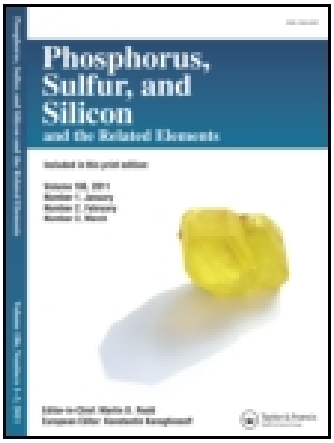

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REACTIVITY STUDY OF 2,4-DINITROBUTA-1,3-DIENES TOWARDS MONO-, POLY-, AND PERSULFANYL CONJUGATED DIENES BY REGIOSPECIFIC VINYL GROUP ACTIVATION

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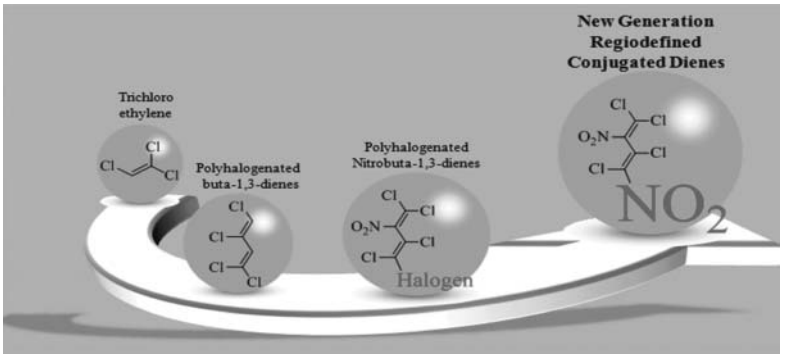
GRAPHICAL ABSTRACT



Abstract *Polyhalogenated nitrobuta-1,3-dienes are unique reagents in organic synthesis and have been employed in several well-known and recently developed areas of application. This study describes the scope and application of 1,1,3,4-tetrachloro-2,4-dinitrobuta-1,3-diene in organic synthesis as well as methods for the preparation of poly- and perfunctionalized 2,4-dinitrobuta-1,3-dienes, and characterization of all obtained compounds.*

Keywords Nitro compounds; dinitrodienes; sulfides; polyhalogenated compounds; polysulfanylbuta-1,3-dienes; persulfanylalkenes; nitroalkenes; click chemistry

INTRODUCTION

Honored in 2010 with the Nobel Prize, one of the prize-winners' main goal was to be able to synthesize regiodefined conjugated dienes by cross-coupling reactions

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between vinylic boranes and vinylic halides in the presence of palladium catalysts.[1] Since regiodefined conjugated dienes provide key intermediates for the formation of complex, bioactive molecules useful as medicinal or agrochemicals, and organic materials with novel electronic and optical properties, the design of a new generation of regiodefined conjugated dienes called "polyhalogenated nitrobuta-1,3-dienes" has been developed.[2,3] First, compared to other novel regiodefined conjugated dienes, nitrobuta-1,3-dienes are highly reactive, unstable, and easily polymerized. Therefore, it was thought that they would be unsuitable as starting compounds. Second, although hexachlorobuta-1,3-diene is stable, it is, unfortunately, chemically less reactive and does not react regiodefined. In consideration of these two aspects, we have decided to investigate the reactions of the new generation of regiodefined conjugated dienes.

In the initial stage of the study, we have analyzed the scope of the reaction and tried several reaction types and we considered that fully substituted regiodefined conjugated dienes could be obtained by sequential reactions of the conjugated dienes.[4] In order to check this possibility, the reaction of octyl (1,3,4-trichloro-2-nitrobuta-1, 3-dien-1-yl) sulfane with amines sequentially was examined. However, no reaction occurred in the presence of a base. The reaction did not proceed in different solvents at reflux temperature even after 2–5 days.

Reactions of polyhalogenated buta-1,3-dienes containing nitro substituents are well-known,[5] but polyhalogenated nitrobuta-1,3-dienes containing an additional electron-withdrawing group (EWG) are rare at all.[6] An EWG such as NO_2, >C=O, or CN significantly activates the vinyl group and causes a change in the electron density distribution, which is responsible for the formation of active reaction centers in the electrophilic molecule. The reactivity of halogen atoms in the nitrobuta-1,3-dienes and the regioselectivity of the molecule towards nucleophiles can be affected if an additional activating EWG group is selectively introduced into the molecule. The presence of two electron-withdrawing nitro groups should significantly affect the reactivity of halogenated buta-1,3-dienes due to its unique electronic properties.

Herein, we focus on the fascinating 1,1,3,4-tetrachloro-2,4-dinitrobuta-1,3-dienes which are much easier accessible than related compounds in three steps starting from radical dimerization of trichloroethylene.[7] However, its chemical properties are hitherto fairly unexplored in contrast to polyhalogenated nitrobuta-1,3-dienes.

RESULTS AND DISCUSSION

These electronically remarkable molecules can be used for a broad variety of synthetic applications since the reactions can be carried out by varied methods ranging from a nucleophilic vinylic substitution (S_NVinylic)[8] pathway via the addition-elimination route and ring cleavage to addition reactions of the trichlorovinyl group activated by the nitro group which also provides regioselectivity to molecule. The regiospecifity is caused by the fact that the LUMO of nitrodienes is located preferentially at the dihalogenonitrovinyl moiety.[9]

Regrettably, polyhalogenated nitrobuta-1,3-dienes react at the terminal C-1 carbon atom to yield the product of a nucleophilic vinylic substitution process by attacking the appropriate nucleophiles.[10] However, possible subsequent substitutions of the chlorine atoms on C-3 and/or C-4 carbon atoms of these compounds are known to occur with difficulty, unless special experimental conditions are adopted: high temperatures, very

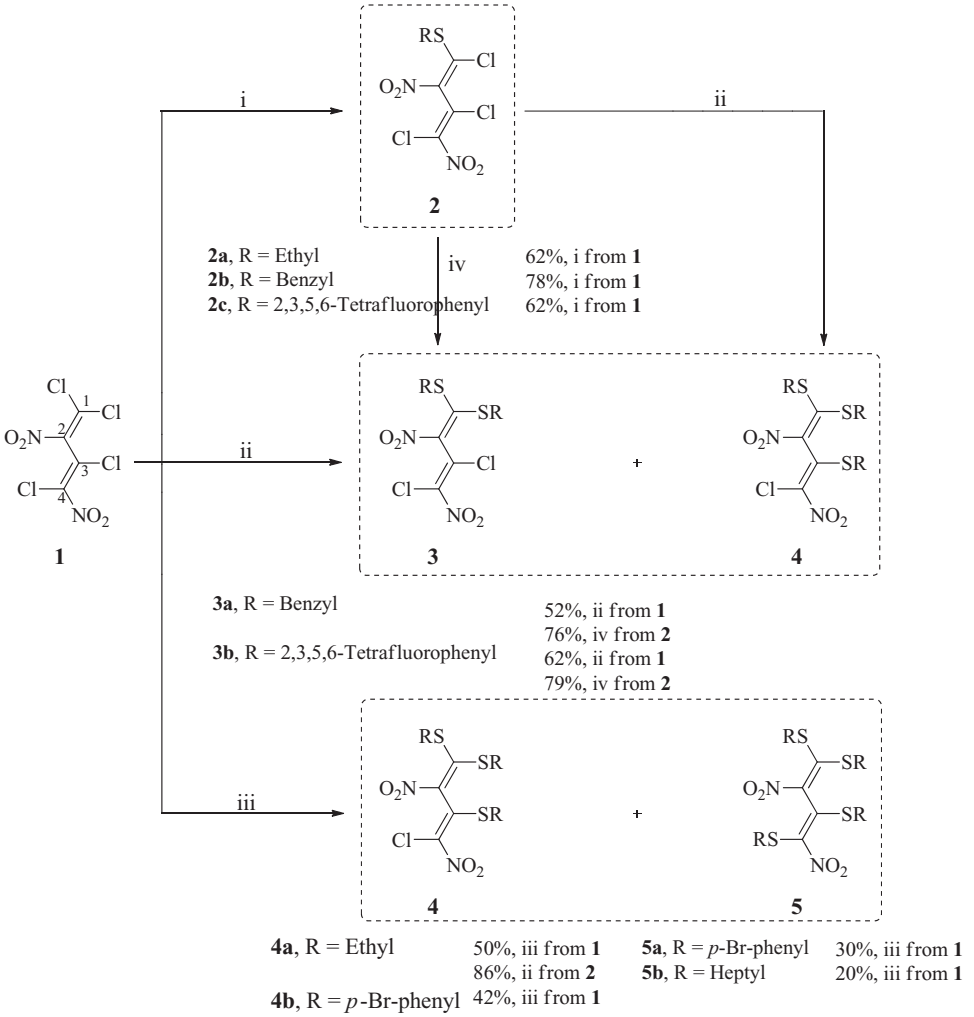
strong bases and nucleophiles, and dipolar aprotic solvents,[11] while 1,1,3,4-tetrachloro-2,4-dinitrobuta-1,3-diene does not require harsh reaction conditions. This has prompted our search for more general, milder routes, high product yields, high regioselectivity, and application in one-pot syntheses. Thus, applying selective and mild reactions, the polyhalogenated nitrobuta-1,3-dienes enable click chemistry-type syntheses.[12]

The product distribution is highly sensitive to modification of the reaction conditions such as molar ratios of substrates, reagents, and basicity of the reaction medium. Thus, increase of the basicity of the reaction medium favors the formation of the di-, tri-, and even tetrasulfanyl 2,4-dinitrobuta-1,3-dienes. Di-, tri-, and tetrasulfanyl 2,4-dinitrobuta-1,3-dienes could be obtained in simple one-pot reactions starting from the mono-, di-, and trisulfanyl 2,4-dinitrobuta-1,3-dienes in the ethanol in the presence of ethoxide, respectively. An attractive feature of this method is that the sulfanyl-substituted 2,4-dinitrobuta-1,3-dienes are also accessible from **2**, **3**, and **4** mediated by ethanol. To the best of our knowledge, poly- and persulfanyl 2,4-dinitrobuta-1,3-dienes have not been reported before in the literature, whereas poly- and persulfanyl buta-1,3-dienes are also rare in literature.[13–16] Thus, it is obvious that the second nitro group at the C-4 carbon atom of buta-1,3-diene promotes the reaction.

The reaction of 1,1,3,4-tetrachloro-2,4-dinitrobuta-1,3-diene (**1**) with one molar equivalent of thiol at room temperature furnishes monosulfanyl 2,4-dinitrobuta-1,3-dienes (Scheme 1). Use of two and three molar equivalents of thiol in the presence of sodium ethoxide in ethanol at 0 °C (dinitrodiene:thiol:EtONa = 1:2:2 and 1:3:3) provides the poly- and persulfanyl 2,4-dinitrobuta-1,3-dienes with up to 86% yield.

Next, the logical question arose whether **1** is also a suitable precursor for amine derivatives or not.[17] Encouraged by the above results, in order to understand how the nitro group exerts an influence on the reaction towards secondary amines by sequential substitutions of two amines, mono- and disulfanyl 2,4-dinitrobuta-1,3-dienes have been used (Scheme 2). Albeit both types of chlorine atoms should in principle be able to react the geminal as well as the inner chlorine atom at C-3 served as the leaving group on nucleophilic attack. Thus, the presence of the second activating nitro group in a buta-1,3-diene promotes the reaction up to the two chlorine substitutions of monosulfanyl 2,4-dinitrobuta-1,3-dienes at moderate temperature, while our efforts to synthesize monosulfanyl 2-nitrobuta-1,3-dienes failed. Few publications dealing with substitution reaction of the C-3 chlorine substituent are available in literature.[11,16] To perform that reaction requires quite sophisticated reaction conditions and base (i.e., refluxing methanol). To the best of our knowledge, such compounds are also rare in the literature.[18] Trisulfanyl 2,4-dinitrobuta-1,3-dienes proved to be unreactive towards further nucleophilic displacement processes even after prolonged reaction times. Thus, the last chlorine atom at C-4 could not be substituted with amine at ambient temperature after countless futile attempts as well as applying harsher conditions such as increasing the amine to diene ratio and refluxing. This unexpected behavior of the dinitrobuta-1,3-diene **1** can be explained in terms of using an amine as a nucleophile decreases the reactivity of the products because of the electron-releasing character of the molecule and the amine decreases the electrophilicity of the butadiene system. It could be feasible to use a Lewis acid in order to activate the butadiene system for the further substitutions.

The exclusive formation of the (*E*)-isomer of **2** is in accordance with the literature.[18] However, the formation of the (*E*)-isomer with the opposite configuration in **6** (with the sulfur substituent and the nitro group in *trans*-position) is possible due to free rotation around the single bond between C-1 and C-2 in the intermediate that is produced during the

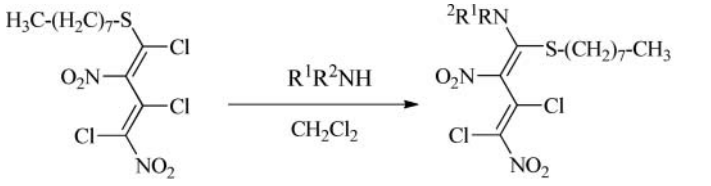


Scheme 1 Synthesis of mono-, poly-, and persulfanyl 2,4-dinitrobuta-1,3-dienes; conditions: (i) 1 eq. RSH, 6 h; (ii) 2 eq. RSH, 2NaOEt, EtOH, 2 h, 0 °C; (iii) 3 eq. RSH, 3NaOEt, EtOH, 2h, 0 °C; (iv) 1 eq. RSH, NaOEt, EtOH, 2 h, 0 °C; isolated yields after column chromatography/recrystallization.

attack of the amine at the C-1 carbon atom.[19] These molecules **6a–b** were obtained with 89% and 84% yield, respectively, upon treatment of the monosulfanyl 2,4-dinitrobuta-1,3-dienes **2** with amines.

With the aim to synthesize *S,S,N*-substituted 2,4-dinitrobuta-1,3-dienes **7** from disulfanyl 2,4-dinitrobuta-1,3-dienes **3**, we continued with S_NVinylic reactions (Scheme 3). With regard to Pearson's HSAB concept,[20] disulfanyl 2,4-dinitrobuta-1,3-dienes **3** should give rise to attack of further amines under formation of **7a–b** (up to 73% yield).

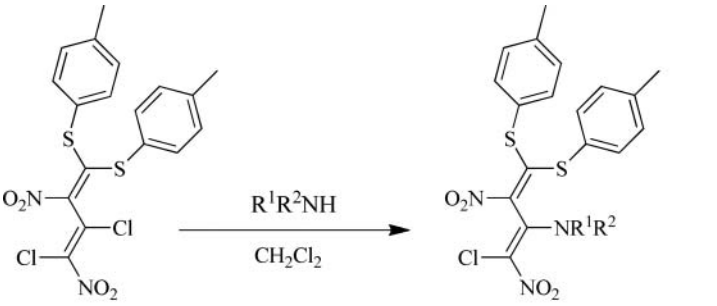
As expected, the preparation of heterocyclic compounds by applying dinitrobuta-1,3-diene **1** as the electrophilic substrate for aromatic *ortho*-substituted difunctional nucleophiles was possible. 2,3-Dihydrobenzo[*d*]thiazole **8** and the interesting 3,11,17,



2 **6**

6a, R^2R^1 = -$(CH_2)_2$-O-$(CH_2)_2$- 89%
6b, R^2R^1 = -$(CH_2)_5$- 84%

Scheme 2 Reactions of monosulfanyl 2,4-dinitrobuta-1,3-dienes with amines; condition: 2 eq. R^1R^2NH, CH_2Cl_2, 2–4 h; isolated yields after column chromatography/recrystallization.



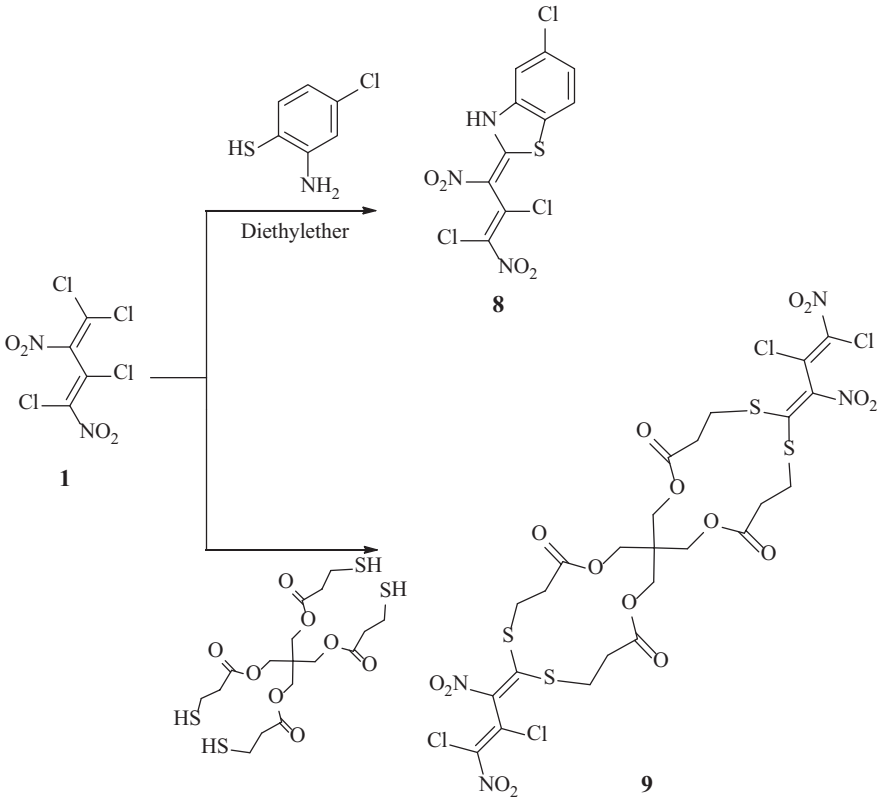
3 **7**

7a, R^2R^1 = -$(CH_2)_2$-O-$(CH_2)_2$- 71%
7b, R^2R^1 = -$(CH_2)_5$- 73%

Scheme 3 Reactions of disulfanyl 2,4-dinitrobuta-1,3-dienes with amines; condition: 2 eq. R^1R^2NH, CH_2Cl_2, 2–4 h; isolated yields after column chromatography/recrystallization.

25-tetraone **9** are obtained with high yields just like polyhalogenated nitrobuta-1,3-dienes reactions (Scheme 4).

The substructure of the 2,3-dihydrobenzo[*d*]thiazole **8** should enable a stabilization caused by a strong hydrogen bond between an oxygen atom of the nitro group and the NH proton of the benzothiazole group. Crystalline 2,3-dihydrobenzo[*d*]thiazole **8** shows a broad absorption band in the IR spectrum with several maxima at 3000–2500 cm^{-1} and a narrower band at 3330 cm^{-1}. The absorption at 3000–2500 cm^{-1} corresponds to the amino group involved in an intramolecular hydrogen bond, and the high-frequency band is due to the heterocyclic amino group connected with the side-chain nitro group through an intramolecular hydrogen bond. The IR spectrum of 2,3-dihydrobenzo[*d*]thiazole **8** in dilute CCl_4 solution ($c = 10^{-3}$ mol/L) lacks absorption bands in the region 3000–2500 cm^{-1} but contains a band at 3330–3400 cm^{-1} belonging to the free amino group. The existence of intramolecular hydrogen bonds is also confirmed by the presence of a characteristic absorption maximum in the 320–400 nm region in the UV spectra of the heterocyclic compounds which is typical of polar, inner salt-like structures.[21] The mixed difunctional 2,3-dihydrobenzo[*d*]thiazole **8** appears as one single isomer with (*E*)-configuration caused by the hydrogen bond stabilization. The low solubility of the 2,3-dihydrobenzo[*d*]thiazole **8** even in DMSO indicates that single hydrogen bonding with the amino and nitro groups



Scheme 4 Cyclization reactions of conjugated diene **1** with multifunctional nucleophiles.

must be important. The latter approach of tetraone **9** mostly will rely on the coordination of transition-metal cations to monosite and/or multisite ligands.

CONCLUSIONS

With the realization of these reactions applying different nucleophiles (thiols, amines, and multifunctional nucleophiles), a highly useful and efficient synthetic methodology is developed. The significance of this project consists in the shortest possible access to highly functionalized sulfur and heterocyclic compounds from very simple precursor in a one-pot operation.

Today, the reactions of "polyhalogenated nitrobuta-1,3-dienes" continue to evolve with many new possibilities reported during the past decade. In particular, we may propose that these reactions would enable to synthesize any fundamentally desired compounds a) in high yields, b) efficiently (in as few steps as possible), and c) selectively. From the perspective of synthesizing polyfunctional hetero(cyclic) and acyclic compounds in this manner, the following must be noted.

There is a need for certain activated and relatively unhindered conjugated dienes for sequentially substitutions with acceptable results.

One of the important prerequisites to synthesize fully substituted conjugated dienes is to insert a second EWG to enhance further reactions. There are clear advantages of employing the second EWG, such as permitting better reactivity/selectivity control, proceeding with stoichiometric amounts of reagents, and expanding the opportunities of organic syntheses. Reactivity restrictions of either the third or the fourth chlorine atoms have been overcome.

The sequential chlorine displacement methodology developed further in this paper has great potential for the production of a wide range of polyfunctional heteroaromatic derivatives. The proposed order for the substitution reaction of the chlorine substituents of dinitrobuta-1,3-diene **1** is C-1 >> C-3 > C-4 by applying thiols and amines, whereas a reaction at C-4 is impossible for amines due to its stepped reactivity in nucleophilic vinylic substitution reactions.

EXPERIMENTAL

All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Petroleum ether (PE) had a boiling range 40–60 °C. Melting points (mp) were determined with a Buchi apparatus B-540 and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian^{UNITY} INOVA spectrometer at frequencies of 500 MHz for ^{1}H and 125 MHz for ^{13}C NMR. Chemical shifts δ (ppm) are reported relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{1}H NMR spectra and ^{13}C NMR spectra in $CDCl_3$ refer to the solvent signal center at $\delta = 7.26$ and $\delta = 77.0$ ppm, respectively. Other solvents are as follows: DMSO-d_6: 2.49, 3.30 ppm (^{1}H), 40.27 ppm (^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz). IR spectra (ν/cm^{-1}) were recorded as ATR on a Perkin Elmer Spectrum 100 UATR FTIR spectrometer. Microanalyses were carried out with a Carlo Erba Elemental Analyzer 1106. UV spectra were recorded in $CHCl_3$ on the UV-VIS spectrophotometer TU-1901. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX MS/MS spectrometer equipped with an ESI (Electrospray ionization) or APCI (Atmospheric pressure chemical ionization) source. N_2 was used as the nebulizing gas. In the MS_1 experiment, He was used as collision gas. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254) based on Merck DC-plates (aluminum based). Visualization of the chromatogram was performed by UV light (254 nm). Column chromatographic separations were carried out using silica gel 60 (Merck, 63–200 μm particle sized, 60–230 mesh).

Reactions of 1,1,3,4-Tetrachloro-2,4-dinitro-1,3-butadiene with Thiols; Standard Procedure 1

At room temperature, dinitrobuta-1,3-diene **1** and 1 equivalent of the thiol were combined and stirred 6 h without a solvent. After this period, the mixture was diluted with MeOH (20 mL). The precipitate that appeared was filtered off, successively washed twice with water (25 mL each portion) and cold MeOH (2 × 25 mL), and finally dried under reduced pressure. If there was no precipitation, the solvent was evaporated and the residue dissolved in CH_2Cl_2 (20 mL). Water (50 mL) was added and the organic layer was separated. The aqueous layer was then extracted with further portions of CH_2Cl_2 (2 × 25 mL), and the

combined organic extracts were dried over $CaCl_2$ and evaporated. Purification by column chromatography on silica gel gave the pure product.

Standard Procedure 2

A solution of NaOEt in 10 mL of EtOH (0 °C) was added dropwise within 10 min to a cold solution (0 °C) of dinitrobuta-1,3-diene **1** or **2** and the thiol (molar ratios of reactions are given in Scheme 1) within 10 min. After 2 h stirring at 0 °C, the solvent was evaporated and the residue dissolved in CH_2Cl_2 (20 mL). Water (50 mL) was added and the organic layer separated. The aqueous layer was then extracted with further portions of CH_2Cl_2 (3 × 25 mL), and the combined organic extracts were dried over $CaCl_2$ and evaporated to yield the product which could be further purified by column chromatography.

1,3,4-Trichloro-1-ethylthio-2,4-dinitrobuta-1,3-diene (2a): **2a** was synthesized according to the standard procedure 1 as yellow oil (0.34 g, 62%). R_f 0.38 (CCl_4). IR: 2962, 2923, 2852 ($CH_{aliphatic}$), 1455 (C=C), 1291, 1529 (NO_2). UV-Vis: λ_{max} 386 nm (lgε 4.64). ^{1}H NMR: 1.36 (t, ^3J = 7.32, 3H, C$\boldsymbol{H_3}$), 3.10 [q, 2H, (C$\boldsymbol{H_2}$)]. ^{13}C NMR: 12.46 ($\boldsymbol{C}H_3$), 29.32 ($\boldsymbol{C}H_2$), 116.22, 122.24, 127.92, 157.36 ($\boldsymbol{C}_{butadien}$). MS (ESI) *m/z* 307 $[M]^+$; MS (ESI-MS/MS) *m/z* 260 $[M - NO_2]^+$. Anal. calcd. for $C_6H_5Cl_3N_2O_4S$ (307.539): C, 23.43; H, 1.64; N, 9.11; S, 10.43; Found: C, 23.09; H, 1.55; N, 9.45; S, 10.50.

1-Benzylthio-1,3,4-trichloro-2,4-dinitrobuta-1,3-diene (2b): 2b was prepared according to the literature.[6]

1,3,4-Trichloro-2,4-dinitro-1-(2,3,5,6-tetrafluorophenylthio)buta-1,3-diene (2c): **2c** was synthesized according to the standard procedure 2 as yellow oil (1.56 g, 69%). R_f 0.52 (PE:$CHCl_3$ = 2:1). IR: 3077 (CH_{arom}), 2963, 1496 (C=C), 1306, 1542 (NO_2), 1261, 803. UV-Vis: λ_{max} 248 nm (lgε 4.92). ^{1}H NMR: 7.11–7.27 (m, 1H, C$\boldsymbol{H}_{arom}$). ^{13}C NMR: 116.70, 153.91 ($\boldsymbol{C}_{arom}$), 108.95 ($\boldsymbol{C}H_{arom}$), 121.15, 129.74, 130.71, 168.14 ($\boldsymbol{C}_{butadien}$). MS (ESI) *m/z* 449 $[M + Na]^+$. Anal. calcd. for $C_{10}HCl_3F_4N_2O_4S$ (427.544): C, 28.09; H, 0.24; N, 6.55; S, 7.50; Found: C, 28.45; H, 0.61; N, 6.27; S, 7.73.

1,1-Bis(benzylthio)-3,4-dichloro-2,4-dinitrobuta-1,3-diene (3a): 3a was synthesized according to the standard procedure 2 as yellow crystals (1.15 g, 52%), mp 96–97.5 °C. R_f 0.59 (PE:$CHCl_3$ = 1:1). IR: 3065, 3029 (CH_{arom}), 1466 (C=C), 1288, 1526 (NO_2). UV-Vis: λ_{max} 392 nm (lgε 4.99). ^{1}H NMR: 4.31 (s, 4H, C$\boldsymbol{H}_2$), 7.25–7.34 (m, 10H, C$\boldsymbol{H}_{arom}$). ^{13}C NMR: 41.18 ($\boldsymbol{C}H_2$), 128.82, 129.65 ($\boldsymbol{C}_{arom}$), 129.41, 129.73 ($\boldsymbol{C}H_{arom}$), 121.50, 128.73, 132.88, 156.98 ($\boldsymbol{C}_{butadien}$). MS (ESI) *m/z* 455 $[M]^+$. Anal. calcd. for $C_{18}H_{14}Cl_2O_4S_2$ (457.351): C, 47.27; H, 3.09; N, 6.13; S, 14.02; Found: C, 46.98; H, 3.21; N, 6.44; S, 14.32.

Alternately, **3a** was prepared from benzylmercaptan (0.067 g, 0.54 mmol) and **2b** (0.20 g, 0.54 mmol) in EtOH at 0 °C for 1 h (0.21 g, 76%).

3,4-Dichloro-2,4-dinitro-1,1-bis(2,3,5,6-tetrafluorophenylthio)buta-1,3-diene (3b): **3b** was synthesized according to the standard procedure 2 as yellow crystals (1.89 g, 62%), mp 126–127.8 °C. R_f 0.43 (PE:$CHCl_3$ = 2:1). IR: 3077 (CH_{arom}), 2964, 1495 (C=C), 1315, 1555 (NO_2), 1541, 920. UV-Vis: λ_{max} 243 nm (lgε 4.83). ^{1}H NMR: 7.11–7.28 (m, 2H, C$\boldsymbol{H}_{arom}$). ^{13}C NMR: 109.14, 145.99 ($\boldsymbol{C}_{arom}$), 108.11 ($\boldsymbol{C}H_{arom}$), 119.49, 129.99, 143.98, 147.85 ($\boldsymbol{C}_{butadien}$). MS (ESI) *m/z* 596 $[M + Na]^+$, *m/z* 522 $[M - NO_2]^+$. Anal. calcd. for $C_{16}H_2Cl_2F_8N_2O_4S_2$ (573.221): C, 33.52; H, 0.35; N, 4.89; S, 11.19; Found: C, 33.35; H, 0.78; N, 4.42; S, 11.62.

Alternately, **3b** was prepared from 2,3,5,6-tetrafluorobenzenethiol (0.051 g, 0.28 mmol) and **2c** (0.12 g, 0.28 mmol) in EtOH at 0 °C for 1 h (0.15 g, 79%).

4-Chloro-1,1,3-tris(ethylthio)-2,4-dinitrobuta-1,3-diene (4a): **4a** was synthesized according to the standard procedure 1 as yellow oil (0.32 g, 50%). R_f (CCl_4) 0.23. IR: 2963, 2926, 2850 ($CH_{aliphatic}$), 1448 (C=C), 1290, 1520 (NO_2). UV-Vis: λ_{max} 385 nm (lgε 4.92). ^{1}H NMR: 1.20 (t, ^3J = 7.32, 3H, C***H*****$_3$**), 1.26 (t, ^3J = 7.32, 3H, C***H*****$_3$**), 1.28 (t, ^3J = 7.32, 3H, C***H*****$_3$**), 2.89 [q, 6H, (C***H*****$_2$**)]. ^{13}C NMR: 13.38, 13.79, 14.02 (***C***H_3), 26.61, 28.97, 29.75 (***C***H_2), 108.77, 124.04, 127.69, 151.68 (***C***$_{butadien}$). MS (ESI) *m/z* 378 $[M + Na]^+$. Anal. calcd. for $C_{10}H_{15}ClN_2O_4S_3$ (358.885): C, 33.47; H, 4.21; N, 7.81; S, 26.80; Found: C, 33.19; H, 4.55; N, 7.49; S, 26.99.

Alternately, **4a** was prepared from EtOH (0.04 g, 0.65 mmol) and **2a** (0.20 g, 0.65 mmol) in ethanol at 0 °C for 1 h (0.20 g, 86%).

1,1,3-Tris(4-bromophenylthio)-4-chloro-2,4-dinitrobuta-1,3-diene (4b): **4b** was synthesized according to the standard procedure 2 as yellow crystals (0.55 g, 42%), mp 152.5–154 °C. R_f 0.24 (PE:$CHCl_3$ = 5:1). IR: 3079, 3048 (CH_{arom}), 1470 (C=C), 1385, 1531 (NO_2). UV-Vis: λ_{max} 386 nm (lgε 4.91). ^{1}H NMR: 6.74–6.77 (m, 4H, C***H*****$_{arom}$**), 6.90–6.93 (m, 4H, C***H*****$_{arom}$**), 7.23–7.32 (m, 4H, C***H*****$_{arom}$**). ^{13}C NMR: 123.62, 125.08, 129.20, 130.15 (***C***$_{arom}$), 132.31, 132.60, 132.93, 136.18 (***C***H_{arom}), 122.13, 128.97, 141.82, 158.22 (***C***$_{butadien}$). MS (ESI) *m/z* 742 $[M + 2H]^+$, 643 $[M - CClNO_2]^+$. Anal. calcd. for $C_{22}H_{12}Br_3ClN_2O_4S_3$ (739.702): C, 35.72; H, 1.64; N, 3.79; S, 13.00; Found: C, 35.99; H, 1.81; N, 3.45; S, 13.25.

1,1,3,4-Tetrakis(4-bromophenylthio)-2,4-dinitrobuta-1,3-diene (5a): **5a** was synthesized according to the standard procedure 2 as yellow crystals (0.48 g, 30%), mp 125.5–127 °C. R_f 0.19 (PE:$CHCl_3$ = 5:1). IR: 3073, 3051 (CH_{arom}), 1470 (C=C), 1386, 1521 (NO_2). UV-Vis: λ_{max} 246 nm (lgε 4.86). ^{1}H NMR: 6.82–6.85 (m, 4H, C***H*****$_{arom}$**), 6.97–7.02 (m, 4H, C***H*****$_{arom}$**), 7.29–7.36 (m, 4H, C***H*****$_{arom}$**). ^{13}C NMR: 120.49, 130.35, 132.08, 132.80, 132.91, 135.52, 137.12, 142.67 (***C***$_{arom}$), 123.45, 124.69, 129.65, 130.72 132.40, 132.66, 133.03, 135.83 (***C***H_{arom}), 120.48, 127.96, 142.67, 157.24 (***C***$_{butadien}$). Anal. calcd. for $C_{28}H_{16}Br_4N_2O_4S_4$ (892.314): C, 37.69; H, 1.81; N, 3.14; S, 14.37; Found: C, 37.45; H, 1.58; N, 3.32; S, 14.23.

1,1,3,4-Tetrakis(heptylthio)-2,4-dinitrobuta-1,3-diene (5b): **5b** was synthesized according to the standard procedure 2 as yellow oil (0.47 g, 20%). R_f 0.46 (PE:$CHCl_3$ = 2:1). IR: 2955, 2926, 2855 ($CH_{aliphatic}$), 1465 (C=C), 1292, 1533 (NO_2). UV-Vis: λ_{max} 249 nm (lgε 4.51). ^{1}H NMR: 0.82 (t, ^3J = 6.84, 12H, C***H*****$_3$**), 1.21–1.71 [m, 40H, (C***H*****$_2$**)$_5$], 2.81 (t, ^3J = 7.57, 2H, SC***H*****$_2$**), 2.86 (t, ^3J = 7.57, 2H, SC***H*****$_2$**), 3.00 (t, ^3J = 7.32, 2H, SC***H*****$_2$**), 3.06 (t, ^3J = 7.32, 2H, SC***H*****$_2$**). ^{13}C NMR: 13.00, 13.01, 13.04 (***C***H_3), 21.51, 21.54, 21.58, 27.41, 27.49, 27.61, 27.67, 27.70, 27.72, 27.75, 27.77, 27.78, 27.82, 27.90, 28.00, 28.06, 28.24, 28.39, 28.55, 28.61, 28.79, 28.97, 28.99, 30.54, 30.62, 30.70, 32.38, 33.56, 34.32, 34.76, 35.05, 35.10, 35.21, 35.58, 36.52, 38.25 [(***C***H_2)$_6$], 119.76, 127.15, 142.73, 156.87 (***C***$_{butadien}$). MS (ESI) *m/z* 664 $[M]^+$, 580 $[M - C_6H_{13}]^+$. Anal. calcd. for $C_{32}H_{60}N_2O_4S_4$ (665.09): C, 57.79; H, 9.09; N, 4.21; S, 19.28; Found: C, 57.54; H, 9.39; N, 4.51; S, 19.55.

Reactions of Monosulfanyl 2,4-Dinitrobuta-1,3-dienes with Amines; Standard Procedure 3

A suspension of monosulfanyl-dinitrobuta-1,3-diene **2** in 25 mL CH_2Cl_2 was added to a solution of amine in 10 mL CH_2Cl_2 with two molar equivalent at room temperature. The mixture was stirred at room temperature for the required reaction time according to TLC (typically 2–4 h). Then, $CHCl_3$ or CH_2Cl_2 was added to the reaction mixture. The organic layer was separated and washed with water (3 × 20 mL) and dried with $CaCl_2$

or $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel.

3,4-Dichloro-1-(morpholin-4-yl)-2,4-dinitro-1-(octylthio)buta-1,3-diene (6a): **6a** was synthesized according to the standard procedure 3 as red oil (0.12 g, 89%). R_f 0.54 (PE:EtAc, 3:1). IR: 2924, 2854 ($CH_{aliphatic}$), 1441 (C=C), 1270, 1521 (NO_2). UV-Vis: λ_{max} 349 nm (lgε 4.81). ^{1}H NMR: 0.81 (t, ^3J = 7.32, 3H, C***H*****$_3$**), 1.19–1.72 [m, 12H, (C***H*****$_2$**)$_6$], 3.18 (t, ^3J = 4.88, 2H, SC***H*****$_2$**), 3.49–3.92 (m, 4H, NC***H*****$_2$**), 3.92 (s, 4H, OC***H*****$_2$**). ^{13}C NMR: 13.42 (***C***H_3), 21.59, 27.90, 28.10, 28.68, 30.72, 32.88, 34.27 [(***C***H_2)$_7$], 51.87, 65.36 (***C***$H_{2Pyrrolidinyl}$), the carbon atoms within the butadiene unit were not detected. MS (ESI) *m/z* 442 $[M]^+$, 364 $[M–NO_2–Cl]^+$. Anal. calcd. for $C_{16}H_{25}Cl_2N_3O_5S$ (442.358): C, 43.44; H, 5.70; N, 9.50; S, 7.25; Found: C, 44.17; H, 5.68; N, 9.67; S, 7.65.

3,4-Dichloro-2,4-dinitro-1-(octylthio)-1-(piperidin-4-yl)buta-1,3-diene (6b): **6b** was synthesized according to the standard procedure 3 as yellow oil (0.142 g, 84%). R_f 0.69 (CH_2Cl_2). IR: 2924, 2854 ($CH_{aliphatic}$), 1442 (C=C), 1272, 1526 (NO_2). UV-Vis: λ_{max} 347 nm (lgε 4.78). ^{1}H NMR: 0.81 (t, ^3J = 7.32, 3H, C***H*****$_3$**), 1.19–1.62 [m, 12H, (C***H*****$_2$**)$_6$], 1.69 (s, 6H, NCH$_2$C***H*****$_2$**), 2.89 (t, ^3J = 7.32, 2H, SC***H*****$_2$**), 3.54 (s, 4H, NC***H*****$_2$**). ^{13}C NMR: 13.04 (***C***H_3), 21.59, 22.82, 27.69, 27.98, 28.68, 28.80 and 30.70 [(***C***H_2)$_7$], 53.80, 28.01, 25.28 (***C***$H_{2Piperidine}$), the carbon atoms within the butadiene unit were not detected. MS (ESI) *m/z* 394 $[M – NO_2]^+$, 348 $[M – 2NO_2]^+$. Anal. calcd. for $C_{17}H_{27}Cl_2N_3O_4S$ (440.385): C, 46.36; H, 6.18; N, 9.54; S, 7.28; Found: C, 46.44; H, 6.70; N, 9.65; S, 7.57.

Reactions of Disulfanyl 2,4-Dinitrobuta-1,3-dienes with Amines; Standard Procedure 4

At room temperature, disulfanyl-dinitrobuta-1,3-diene **3** and amine were dissolved in CH_2Cl_2 in a round-bottomed flask and stirred for 2–4 h, according to TLC. Water (25 mL) was added and the organic layer separated. The aqueous layer was then extracted with further portions of CH_2Cl_2 (3 × 25 mL), and the combined organic extracts were dried ($MgSO_4$), filtered, and evaporated to yield the product which could be further purified by recrystallization.

4-Chloro-1,1-bis(4-methylphenylthio)-3-(morpholin-4-yl)-2,4-dinitrobuta-1,3-diene (7a): **7a** was synthesized according to the standard procedure 4 as orange oil (0.31 g, 70%). R_f 0.11 (CH_2Cl_2). IR: 3022 (CH_{arom}), 2962, 2921, 2856 ($CH_{aliphatic}$), 1491 (C=C), 1257, 1539 (NO_2). UV-Vis: λ_{max}: 242 nm (lgε 4.87). ^{1}H NMR: 2.29 (s, 6H, 2C***H*****$_3$**), 3.39 (s, 4H, NC***H*****$_2$**), 3.58–3.81 (m, 4H, OC***H*****$_2$**), 7.08–7.19 (m, 8H, C***H*****$_{arom}$**). ^{13}C NMR: 20.27 (***C***H_3), 53.03, 65.18 (***C***$H_{2Morpholine}$), 129.57, 131.48 (***C***H_{arom}), 122.90, 139.42 (***C***$_{arom}$), 114.98, 122.93, 130.83, 171.11 (***C***$_{butadien}$). MS (ESI) *m/z* 484 $[M–CClNO_2]^+$, 414 $[M–2NO_2]^+$, 397 $[M–2NO_2–CH_3]$. Anal. calcd. for $C_{22}H_{22}ClN_3O_5S_2$ (508.010): C, 52.01; H, 4.37; N, 8.27; S, 12.62; Found: C, 52.35; H, 4.88; N, 8.42; S, 12.53.

4-Chloro-1,1-bis(4-methylphenylthio)-2,4-dinitro-3-(piperidin-4-yl)buta-1,3-diene (7b): **7b** was synthesized according to the standard procedure 4 as orange oil (0.32 g, 73%). R_f 0.18 (CH_2Cl_2). IR: 2932, 2856 ($CH_{aliphatic}$), 1444, 1413 (C=C), 1218, 1539 (NO_2). UV-Vis: λ_{max}: 251 nm (lgε 4.91). ^{1}H NMR: 1.59–1.71 (m, 6H, C***H*****$_{2Piperidine}$**), 2.28 (s, 6H, 2C***H*****$_3$**), 3.76 (m, 4H, NC***H*****$_2$**), 7.10–7.16 (m, 8H, C***H*****$_{arom}$**). ^{13}C NMR: 20.29 (***C***H_3), 54.29, 25.16, 22.76 (***C***$H_{2Piperidine}$), 129.41, 131.94 (***C***H_{arom}), 123.21, 139.32 (***C***$_{arom}$), 118.11, 123.18, 125.68, 172.89 (***C***$_{butadien}$). MS (ESI) *m/z* 415 $[M–2NO_2]^+$,

395 $[M–2NO_2–CH_3]^+$. Anal. calcd. for $C_{23}H_{24}ClN_3O_4S_2$ (506.037): C, 45.94; H, 4.10; N, 10.05; S, 7.67; S, 11.73; Found: C, 46.15; H, 3.88; N, 10.32; S, 7.53.

Cyclization Reactions of 1,1,3,4-Tetrachloro-2,4-dinitrobuta-1,3-diene with Multifunctional Nucleophiles

A solution of 2-amino-4-chlorothiophenol in diethylether was added dropwise at –20 °C to a solution of dinitrobuta-1,3-diene **1** in diethylether within 30 min. After stirring for 1 h at –20 °C, the precipitate was filtered off, successively washed twice cold methanol (2 × 25 mL), PE (2 × 25 mL), and diethylether (2 × 25 mL), and finally dried under reduced pressure.

5-Chloro-2-(2,3-dichloro-1,3-dinitroallylidene)-2,3-dihydrobenzo[*d*]thiazole (8): **8** was synthesized as grey crystals (1.50 g, 77%), mp 160–161.5 °C. R_f 0.54 ($CHCl_3$). IR: 3450, 3363 (NH), 3016 (CH_{arom}), 1487, 1470 (C=C), 1399, 1559 (NO_2). UV-Vis: λ_{max} 377 nm (lgε 4.82). ^{1}H NMR (DMSO-d_6): 7.27 (s, 1H, NH), 6.46 (dd, ^3J = 2.44 Hz, ^3J = 8.30, 2H, C***H***$_{arom}$), 6.81 (d, ^3J = 1.95, 1H, C***H***$_{arom}$), 6.92 (d, ^3J = 8.30, 2H, C***H***$_{arom}$). ^{13}C NMR (DMSO-d_6): 118.09, 137.49, 149.46 (***C***$_{arom}$), 115.93, 117.55, 136.36 (***C***H$_{arom}$), 118.03, 118.07, 137.50, 149.65 (***C***$_{butadien}$). MS (ESI) *m/z* 371 $[M + 2H]^+$, 319 $[M – NO_2]^+$. Anal. calcd. for $C_{10}H_4Cl_3N_3O_4S$ (368.580): C, 32.59; H, 1.09; N, 11.40; S, 8.70; Found: C, 32.81; H, 1.58; N, 11.02; S, 8.53.

Dinitrobuta-1,3-diene **1** and pentaerythritol tetrakis(3-mercaptopropionate) were combined and stirred 10 h without a solvent at 0 °C. After this period, the solvent was evaporated and the residue dissolved in CH_2Cl_2 (20 mL). Water (50 mL) was added and the organic layer separated. The aqueous layer was then extracted with further portions of CH_2Cl_2 (2 × 25 mL) and the combined organic extracts were dried over $CaCl_2$ and evaporated. Purification by column chromatography on silica gel gave pure product.

7,21-Bis(2,3-dichloro-1,3-dinitroallylidene)-2,12,16,26-tetraoxa-6,8,20,22-tetrathiaspiro[13.13]heptacosane-3,11,17,25-tetraone (9): 9 was synthesized as brown oil (0.41 g, 21%). R_f 0.60 ($CHCl_3$). IR: 2900, 2936, 2981 ($CH_{aliphatic}$), 1616, 1660 (C=O), 1474 (C=C), 1388, 1552 (NO_2). UV-Vis: λ_{max}: 383 nm (lgε 4.97). ^{1}H NMR: 4.12 (s, 8H, >C-C***H$_2$***), 2.60–2.63 (m, 8H, SC***H$_2$***), 2.68–2.73 (m, 8H, (C=O)-C***H$_2$***). ^{13}C NMR: 18.63 (S***C***H$_2$), 37.27 (>***C***<), 41.12 (O***C***H$_2$), 61.23 (>C***C***H$_2$), 170.06 (***C***=O), 169.65, 170.09, 170.28, 170.53 (***C***$_{butadien}$). MS (ESI) *m/z* 909 $[M + 2H]^+$, 802 $[M – 3Cl]^+$. Anal. Calcd. for $C_{25}H_{24}Cl_4N_4O_{16}S_4$ (906.547): C, 33.12; H, 2.67; N, 6.18; S, 14.15; Found: C, 33.45; H, 2.88; N, 6.32; S, 14.53.

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