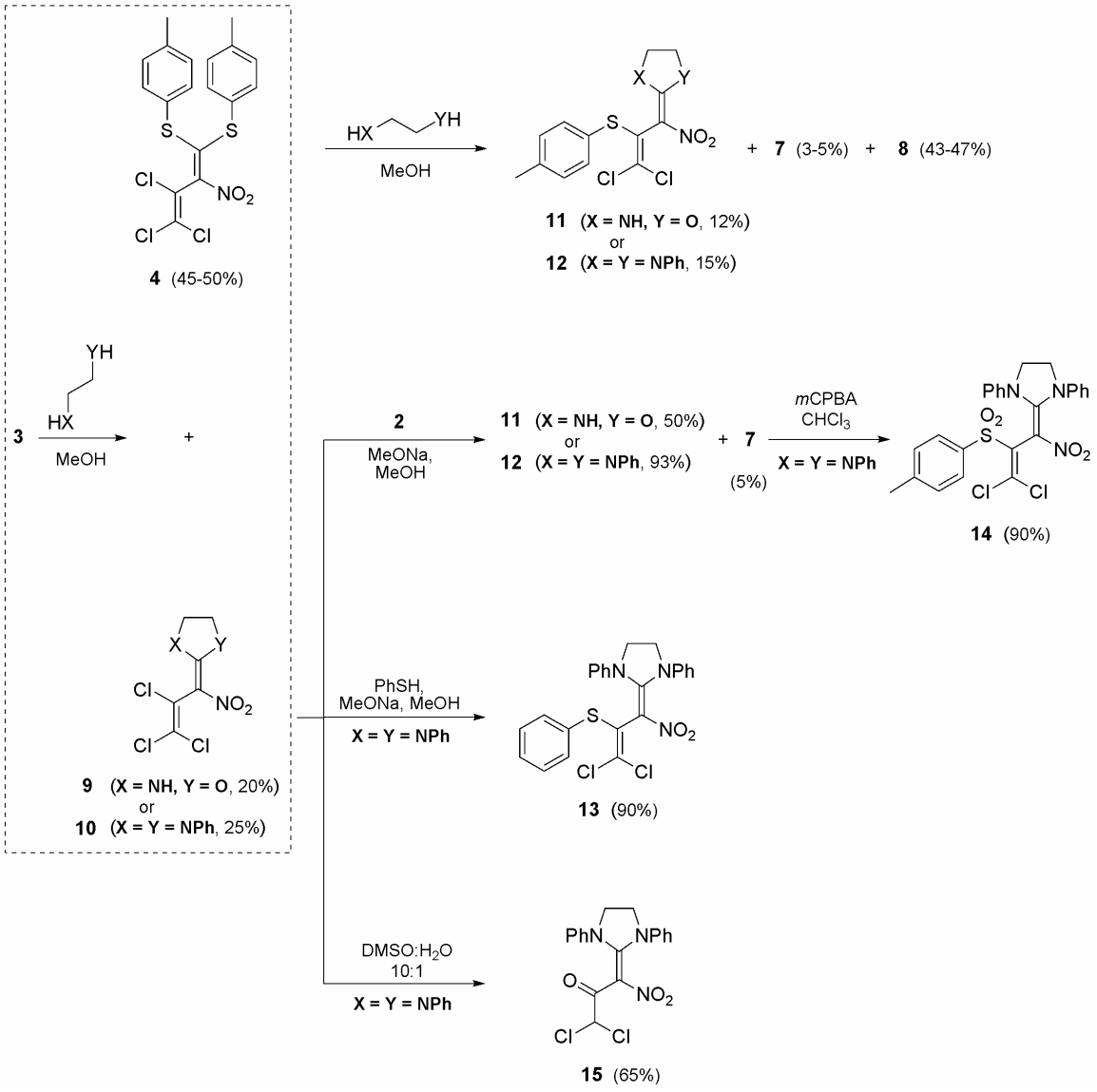
The nmr shifts of the C-1 carbon atoms of compounds **3**, **4**, and **8** (the atom numbering of these non-heterocyclic compounds follows the example in Scheme 1) appear relatively downfield around 160 ppm, whereas the NO_2-bearing carbon atoms C-2 each show their resonance, a broadened less intense peak, between 138 and 141 ppm. In accordance with the

assignment of carbon nmr data for similar nitrobutadienes,[5] the individual C-3 and C-4 carbons each provide chemical shift values around 122 ppm and 129 ppm, respectively. In addition, the ^{13}C-NMR shifts within the thioaryl units of **3**, **4**, and **8** have been assigned by appropriate incremental shifts for substituted benzene derivatives.[6] The proton nmr data show typical ppm values and splitting patterns (AA'BB'- system of the aromatic protons within the range 6.63-7.60 ppm and 2.30-2.43 ppm for the methyl singlets, respectively). Furthermore, some characteristic bands in the IR spectra of compound **3**, **4**, and **8** should be mentioned: The C=C stretching band is observed within the range 1572-1606 cm^{-1}, and the NO_2 groups range from 1512 to 1531 cm^{-1} (asymmetric stretching) and from 1310 to 1321 cm^{-1} (symmetric stretching). An IR band around 510 cm^{-1} is assumed to stem from the C-S vibration, even though somewhat higher values can be found in the literature.[7]

In the course of the vinylic substitutions, the reaction of the monothio derivative **3** with ethanolamine or *N,N'*-diphenyl-ethylenediamine in methanol afforded the bis(4-tolylthio)diene **4** (45-50%) and the corresponding heterocyclic compounds, *i.e*. the oxazolidine **9** or the imidazolidine **10**, respectively, in 20 to 25% chemical yield. The disproportionation of the bis(arylthio)nitrodiene **4**, effected by one of the bisnucleophiles mentioned above at room temperature, revealed the tris(arylthio)butadiene **8** (43-47%), the disulfide **7** (3-5%), and the heterocycles **11** or **12** (12-15%). In analogy to the reaction of the imidazolidine **6** with 4-tolylthiol (**2**), the pre-formed heterocycle **9** was reacted with **2**, whereas **10** additionally was combined with the unsubstituted benzenethiol in sodium methoxide solution at slightly elevated temperature. Even though the resulting oxazolidine derivative **11** was obtained in 50% yield, the imidazolidines **12** and **13** were accessible in 90-93% yield (with traces of the side product **7**). Some further attempts to convert the tris(4-tolylthio)butadiene **8** to the oxazolidine **11** or to the imidazolidine **12** with ethanolamine or *N,N'*-diphenyl-ethylenediamine, respectively, were unsuccessful. In detail, at room temperature no reaction occurs, whereas at elevated temperatures (60-65°C) an inseparable complex mixture of products was obtained. Aside from steric reasons (*i.e*. the presence of three aromatic rings has to be taken into account), especially in the case of ethanolamine, this result was not unexpected due to the fact that the nucleophilic oxygen of ethanolamine represents a harder nucleophilic center (following Pearson´s concept[8]) than the nitrogen of the amino group. The former should be able to initiate the fragmentation of the double bond of the C(NO_2)=C(S-)S- unit, as is known from the alcoholysis of 2-nitroperchloro-1,3-butadiene (**1**), which leads to 1,1,2-trichloro-3-nitro-1-propene as well as to the corresponding esters of 2-nitro-3,4,4-trichlorocrotonic acid.[9] Additionally, with the imidazolines **12** and **13** in hand, some subsequent synthetic steps appeared to be useful. Thereby, the oxidation of the sulfur in **12** by means of 77% *m*-chloroperbenzoic acid was performed ($CHCl_3$, r.t., 30 h), providing the sulfone **14** in 90% yield. In addition, the saponification of the internal chloro substituent of the trichlorvinyl group in **10** with aqueous dimethylsulfoxide at 80°C gave the synthetically interesting nitrobutenone **15** in 65% yield (Scheme 4).

Applying sulfur-containing nucleophiles, the reaction of monothiobutadiene **3** with cysteamine hydrochloride (MeOH, 0°C) in the presence of sodium methoxide

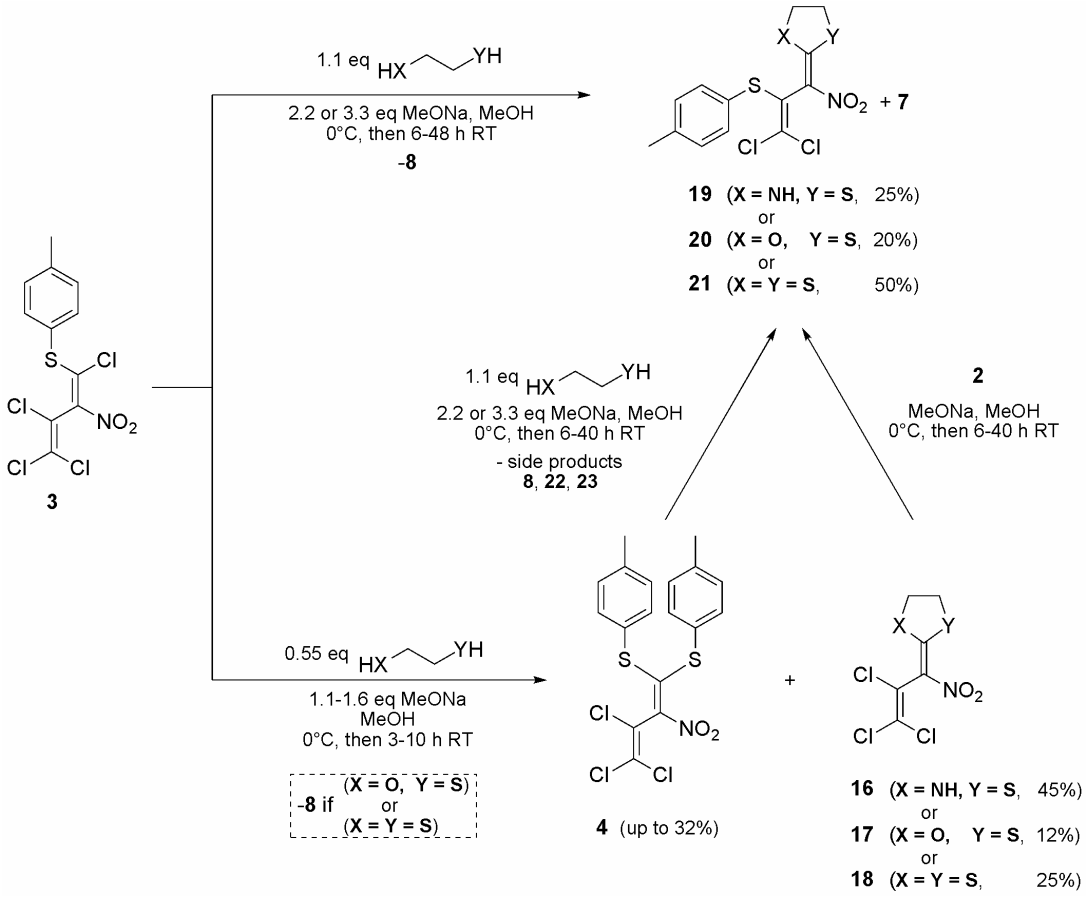
(**3**:cysteamine:MeONa = 2:1.1:3.3) furnished the bis(4-tolylthio)diene **4** (32%) as well as the thiazolidine **16** (45%). It is noteworthy that the corresponding reaction of **3** with other *S*-nucleophiles (e.g. 2-mercaptoethanol or 1,2-ethanedithiol with the ratio **3**:thiol:MeONa = 1:0.55:1.1) occurred with drastically decreased selectivity, in comparison to *N*,*N*-, *N*,*O*-, or *N*,*S*-bisnucleophilic reagents. In detail, the dithiobutadiene **4** was found (10-15%) as well as the tris(arylthio)nitrodiene **8** (5-10%) and the oxathiolane **17** (12%) or the dithiolane **18** (25%), respectively. Unfortunately, as a side-product the disulfide **7** was formed in about 5% yield.



Scheme 4

Under room temperature conditions and with an excess of sodium methoxide (*i.e.* **3**:cysteamine hydrochloride:MeONa = 1:1.1:3.3 or otherwise **3**:mercaptoethanol or 1,2-

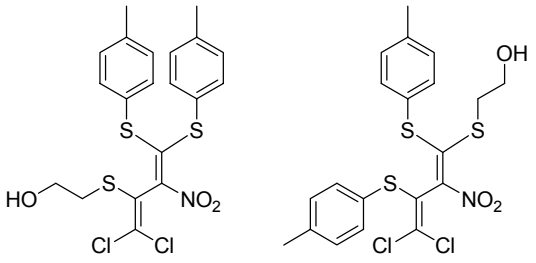
ethanedithiol:MeONa = 1:1.1:2.2), the formation of tris(arylthio)nitrodiene **8** (5-13%), the corresponding heterocyclic 4-tolylthio derivatives **19**, **20** or **21** (in 25%, 20% and 50% yield, respectively), and the disulfide **7** (5-8%) was observed. Applying bisthionitrobutadiene **4** as starting material (and cysteamine hydrochloride, or 2-mercaptoethanol or 1,2-ethanedithiol, respectively), the tris-thiobutadiene **8** (5-20%) and the disulfide **7** (5%) were observed together with the expected cyclic products, thiazolidine **19** (75%), oxathiolane **20** (15%), or dithiolane **21** (40%) (Scheme 5).



Scheme 5

The distribution of reaction products again underlines the higher selectivity of cysteamine contrary to the conversion of **4** using 1,2-ethanedithiol or mercaptoethanol. In the latter case, additionally a regioisomeric mixture of 1,1-bis(4-tolylthio)-4,4-dichloro-3-(2-hydroxyethyl)thio-2-nitro-1,3-butadiene (**22**) (6%) and the corresponding 1,3-bis(4-tolylthio)-4,4-dichloro-1-(2-hydroxyethyl)thio-2-nitro-1,3-butadiene (**23**) (9%) was isolated and investigated by nmr spectroscopy. The aforementioned threefold sulfur-substituted nitrobutadiene **22** obviously is generated *via* a competitive reaction pathway where the internal carbon atom of the

trichlorovinyl group is attacked by mercaptoethanol. On the other hand, **23** seemed to be a precursor of the oxathiolane derivative **20**.



22 **23**

Figure 1. Isolated side products.

As a particular conclusion, the sulfur-substituted heterocyclic compounds **19-21** each are accessible in good yields (60-65%) starting from the heterocyclic trichloro-substituted precursors **16-18** and the sodium salt of 4-tolylthiol (reaction conditions: MeOH, 0°C to r.t., 6-8 h).

Furthermore we have to discuss our own results in contrast to a previous structural proposal: It was recently published by Ibis[2a] that the reaction of monothionitrodiene **3** with cysteamine hydrochloride or with 1,2-ethanedithiol (EtOH/NaOH, NaOH, r.t., 1-2 h) led to 3,4-dihydro-2*H*-1,4-thiazocine or 2,3-dihydro-1,4-dithiocine derivatives, respectively. In this paper, we wish to present proof of formation of the five-membered 2-[2-(4-tolyl)thio-3,3-dichloro-1-nitroallylidene]thiazolidine (**19**) or dithiolane **21**, instead. Indeed, due to their molecular structure, formation of eight-membered rings seems to be feasible, though less likely. Therefore, we repeated the synthesis described in the literature and, additionally, synthesized the compound in question by applying an alternative reaction pathway. More precisely, we started also from thiazolidine **16** and sodium 4-tolylthiolate and thus obtained the same five-membered compound **19** which had been identified by us previously, initially by nmr methods. To put all doubts aside, we repeated the reaction with diene **3** / 1,2-ethanedithiol and dithiolane **18** / sodium 4-tolylthiolate, respectively. Both of these reactions revealed the spectroscopically identical product, i.e. dithiolane **21**. Finally, an X-ray analysis of the corresponding oxathiolane **20** unambiguously proved the presence of only five-membered heterocyclic ring systems (Figure 2).

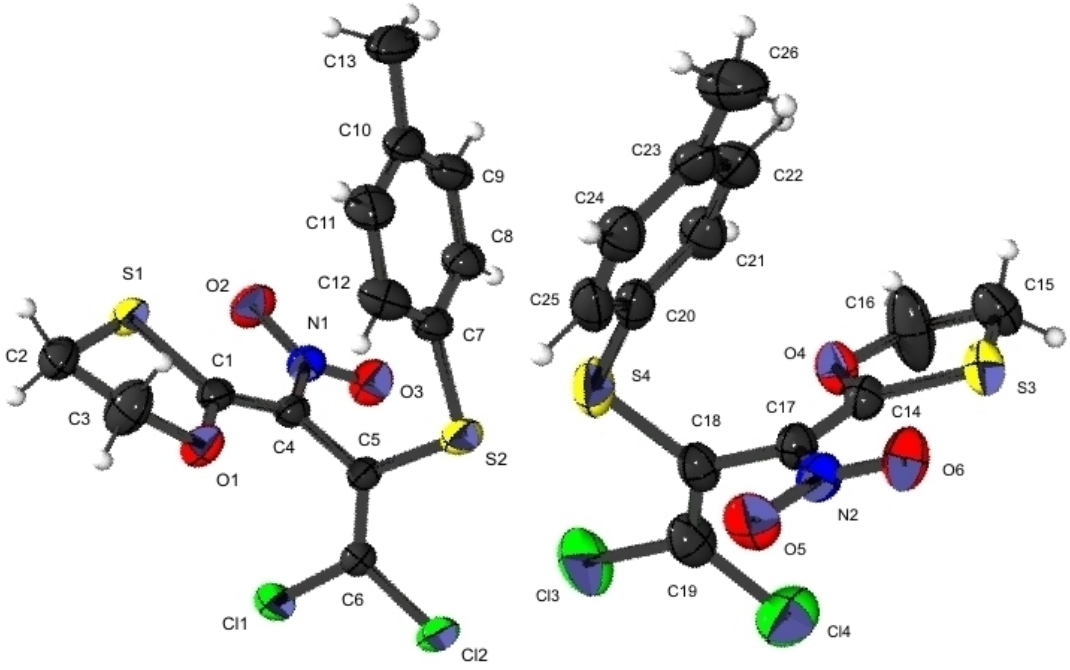


Figure 2. X-ray analysis of 2-[1-(*Z*)-nitro-2-(4-tolyl)thio-3,3-dichloro-allylidene]-[1,3]oxathiolane (**20**).

Moreover, the reaction of the monothio derivative **3** with the disodium salt of 1,2-ethanediol initially failed, but raising the temperature to 50°C revealed the bis(4-tolylthio)diene **4** (45%), but not the corresponding heterocyclic 2-(2,3,3-trichloro-1-nitroallylidene)-1,3-dioxolane. In the case of the reaction of nitrodiene **3** and an equimolar amount of 1,2-ethanediol and sodium metal in benzene, again **4** was formed (45%). Applying the same reaction conditions to compound **4** as the substrate furnished the tris(arylthio)nitrobutadiene **8** (43%) and the disulfide **7** (5%).

Discussion of the NMR data for compounds 5, 6, 9-14, and 16-21

The particular carbon atoms in the 2-position of these heterocyclic compounds (for atom numbering refer to compound **6** in Scheme 2) show their resonance in a range between 155 and 178 ppm, depending on the kind of heteroatoms, *i.e.* 155 to 159 ppm (N-*C*-N), around 165 ppm (N-*C*-O), 168 ppm (N-*C*-S), 171 ppm (S-*C*-S), and 177 ppm (S-*C*-O) ppm. The ppm value for the broad resonance of the C-6 carbon atom shows by far the highest range: 102.6 to 105.8 ppm (imidazolidines and oxazolidines), and 113.1 to 130.1 ppm (thiazolidines, oxathiolanes, and dithiolanes). Moreover, apart from the sulfone **14** and nitrobutenone **15**, the ^{13}C-NMR peaks of the C-7 and C-8 carbon atoms of **5**, **6**, **9-14**, and **9-21** were found within 117.0-125.8 ppm (C-8), and 125.7-131.0 ppm (C-7), respectively. Consequently, the C-7 and C-8 carbon atoms of the sulfone **14** resonate much deeper, *i.e.* at 136.9 and 137.4 ppm. Among the expected appearance of the proton nmr spectra of **6**, **11**, **12**, **14**, and **19-21**, especially as AA'BB'- systems, the NH group of imidazolidine **5** exhibits a proton signal around 8.5 ppm. This chemical shift, typical for

nitroenamines[4,10] is a result of the intramolecular hydrogen bonding shown in Fig. 2. In addition, both of the amino groups in **5** are spectroscopically identical on account of the tautomerism (see Fig. 2). After introduction of the bulky 4-tolylthio substituent, the former free rotation around the partial C(2)-C(6) single bond becomes a hindered one. Thus, two separate proton nmr signals of the amino groups are observed in **6**. The associated NH proton appears at 8.4 ppm, whereas the unassociated NH group resonates at 5.7 ppm (in $CDCl_3$).

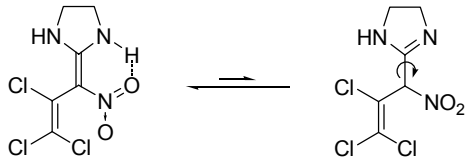


Figure 3. Tautomeric forms of **5**.

Experimental Section

General Procedures. Melting points were measured on a Büchi 520 apparatus and were uncorrected. NMR spectra were obtained on a BRUKER Avance with 400 MHz proton frequency. ^{1}H-NMR spectra in $CDCl_3$ were referenced to tetramethylsilane (TMS) as internal standard at 0.0 ppm; ^{13}C-NMR spectra refer to the solvent signal center at 77.0 ppm ($CDCl_3$). In case of DMSO-d_6, the solvent peak was set to 2.50 ppm (^{1}H) and 39.70 ppm (^{13}C), respectively. Coupling constants are given in Hertz. IR spectra were obtained on a BRUKER 'Vector 22' FT IR as film between NaCl plates or as KBr pellet. UV/Vis spectra were measured on a HP 8452a (Hewlett-Packard) and refer to ethanol as solvent and a concentration of 10^{-4} mol/l. Mass spectra were recorded on a Hewlett Packard 'MS 5989B' with direct inlet. All masses of chlorine containing molecules or fragments refer to the isotope ^{35}Cl. High-resolution mass spectra were measured with a Bruker Daltonik 'APEX IV' 7 T fourier transform ion cyclotron resonance mass spectrometer with electrospray ionisation at Institute of Organic Chemistry, University of Göttingen. Elemental analyses were performed by the Institute of Pharmaceutical Chemistry, Braunschweig Technical University. TLC analyses were carried out on Merck-plates coated with silica gel (60 F 254). Silica gel 60 was used also for column chromatography.

Pentachloro-2-nitro-1,3-butadiene (**1**) was prepared from 2*H*-pentachloro-1,3-butadiene in 53% yield (bp 69-71°C) following the literature procedure.[12]
IR (neat, cm^{-1}) 1616, 1570, 1544 (NO_2), 1330 (NO_2), 1190, 1003, 947, 911, 834, 764, 738, 703, 676; ^{13}C-NMR ($CDCl_3$) δ 143.1, 136.8, 130.6, 119.1
1,3,4,4-Tetrachloro-2-nitro-1-(4-tolylthio)-1,3-butadiene (**3**). At room temperature mercaptan **2** (4.72 g 38.0 mmol) was added to a stirred solution of nitrobutadiene **1** (10.0 g, 36.9 mmol) in diethyl ether (20 ml). After stirring for 20 h the solvent was removed *in vacuo*. Subsequent

addition of methanol (20 ml) afforded a solid which was filtered off and washed twice with cold methanol (2 × 10 ml). The resulting product was dried *in vacuo* to give 9.94 g of the thiodiene **3** (75%), R_f = 0.72 (diethyl ether/petrol ether 1:3); mp 110-111°C (Lit.[2a] 112-113°C). IR (KBr, cm^{-1}) 1606, 1595 (C=C), 1531 (NO_2), 1492, 1475, 1321 (NO_2), 1295, 1195, 1003, 923, 826, 809, 759, 686; ^{1}H-NMR ($CDCl_3$) δ 7.42 (2H, d, *J*=8.0 Hz), 7.28 (2H, d, *J*=8.0 Hz), 2.43 (3H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 158.5 (C-1), 142.1 (C-8), 137.8 (C-2), 135.8 (C-6), 130.4 (C-7), 128.6 (C-3), 125.0 (C-5), 121.3 (C-4), 21.4 (Me).

1,1-Bis(4-tolylthio)-3,4,4-trichloro-2-nitro-1,3-butadiene (**4**). To a cold solution of 10.00 g (36.9 mmol) nitrodiene **1** and 9.32 g (75 mmol) of thiol **2** in ethanol (50 ml) was added dropwise at 0°C a solution of 5.02 g (74 mmol) sodium ethoxide in 10 ml of ethanol within 10 min. After 2 h at 0°C with stirring the precipitate was filtered off, washed with water and twice with cold methanol (2 × 20 ml). Removal of the solvents afforded 14.50 g (88%) pure product. R_f = 0.68 (diethyl ether/petrol ether 1:3), mp 117-118°C (Lit.[2a] 89-91°C). IR (KBr, cm^{-1}) 1596 (C=C), 1512 (NO_2), 1456, 1315 (NO_2), 1285, 1193, 998, 932, 905, 819, 798, 761, 684; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.01 (4H, m), 6.96 (2H, d, *J*=8.0 Hz), 6.85 (2H, d, *J*=8.0 Hz), 2.35 and 2.32 (each 3H, s, Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3 (C-1), 140.7 (C-2), 140.2 and 139.2 (C-8), 134.5 and 131.7 (C-6), 129.8 and 129.5 (C-7), 128.1 (C-3), 127.5 and 126.6 (C-5), 122.5 (C-4), 21.4 and 21.2 (Me).

General procedure 1. Reaction of diene 3 with 1,2-ethylenediamine to give 4 and 2-(2,3,3-trichloro-1-nitroallylidene)imidazolidine (5)

A solution of 0.36 g (6.0 mmol) 1,2-ethylenediamine in methanol (5 ml) was added to a suspension of 1.08 g (3.0 mmol) nitrodiene **3** in methanol (10 ml) at 0°C and stirred for 1 h at the same temperature. The precipitated bisthiodiene **4** was filtered off, washed with water and cold methanol (2 × 3 ml) and dried under reduced pressure to yield 0.64 g of **4** (48%). The collected filtrates were carefully neutralized by means of hydrochloric acid and stirred with additional 50 ml of water. Again, the solid was filtered off, then washed with water and small portions of diethyl ether (3 × 5 ml). Recrystallization from methanol gave 0.27 g (35%) of imidazolidine **5**. R_f = 0.66 (diethyl ether/acetonitrile 5:1); mp 184-185°C (Lit.[14] 185°C); IR (KBr, cm^{-1}) 3371, 3108, 1612 (C=C), 1588, 1551 (NO_2), 1474, 1371 (NO_2), 1288, 1107, 942, 900, 818, 706; UV: λ (log ε) 216 (4.47), 324 (4.55); ^{1}H-NMR (DMSO-d_6) δ 8.52 (2H, br s, NH), 3.66 (4H, br s, NCH_2); ^{13}C-NMR (DMSO-d_6) δ 157.6 (C-2), 125.7 (C-7), 124.5 (C-8), 103.4 (C-6), 43.7 (C-4,5).

General procedure 2. Reaction of monothiodiene 3 with 1,2-ethylenediamine to give 2-[3,3-dichloro-1-nitro-2-(4-tolyl)thio-allylidene]imidazolidine (6) accompanied by disulfide 7

A suspension of 1.0 g (2.8 mmol) of **3** and 1.7 g (28 mmol) 1,2-ethylenediamine in methanol (15 ml) was stirred for 6 h at room temperature and subsequently heated to reflux (10 h). After cooling down to 5°C the surplus amine was slowly neutralized with hydrochloric acid. The resulting salt then was removed by means of cold water (100 ml). The residual solid was sucked

off and washed subsequently with water and petrol ether (4 × 10 ml). The resulting crude product was recrystallized from dichloromethane to afford 0.48 g (50%) of imidazolidine **6**. The mother liquor contained 0.10 g (15%) of disulfide **7**.

The reaction of bisthiodiene **4** with 1,2-ethylenediamine to give imidazolidine **6** (65%) and disulfide **7** (5%) was also carried out according to this general procedure 2. The reaction time was 2 h at 20°C and 7 h at methanol reflux conditions.

2-[3,3-Dichloro-1-nitro-2-(4-tolyl)thioallylidene]imidazolidine (6). $R_f = 0.70$ (diethyl ether/acetonitril 5:1); mp 194-195°C; IR (KBr, cm^{-1}) 3382, 3110, 1601 (C=C), 1576, 1549 (NO_2), 1491, 1376 (NO_2), 1291, 1110, 935, 895, 816, 701; UV: λ (log ε) 208 (4.28), 254 (4.11), 330 (4.15); ^{1}H-NMR ($CDCl_3$) δ 8.43 (1H, br s, NH), 7.31 (2H, d, *J*=8.2 Hz, Ph), 7.08 (2H, d, *J*=8.2 Hz, Ph), 5.51 (1H, br s, NH), 3.70 (4H, br s, NCH_2), 2.31 (3H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 159.2 (C-2), 139.8 (C-12), 134.6 (C-10), 129.6 (C-11), 129.1 (C-7), 126.3 (C-9), 119.2 (C-8), 104.6 (C-6), 43.9 (C-4,5), 21.3 (Me); MS (EI), *m/z*: 345 (M^+). HRMS calcd. for $C_{13}H_{13}Cl_2N_3O_2S+H^+$: 346.0178, found: 346.0181.

Di(4-tolyl)disulfide (7). $R_f = 0.79$ (diethyl ether/petrol ether 1:10); mp 43-45°C. (Lit.[15] 44-45°C); IR (KBr, cm^{-1}) 2914, 1633, 1488, 1397, 1117, 1076, 1014, 835, 801; ^{1}H-NMR ($CDCl_3$) δ 7.35 (4H, d, *J* = 8.0 Hz), 7.05 (4H, d, *J* = 8.0 Hz), 2.27 (6H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 137.3 (C-4), 133.8 (C-1), 129.7 (C-2), 128.4 (C-3), 21.0 (Me).

General procedure 3. Reaction of bisthiodiene 4 with 1,2-ethylenediamine to give imidazolidine 6 and tristhiodiene 8

A suspension of 1.07 g (2.4 mmol) diene **4** and 0.85 g (14 mmol) 1,2-ethylenediamine in methanol (15 ml) was stirred for 10 h at room temperature. After cooling down to 5°C the waste amine was carefully neutralized by means of hydrochloric acid. The precipitate of **8** was sucked off and washed with methanol (3x7 ml), petrol ether (3x7ml) and finally with water (3x15 ml). The solid was dried under reduced pressure to give 0.45 g (35%) diene **8**. Subsequently, the collected solvents were combined with cold water (100 ml) to obtain an additional solid which was filtered off, washed with water and petrol ether (4x10 ml). Recrystallization from dichloromethane gave 0.37 g (45%) of imidazolidine **6**.

1,1,3-Tris(4-tolylthio)-4,4-dichloro-2-nitro-1,3-butadiene (8). $R_f = 0.58$ (diethyl ether/petrol ether 1:3); mp 163-165°C (Lit.[17] 165-167°C); IR (KBr, cm^{-1}) 1594, 1572 (C=C), 1513 (NO_2), 1490, 1463, 1310 (NO_2), 1282, 1191, 997, 924, 818, 806, 754, 690; UV: λ (log ε) 206 (4.62), 223 (4.53), 262 (4.26), 386 (4.00); ^{1}H-NMR ($CDCl_3$) δ 7.45 (2H, d, *J*=8.0 Hz), 7.17 (2H, d, *J*=7.8 Hz), 6.88 (4H, d, *J*=8.0 Hz), 6.63 (4H, dd, *J*=7.3, 7.8 Hz), 2.40 and 2.30 (each 3H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 158.7 (C-1), 140.5 (C-2), 140.3, 139.4, and 138.6 (C-8), 135.8, 133.8, and 131.6 (C-6), 130.0, 129.3, and 129.1 (C-7), 129.9 (C-3), 127.8, 127.5, and 125.4 (C-5), 121.3 (C-4), 21.4, 21.3, and 21.2 (Me); MS (EI), *m/z*: 533 (M^+).

General procedure 4. Reaction of imidazolidine 5 with sodium 4-tolyl-thiolate

A solution of 0.22 g (4.0 mmol) sodium methylate in methanol (5 ml) was added at 0°C to a vigorously stirred suspension of 1.0 g (3.9 mmol) of **5** and 0.50 g (4.0 mmol) 4-tolylmercaptane in 15 ml of methanol. The mixture was stirred for 2 h at room temperature and for additional 6 h at 35°C. Subsequently, after cooling down to 5°C, a few drops of conc. hydrochloric acid were added and the reaction mixture was taken up in cold water (100 ml). A precipitate was obtained which was sucked off and successively washed with methanol (3 × 7 ml), petrol ether (3 × 7 ml) and water (3 × 15 ml). Finally, recrystallization from dichloromethane yielded 1.16 g of imidazolidine **6** (90%). In addition, 0.03 g (5%) of the disulfide **7** were received from the mother liquor.

The reactions of monothiodiene **3** with ethanolamine (to give 55% of bisthiodiene **4**) and 1,2-ethylenediamine (50% of **4**) have been performed in accordance with the general procedure 1. In the latter case, the reaction required 3 h at room temperature.

2-(2,3,3-Trichloro-1-nitroallylidene)oxazolidine (9). Yield: 20%. $R_f = 0.64$ (diethyl ether/acetonitrile 5:1); mp 156-158°C (Lit.[18] 156-157°C); IR (KBr, cm^{-1}) 3345, 1621 (C=C), 1589 (NO_2), 1478, 1429, 1365 (NO_2), 1313, 1259, 1093, 967, 933, 825, 712; UV: λ (log ε) 214 (4.07), 322 (4.02). ^{1}H-NMR ($CDCl_3$) δ 9.24, br s (1 H, NH); 4.80, t (2 H, *J*=8.9 Hz, OCH_2); 4.08, t (2 H, *J*=8.9 Hz, NCH_2); ^{13}C-NMR ($CDCl_3$) δ 164.9 (C-2), 127.0 (C-7), 121.3 (C-8), 106.4 (C-6), 70.1 (C-5), 43.9 (C-4).

2-(2,3,3-Trichloro-1-nitroallylidene)-1,3-diphenylimidazolidine (10). Yield: 25%.

$R_f = 0.68$ (diethyl ether/acetonitrile 5:1); mp 250-251°C; IR (KBr, cm^{-1}) 3059, 2887, 1595 (C=C), 1525 (NO_2), 1500, 1449, 1333 (NO_2), 1295, 1153, 1019, 921, 812, 760, 693; UV: λ (log ε) 206 (4.34), 226 (4.19), 302 (4.17), 368 (3.91); ^{1}H-NMR (DMSO-d_6) δ 7.35 (10H, m, Ph), 4.31 (4H, br s, NCH_2); ^{13}C-NMR (DMSO-d_6) δ 155.9 (C-2), 139.9 (C_{aryl}-1'), 129.5 (C_{aryl}-3'), 127.1 (C_{aryl}-4'), 126.6 (C-7), 122.5 (C_{aryl}-2'), 119.6 (C-8), 104.2 (C-6), 50.9 (C-4,5); MS (EI), *m/z*: 409 (M^+). HRMS calcd. for $C_{18}H_{14}Cl_3N_3O_2+H^+$: 410.0224, found: 410.0223.

The reaction of bisthionitrodiene **4** with ethanolamine or 1,2-ethylenediamine to give tristhiodiene **8** (43-47%), disulfide **7** (3-5%), and the heterocyclic compounds **11** or **12**, respectively, was carried out according to the general procedure 3.

2-[3,3-Dichloro-1-nitro-2-(4-tolyl)thioallylidene]oxazolidine (11). Yield: 12%. $R_f = 0.72$ (diethyl ether/acetonitrile 5:1); mp 132-133°C; IR (KBr, cm^{-1}) 3342, 2921, 1620 (C=C), 1572 (NO_2), 1479, 1428, 1373, 1319 (NO_2), 1086, 934, 900, 818, 692; ^{1}H-NMR ($CDCl_3$) δ 8.88 (1H, br s, NH), 7.29 (2H, d, *J*=8.0 Hz, Ph), 7.07 (2H, d, *J*=8.0 Hz, Ph), 4.67 (1H, m,OCH_2), 4.44 (1H, m, OCH_2), 3.88 (1H, m, NCH_2), 3.70 (1H, m, NCH_2), 2.32 (3H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 164.9 (C-2), 139.5 (C-12), 134.8 (C-10), 129.4 (C-11), 128.0 (C-7), 127.0 (C-9), 119.6 (C-8), 106.1 (C-6), 69.6 (C-5), 43.5 (C-4), 21.2 (Me); MS (EI), *m/z*: 346 (M^+). HRMS calcd. for $C_{13}H_{12}Cl_2N_2O_3S+H^+$: 347.0018, found: 347.0022.

2-[3,3-Dichloro-1-nitro-2-(4-tolyl)thioallylidene]-1,3-diphenylimidazolidine (12).

Yield: 15%. $R_f = 0.65$ (diethyl ether/acetonitrile 5:1); mp 192-193°C; IR (KBr, cm^{-1}) 3065, 2880, 1594 (C=C), 1520 (NO_2), 1452, 1405, 1302 (NO_2), 1278, 1155, 912, 802, 764, 692; UV: λ (log ε) 206 (4.50), 230 (4.33), 316 (4.21), 384 (3.87); ^{1}H-NMR (DMSO-d_6) δ 7.24 (10H, m, Ph), 6.93

(4H, d, *J*=6.5 Hz, Ph), 4.29 (4H, br s, NCH_2), 2.28 (3H, s, Me); ^{13}C-NMR (DMSO-d_6) δ 155.4 (C-2), 140.4 (C_{aryl}-1'), 137.1 (C-12), 130.6 (C-7), 130.1 (C_{aryl}-3'), 129.0 (C-10,11), 127.5 (C-9), 126.4 (C_{aryl}-4'), 124.3 (C-8), 122.4 (C_{aryl}-2'), 106.8 (C-6), 51.2 (C-4,5), 20.8 (Me); MS (EI), *m/z*: 497 (M^+). HRMS calcd. for $C_{25}H_{21}Cl_2N_3O_2S+H^+$: 498.0804, found: 498.0804.

The reactions of the heterocyclic compounds **9** or **10** with sodium thioarylates to give oxazolidine **11** (50%) or imidazolidine **12** (93%), or imidazolidine **13** (90%), respectively, have been accomplished applying general procedure 4.

2-(3,3-Dichloro-1-nitro-2-phenylthioallylidene)-1,3-diphenylimidazolidine (13).

R_f = 0.68 (diethyl ether/acetonitrile 5:1); mp 191-193°C; IR (KBr, cm^{-1}) 3051, 2887, 1596 (C=C), 1540, 1515 (NO_2), 1453, 1403, 1300 (NO_2), 1276, 1154, 1083, 915, 818, 743, 694; ^{1}H-NMR (DMSO-d_6) δ 7.30 (10H, m, Ph), 7.01 (4H, d, *J*=7.0 Hz, Ph), 4.31 (4H, br s, NCH_2); ^{13}C-NMR (DMSO-d_6) δ 155.9 (C-2), 140.3 (C_{aryl}-1'), 134.8 (C-9), 129.4 (C-10), 129.2 (C_{aryl}-3'), 128.8 (C-12), 126.9 (C_{aryl}-4'), 126.6 (C-11), 126.5 (C-7), 125.9 (C-8), 122.5 (C_{aryl}-2'), 106.8 (C-6), 51.1 (C-4,5); MS (EI), *m/z*: 483 (M^+). HRMS calcd. for $C_{24}H_{19}Cl_2N_3O_2S+H^+$: 484.0648, found: 484.0649.

2-[3,3-Dichloro-1-nitro-2-(4-tolyl)sulfonylallylidene]-1,3-diphenylimidazolidine (**14**).

A mixture of 0.45 g (2.0 mmol) 77% 3-chloroperoxybenzoic acid and 0.40 g (0.8 mmol) imidazolidine **12** in 10 ml of chloroform was stirred for 30 h at room temperature. Subsequently, 50 ml of chloroform were added, and the reaction mixture was washed thrice with 2N NaOH and with 20 ml of water. The organic phase was dried with Na_2SO_4 and evaporated to dryness to afford an oil (0.38 g, 90%) that crystallized after some days. R_f = 0.70 (diethyl ether/acetonitrile 5:1); mp 153-155°C; IR (KBr, cm^{-1}) 3045, 2880, 1594 (C=C), 1522 (NO_2), 1496, 1448, 1330 (NO_2), 1319 (SO_2), 1296, 1160 (SO_2), 1143, 1083, 970, 814, 760, 696, 662; UV: λ (log ε) 206 (4.49), 224 (4.43), 316 (4.06), 360 (4.10); ^{1}H-NMR (DMSO-d_6) δ 7.70 (2H, d, *J*=7.8 Hz, Ph), 7.44 (12H, m, Ph), 4.59 (2H, br s, NCH_2), 4.06 (2H, br s, NCH_2), 2.40 (3H, s, Me); ^{13}C-NMR (DMSO-d_6) δ 158.4 (C-2), 144.8 (C_{aryl}-1'), 140.4 (C-12), 137.6 (C-9), 137.4, 136.9 (C-7,8), 129.8 (C-10), 129.4 (C_{aryl}-3'), 127.5 (C-11), 127.1 (C_{aryl}-4'), 123.6 (C_{aryl}-2'), 102.6 (C-6), 51.6 (C-4,5), 21.3 (Me); MS (EI), *m/z*: 529 (M^+). HRMS calcd. for $C_{25}H_{21}Cl_2N_3O_4S+H^+$: 530.0703, found: 530.0703.

1,1-Dichloro-3-nitro-(1,3-diphenyl-imidazolidin-2-ylidene)-propan-2-one (**15**)**.** A solution of 0.50 g (1.22 mmol) imidazolidine **10** in 15 ml of DMSO/H_2O 10:1 was heated to 80-85°C for 3 h, then cooled down and subsequently poured onto an ice/water mixture. The precipitate was sucked off, washed with water (3 × 20 ml) and twice with diethyl ether. After drying *in vacuo*, 0.31g (65%) of the nitropropanone **15** was obtained; mp 204-205°C; IR (KBr, cm^{-1}) 3043, 1607 (C=O), 1562, 1498, 1454, 1428, 1355, 1295, 1193, 1154, 1011, 814, 758, 691; ^{1}H-NMR (DMSO-d_6) δ 7.44 (6H, m), 7.32 (4H, m), 7.19 (1H, s, $CHCl_2$), 4.64 (4H, s, NCH_2); ^{13}C-NMR (DMSO-d_6) δ 175.0 (C-3), 160.6 (C-1), 136.6 (C_{aryl}-1'), 129.7 (C_{aryl}-3'), 128.9 (C_{aryl}-4'), 123.4 (C_{aryl}-2'), 108.5 (C-2), 68.6 (C-4), 50.5 (2 NCH_2); MS (EI), *m/z*: 391 (M^+). HRMS calcd. for $C_{18}H_{15}Cl_2N_3O_3+H^+$: 392.0563, found: 392.0565.

General procedure 5. Reaction of monothiodiene 3 with cysteamine hydrochloride to give bisthiobutadiene 4 and thiazolidine 16

A solution of 0.26 g (4.8 mmol) sodium methoxide in methanol (10 ml) was added at 0°C to a vigorously stirred suspension of 1.08 g (3.0 mmol) of **3** and 0.18 g (1.6 mmol) cysteamine hydrochloride in 10 ml of methanol. The mixture was stirred for 2 h at 0°C and for additional 3 h at room temperature. After work-up as described for general procedure 1, 0.43g (32%) diene **4** and 0.37 g (45%) thiazolidine **16** were obtained.

2-(2,3,3-Trichloro-1-nitroallylidene)thiazolidine (16). $R_f = 0.71$ (petrol ether/diethyl ether 3:1); mp 135-136°C (Lit.[13] 125-127°C); IR (KBr, cm^{-1}) 3342, 2890, 1603 (C=C), 1547 (NO_2), 1452, 1358 (NO_2), 1273, 1059, 1002, 941, 810, 757, 689; UV: λ (log ε) 228 (4.09), 272 (3.70), 332 (4.16); ^{1}H-NMR ($CDCl_3$) δ 9.57 (1H, br s, NH), 4.20 (2H, t, *J*=7.8 Hz, NCH_2), 3.49 (2H, t, *J*=7.8 Hz, SCH_2); ^{13}C-NMR ($CDCl_3$) δ 167.9 (C-2), 128.4 (C-7), 124.0 (C-8), 113.1 (C-6), 51.4 (C-4), 30.4 (C-5); MS (EI), *m/z*: 274 (M^+). $C_6H_5Cl_3N_2O_2S$ (273.91).

The reaction of monothiodiene **3** with 2-mercaptoethanol or 1,2-ethanedithiol, respectively, to give bisthiodiene **4**, tristhiodiene **8**, or the thiolanes **17** and **18**, respectively, was performed in virtue of general procedure 5. The reaction times were 8 to 10 h; the reagent ratio was **3**:thiol:MeONa 1:0.55:1.1. Bisthiodiene **4** (10-15%), tris(4-tolylthio)diene **8** (5-10%), oxathiolane **17** (12%) and dithiolane **18** (25%), respectively, as well as disulfide **7** (about 5%) were isolated. The dienes **4** and **8** were separated by column chromatography using petrol ether/diethyl ether 3:1 as eluent.

(*Z*)-2-(2,3,3-Trichloro-1-nitroallylidene)-1,3-oxathiolane (17). $R_f = 0.30$ (petrol ether/diethyl ether 3:1); mp 115-116°C; IR (KBr, cm^{-1}) 2973, 1605 (C=C), 1542 (NO_2), 1454, 1383, 1310 (NO_2), 1280, 1158, 1055, 945, 923, 866, 822, 695, 635; UV: λ (log ε) 218 (4.13), 330 (4.10); ^{1}H-NMR ($CDCl_3$) δ 4.86 (2H, t, *J*=7.4 Hz, OCH_2), 3.48 (2H, t, *J*=7.4 Hz, SCH_2); ^{13}C-NMR ($CDCl_3$) δ 178.0 (C-2), 127.5 (C-7), 123.5 (C-6), 119.6 (C-8), 76.1 (C-5), 31.6 (C-4); MS (EI), *m/z*: 275 (M^+). HRMS calcd. for $C_6H_4Cl_3NO_3S+H^+$: 275.9050, found: 275.9052.

2-(2,3,3-Trichloro-1-nitroallylidene)-1,3-dithiolane (18). $R_f = 0.36$ (petrol ether/diethyl ether 3:1); mp 109-111°C (Lit.[19] 110-112°C) ; IR (KBr, cm^{-1}) 2990, 2933, 1595 (C=C), 1513 (NO_2), 1444, 1415, 1310 (NO_2), 1272, 1152, 926, 851, 816, 765, 691, 678; UV: λ (log ε) 218 (4.12), 352 (4.18); ^{1}H-NMR ($CDCl_3$) δ 3.65 (4H, m, 2 SCH_2); ^{13}C-NMR ($CDCl_3$) δ 172.1 (C-2), 129.4 (C-6), 128.5 (C-7), 122.5 (C-8), 38.0, 40.3 (C-4,5); MS (EI), *m/z*: 291 (M^+). $C_6H_4Cl_3NO_2S_2$ (290.87).

The reaction of monothiodiene **3** with cysteamine hydrochloride, 2-mercaptoethanol, and 1,2-ethanedithiol, respectively, to give tristhiodiene **8**, and the heterocycles **19**-**21** was carried out according to general procedure 5. The reaction time was 6 h for cysteamine hydrochloride, 20 h for mercaptoethanol, and 48 h for 1,2-ethanedithiol. The reagent ratio in case of cysteamine hydrochloride was **3**:aminothiol:MeONa 1:1.1: 3.3, but, in case of mercaptoethanol and ethanedithiol was **3**:thiol:MeONa 1:1.1:2.2. Products yields, starting from the cysteamine salt, were 25% for thiazolidine **19** and 5% for tris(4-tolylthio)diene **8**. The conversion applying mercaptoethanol gave oxathiolane **20** (20%) and diene 8 (13%), whereas dithiolane **21** was

obtained in 50% yield accompanied by 10% of diene **8.** In addition, in all three cases the disulfide **7** was isolated in about 5% yield.

2-[3,3-Dichloro-1-nitro-2-(4-tolyl)thioallylidene]thiazolidine (19). $R_f = 0.75$ (diethyl ether/acetonitrile 5:1); mp 126-127°C; IR (KBr, cm^{-1}) 3215, 2949, 1583 (C=C), 1557 (NO_2), 1491, 1448, 1349 (NO_2), 1298, 1042, 985, 927, 824, 778, 694; UV: λ (log ε) 220 (4.27), 256 (4.13), 352 (4.23); ^{1}H-NMR ($CDCl_3$) δ 9.25 (1H, br s, NH), 7.37 (2H, d, *J*=8.2 Hz, Ph), 7.06 (2H, d, *J*=8.2 Hz, Ph), 3.99 (1H, m, NCH_2), 3.89 (1H, m, NCH_2); 3.35 (1H, m, SCH_2), 3.25 (1H, m, SCH_2), 2.31 (3H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 167.9 (C-2), 139.9 (C-12), 135.5 (C-10), 131.0 (C-7), 129.4 (C-11), 125.7 (C-9), 118.9 (C-8), 113.2 (C-6), 51.0 (C-4), 30.5 (C-5), 21.3 (Me); MS (EI), *m/z*: 362 (M^+). HRMS calcd. for $C_{13}H_{12}Cl_2N_2O_2S_2$+$H^+$: 362.9790, found: 362.9792.

(*Z*)-2-[3,3-Dichloro-1-nitro-2-(4-tolyl)thioallylidene]-1,3-oxathiolane (20). $R_f = 0.48$ (diethyl ether); mp 111-112°C; IR (KBr, cm^{-1}) 3015, 2900, 1587 (C=C), 1543 (NO_2), 1491, 1456, 1373, 1305 (NO_2), 1284, 1148, 936, 815, 691, 633; UV: λ (log ε) 212 (4.22), 226 (4.24), 256 (4.11), 340 (3.94); ^{1}H-NMR ($CDCl_3$) δ 7.25 (2H, d, *J*=8.0 Hz, Ph), 7.08 (2H, d, *J*=8.0 Hz, Ph), 4.74 (1H, m, OCH_2), 4.36 (1H, m, OCH_2), 3.30 (1H, m, SCH_2), 3.14 (1H, m, SCH_2), 2.32 (3H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 176.1 (C-2), 139.9 (C-12), 135.0 (C-10), 129.5 (C-11), 127.4 (C-7), 126.3 (C-9), 123.5 (C-6), 120.1 (C-8), 75.3 (C-5), 31.3 (C-4), 21.2 (Me); MS (EI), *m/z*: 363 (M^+). $C_{13}H_{11}Cl_2NO_3S_2$ (362.96). Anal. Calcd. for $C_{13}H_{11}Cl_2NO_3S_2$, %: C, 42.86; H, 3.04; Cl, 19.47; N, 3.85; S, 17.60. Found, %: C, 42.81; H, 3.04; Cl, 19.52; N, 3.82; S, 17.56.

An X-ray crystallographic analysis of $C_{26}H_{22}Cl_4S_4N_2O_6$ was performed at 223(2) K by using a STOE IPDS II diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. Crystal system: triclinic, SG P1 (No. 2), Z = 2, a = 897.18(9) pm, b = 1181.3(1) pm, c = 1508.6(2) pm, α = 86.55(1) °, β = 80.45(1) °, γ = 85.35(1) °, V_{EZ} = 1569.8(3) 10^6 pm^3. The crystal structures were dissolved by direct methods using SHELXS-97 and refined using alternating cycles of least squares refinements against F^2 (SHELXL-97)[20]. All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by final difference Fourier syntheses. The refinement converged to a final ω*R*2 = 0.0731 and *R*1 = 0.0355 for 5274 unique reflections and 471 refined parameters with a goodness-of-fit of 1.049. Further details of the crystal structure investigations have been deposited with the Cambridge Crystallographic Data Centre, CCDC 630118. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44(1223)-336 033; e-mail: fileserv@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).

2-[3,3-Dichloro-1-nitro-2-(4-tolyl)thioallylidene]-1,3-dithiolane (21). $R_f = 0.40$ (petrol ether/diethyl ether 3:1); mp 126-128°C; IR (KBr, cm^{-1}) 3022, 2924, 1580 (C=C), 1519 (NO_2), 1490, 1463, 1419, 1305 (NO_2), 1269, 1157, 918, 813, 692, 631; UV: λ (log ε) 204 (4.20), 224 (4.04), 260 (3.87), 360 (3.75); ^{1}H-NMR ($CDCl_3$) δ 7.34 (2H, d, *J*=8.0 Hz, Ph), 7.06 (2H, d, *J*=8.0 Hz, Ph), 3.46 (3H, m, SCH_2), 3.30 (1H, m,SCH_2), 2.33 (3H, s, Me); ^{13}C-NMR ($CDCl_3$) δ 169.7 (C-2), 140.4 (C-12), 135.6 (C-10), 130.8 (C-7), 130.1 (C-6), 129.5 (C-11), 124.7 (C-9), 119.1 (C-

8), 40.0, 37.7 (C-4,5), 21.3 (Me); MS (EI), *m/z*: 379 (M^+). HRMS calcd. for $C_{13}H_{11}Cl_2NO_2S_3+H^+$: 379.9402, found: 379.9402.

The reaction of bisthiodiene **4** with cysteamine hydrochloride, 2-mercaptoethanol, or 1,2-ethandithiol, respectively, to give the dienes **8**, **22** and **23** as well as the heterocycles **19-21**, respectively, was successful following the general procedure 5. The reaction time was 6 h for cysteamine hydrochloride, 25 h for mercaptoethanol, and 40 h for 1,2-ethanedithiol. The cysteamine hydrochloride yielded diene **8** (5%), thiazolidine **19** (75%), and disulfide **7** (5%), whereas mercaptoethanol afforded diene **8** (5%), oxathiolane **20** (15%), disulfide **7** (below 5%), and as additional side products the tristhiodienes **22** and **23** (15% in total, not separable by column chromatography). In the case of ethanedithiol, diene **8** (20%), dithiolane **21** (40%), and disulfide **7** (about 5%) were obtained.

1,1-Bis(4-tolylthio)-4,4-dichloro-3-(2-hydroxyethyl)thio-2-nitro-1,3-butadiene (**22**) **and 1,3-Bis(4-tolylthio)-4,4-dichloro-1-(2-hydroxyethyl)thio-2-nitro-1,3-butadiene (23).** The 2-hydroxyethyl-substituted compounds **22** and **23** were obtained as a viscous yellow mixture. The isomeric ratio (2:3) was determined by ^{13}C-NMR. R_f = 0.45 (petrol ether/diethyl ether 3:1). IR (neat, cm^{-1}) 3450 (OH), 3023, 2922, 2871 (C-H), 1595 (C=C), 1520 (NO_2), 1491, 1400, 1378, 1297 (NO_2), 1279, 1181, 1047, 992, 900, 811, 690; ^{1}H-NMR ($CDCl_3$) δ 7.42 (2H, d, *J* = 8.2 Hz, Ph), 7.40 (2H, d, *J* = 8.2 Hz, Ph), 7.13 (12H, m, Ph), 3.53 (4H, m, OCH_2), 2.73 (4H, m, SCH_2), 2.39 (3H, s, Me), 2.36 (3H, s, Me), 2.35 (3H, s, Me), 2.34 (3H, s, Me), 1.86 (2H, br s, OH); ^{13}C-NMR ($CDCl_3$) δ 155.0, 154.4, 143.0, 142.3, 140.4, 140.3, 139.9, 139.1, 135.6, 135.5, 133.1, 130.9, 130.2, 130.0, 129.7, 129.6, 128.3, 128.1, 125.5, 125.0, 122.6, 121.9, 60.9, 60.8, 38.4, 37.8, 21.3, 21.2. HRMS calcd. for $C_{20}H_{19}Cl_2NO_3S_3+H^+$: 487.9977, found: 487.9981.

The reactions of the heterocyclic compounds **16-18** with sodium 4-tolylthiolate to give the thiazolidine **19** (65%), oxathiolane **20** (60%), and dithiolane **21** (60%) were performed in accordance with the general procedure 4 at room temperature within 6 to 8 h. The reaction of monothiodiene **3** with bissodium ethyleneglycolate proceeded at 45-50°C in ethylene glycol following the general procedure 1 and furnished the bisthio compound **4** in 45% yield. Applying **4** as the substrate, the tristhiodiene **8** (43%) accompanied by the disulfide **7** (5%) was obtained.

Acknowledgements

Support of this work by BAYER AG (Leverkusen, Germany) is most gratefully acknowledged. We thank Dr. H. Frauendorf, University of Göttingen, Germany, for HRMS data.

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