Chemistry of Polyhalogenated Nitrobutadienes, 3: [4+2] Cycloadditions of (*Z*)-1,1,4-Trichloro-2,4-dinitrobuta-1,3-diene and Subsequent Reactions

Viktor A. Zapol'skii,[a] Jan C. Namyslo,[a] Björn Blaschkowski,[b] Dieter E. Kaufmann*[a]

[a] Institut für Organische Chemie, Technische Universität Clausthal, Leibnizstraße 6, 38678 Clausthal-Zellerfeld, Germany
Fax +49(5323)722834; E-mail: dieter.kaufmann@tu-clausthal.de

[b] Institut für Anorganische und Analytische Chemie, Technische Universität Clausthal, Leibnizstraße 6, 38678 Clausthal-Zellerfeld, Germany

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Abstract: The multifaceted chemical behavior of polyhalogenated nitrobutadienes, such as **1** and **2**, inspired us to test their features in [4+2] cycloaddition reactions. It appears that in the presence of an appropriate diene only the β-chloro-β-nitro vinyl moiety of **1** acts as an efficient dienophile. The resulting cycloaddition products were subsequently converted at the β,β-dichloro position by means of a suitable N,O- and N,N-bisnucleophile to give benzoxazole or benzimidazole derivatives. The latter reaction products proved valuable for crop protection.

Key words: nitro compound, haloalkene, cycloaddition, Diels–Alder, heterocycle

Nitro-substituted polyhalogenobuta-1,3-dienes are members of a rather new class of organic compounds which became the topic of recent investigations due to interesting chemical characteristics as well as biological properties.[1,2] Among these, (*Z*)-1,1,4-trichloro-2,4-dinitrobuta-1,3-diene (**1**) is less easily accessible than **2**; it was prepared for the first time in 1993 by means of nitration of 1-bromo-1,4,4-trichlorobuta-1,3-diene.[3] However, its chemical properties are hitherto fairly unexplored, in contrast to, for example, pentachloro-2-nitrobuta-1,3-diene (**2**, Figure 1).[4]

Figure 1 Nitro-substituted polyhalogenobuta-1,3-dienes

In the present paper we mainly focus on (*Z*)-1,1,4-trichloro-2,4-dinitrobuta-1,3-diene (**1**) as a novel dienophile for Diels–Alder reactions. The resulting cycloadducts serve as useful precursors for the synthesis of physiologically active substances, for example pesticides, as evidenced by the structural formula of potent agents like aldrin or captafol (Figure 1) that are similarly accessible by [4+2] cycloadditions. In almost the same manner as it is known from these highly chlorinated compounds, the additional presence of a nitro substituent enforces the biological activity.[5] For example, this is the case for the herbicide nitrofen[6] and the fungicide pentachloronitrobenzene (Figure 2).

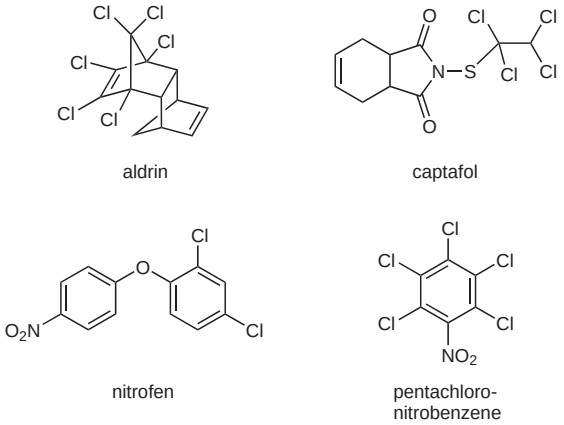
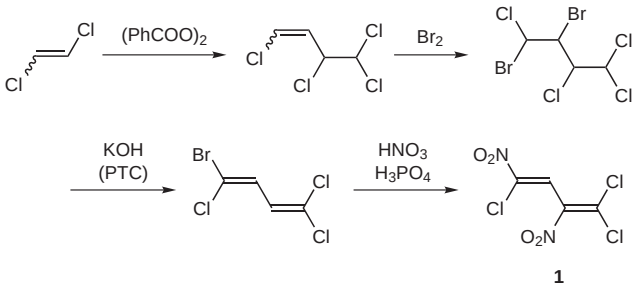


Figure 2 Pesticides based on chlorinated compounds

Moreover, with the new Diels–Alder products in hand, we subsequently took advantage of the high reactivity of the remaining dichloro-substituted olefinic carbon. Thus, by reaction of this electron-deficient center with an appropriate aromatic N,O- or N,N-bisnucleophile (e.g. 2-aminohydroxy- or 1,2-diaminobenzene), interesting benzoxazole or benzimidazole derivatives were synthesized which are currently under biological screening.

In detail, our investigations started with the synthesis of (*Z*)-1,1,4-trichloro-2,4-dinitrobuta-1,3-diene (**1**) which was obtained in four steps from 1,2-dichloroethylene (Scheme 1).[3]



Scheme 1

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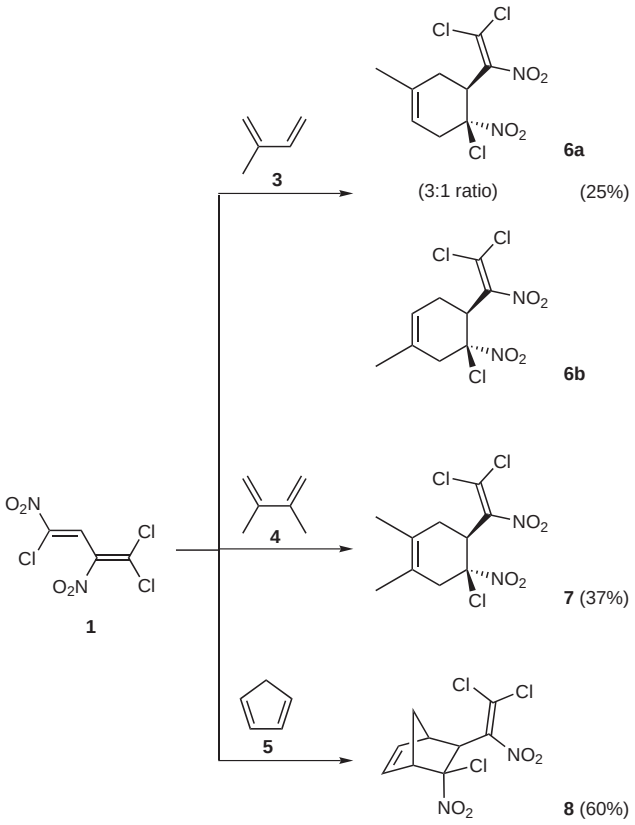
The first synthetic step is the radical dimerization of 1,2-dichloroethylene producing a mixture of isomers. The resulting 1,3,4,4-tetrachlorobut-1-ene then is brominated. Subsequent twofold dehydrobromination by means of potassium hydroxide under phase-transfer-catalysis conditions, followed by nitration of the intermediate bromobuta-1,3-diene, gave the desired trichloro-dinitrodiene **1**. In general, cycloaddition reactions of unsaturated nitrohalo compounds are fairly rare in the literature. Among these, some examples are known with halonitroethylenes.[7] To the best of our knowledge, cycloadditions with polyhalogenated nitrobuta-1,3-dienes are unknown up to now. However, the less substituted 2,3-dichlorobuta-1,3-diene as well as the 1,4-dichloro isomer act as a diene in Diels–Alder reactions, whereas both, the 1,1,2- and 1,2,3-trichloro derivatives are good dienophiles.[8] In conjunction with this work we became interested in the cycloaddition modes of (*Z*)-1,1,4-trichloro-2,4-dinitrobuta-1,3-diene (**1**) and perchloro-2-nitrobuta-1,3-diene (**2**). By means of X-ray analysis it had been confirmed that in the solid state these nitrodienes exist in an *s-trans* form,[9] due to their bulky substituents. In our experiments, nitrodiene **1** exclusively acted as a dienophile, whereas reactive dienes such as isoprene (**3**), 2,3-dimethylbuta-1,3-diene (**4**), cyclopentadiene (**5**), or cyclohexa-1,3-diene undertook the task of the diene (Scheme 2).

For example, diene **1** reacts with a fivefold excess of isoprene (**3**) in a sealed ampule at 80–85 °C within 60 hours to give the cyclohexene derivatives **6a**,**b** as an inseparable mixture of regioisomers (3:1 ratio as evidenced by ^{1}H NMR), albeit in low yield (25%). Addition of hydroquinone could not prevent polymerization of **3**. An increased yield (37%) was obtained in the case of diene **4** under similar conditions (65–70 °C, 40 h), whereupon in a regioselective manner the dimethylcyclohexene **7** was formed. Attempted cycloadditions with 1-methoxy-1,3-butadiene or 1-methoxy-3-trimethylsiloxybuta-1,3-diene (Danishefsky's diene) led to the formation of polymers exclusively or predominantly. Best results were achieved with cyclopentadiene (**5**) applying very mild conditions (20 °C, 96 h). The expected bicyclic stereoisomer **8** was diastereoselectively synthesized this way in 60% yield. The similar reaction of the dinitrobutadiene **1** with cyclohexa-1,3-diene unexpectedly delivered a complex mixture of products that could not be separated by column chromatography. All attempts to force **1** as well as **2** to react as a diene with dienophiles such as ethylenetetracarbonitrile, acrylonitrile, ethyl acrylate, 3-bromoprop-1-ene, 2-methylbut-2-ene, or styrene remained unsuccessful.



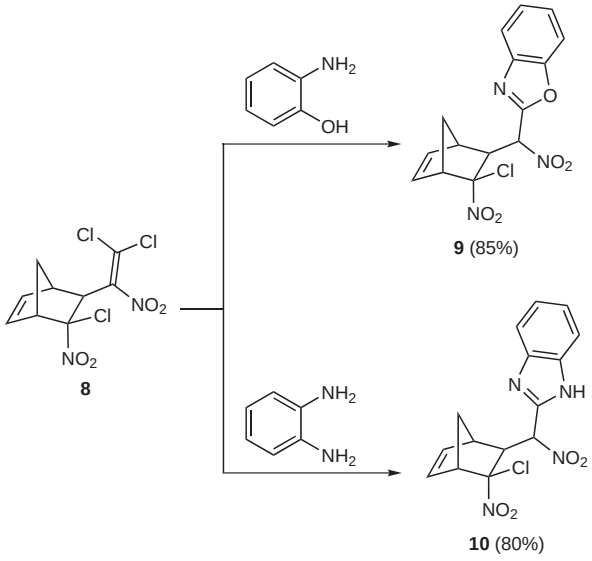
Scheme 2

From a mechanistic viewpoint it is interesting to know, that even though the α-nitro-β,β-dichloro vinyl moiety within **1** is even more electron-deficient, only the β-chloro-β-nitro vinyl group undergoes the [4+2] cycloaddition as the dienophile, probably due to a lower sterical demand. Additional synthetic examples illustrate the chemical behavior of this unusual disubstituted vinyl group such as the selective reduction of the C=C double bond by means either of sodium borohydride[10a] or with molecular hydrogen and palladium on charcoal,[10b] in both cases leaving the chloro as well as the nitro substituent unchanged. Furthermore, interesting condensation reactions have been published to give highly substituted 2*H*-1-benzopyranes,[10c–f] furo[3,2-*c*]pyran-4-ones,[10g] furo[2,3-*d*]pyrimidin-4(3*H*)-ones,[10h,i] anthracene-9,10-diones,[10j] furans, tetrahydro-4(2*H*)benzofuranones, and analogues,[10k] or chromane derivatives.[10g,l,m] In addition, the formation of 4-oxospiro[2.5]octanes[10n] is worth mentioning. Other synthetic strategies using the β-chloro-β-nitro vinyl group, involve the cyclization with ethane-1,1,2,2-tetracarbonitrile to give a hepta-substituted cyclopentene,[10o] use the formation of a substituted isoxazole[10p] or create a 5,6-dihydro-4*H*-[1,2]oxazine *N*-oxide.[10q] Moreover, addition reactions of arylsulfinic acid derivatives have been pointed out.[10r,s] Last, but not least in this context, the rare vinylic substitution of the nitro group of this β-chloro-β-nitro vinyl fragment **1** has been demonstrated by using 1*H*-benzotriazole or butanethiol as the nucleophile.[11,12]

However, all attempts to use pentachloro-2-nitrobuta-1,3-diene (**2**) as the dienophile along with the dienes **3**–**5** failed, regardless of the presence or absence of a Lewis acid such as zinc dichloride, lithium chloride, or aluminum trichloride. Either no conversion or polymerization was observed, even though hydroquinone had been added. Solely the combination of aluminum trichloride and cyclopentadiene (**5**) gave an inseparable mixture of cycloaddition products. Despite this unwanted behavior, it is well

known that the trichlorovinyl group in **2** generally allows for rich chemistry, e.g. halogenations,[13a,b] epoxidations,[13c] saponification,[13d] or other types of addition reactions.[13d–h] But cycloadditions, predominantly of the [2+2]-type, with this trichlorovinyl double bond taking part, need harsh conditions: among these, irradiations,[14a–d] high-temperature reactions,[14e] or the application of Friedel–Crafts-type catalysts[14f] have been published. As a tentative result, the lower reactivity of the perchlorinated nitrodiene **2** in general compared to the title compound **1** may be due to the distinct steric hindrance caused by a total of five chloro substituents. The α-nitro-β,β-dichloro vinyl group within these molecules exhibits no reactivity towards cycloaddition reactions, whereas its tendency to undergo vinylic S_N reactions exceeds the reactivity of both the β-chloro-β-nitro vinyl group of **1** and the trichloro vinyl group within the pentachloro compound **2**, with respect to such vinylic substitution reactions.

In addition, the highly substituted Diels–Alder products **6**–**8** turned out to be promising substrates for a subsequent vinylic substitution with appropriate nucleophiles, in fact at the terminal carbon atom of the remaining α-nitro-β,β-dichloro moiety. By means of *o*-aminophenol or *o*-phenylenediamine, the twofold vinylic S_N reaction of **8** afforded the benzoxazole **9** in 85% yield or benzimidazole **10** in 80% yield, respectively. As it is known from such α-nitro-β,β-dichloro compounds, these reactions involve the formation of intermediate 2,3-dihydro derivatives which subsequently aromatize to give the heterocycles **9** and **10** (Scheme 3).



Scheme 3

Besides the characterization of all new compounds by one- and two-dimensional NMR spectroscopy as a matter of routine, we were fortunate to get an X-ray analysis of **9** (Figure 3). This way we are able to proof the conservation of the stereochemistry of **1** unambiguously, with the big heterocyclic substituent in an *exo*-position.

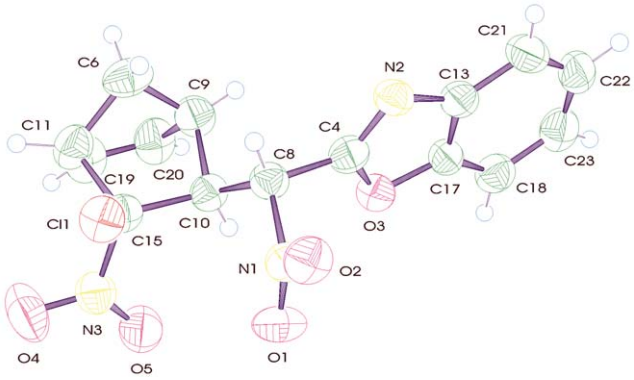


Figure 3 X-ray structure of 2-*exo*-[(3-*exo*-chloro-3-nitrobicyclo[2.2.1]hept-5-en-2-yl)nitromethyl]benzooxazole (**9**)[15]

In conclusion, the β-chloro-β-nitro vinyl moiety within (*Z*)-1,1,4-trichloro-2,4-dinitrobuta-1,3-diene (**1**) acts as an efficient dienophile in [4+2]-cycloaddition reactions with classical electron-rich dienes, whereas the additional α-nitro-β,β-dichloro vinyl group shows no such reactivity with respect to Diels–Alder reactions. However, the latter vinyl group offers great potential in vinylic substitution of the two chloro substituents, due to the activating α-nitro group. Thus, the Diels–Alder products were subsequently reacted with appropriate aromatic N,O- or N,N-bisnucleophiles. The resulting benzoxazole or benzimidazole derivatives show promising physiological activity, probably as candidates for application as pesticides. Further biological testing is underway.

Acknowledgment

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(15) **Crystal Data for 9.**
$C_{15}H_{12}ClN_3O_5$, M = 349.73 g mol^{-1}, crystal size 0.2 × 0.2 × 0.5 mm were collected on a Stoe IPDS II diffractometer using λ = 0.71073 Å [T = 223(2) K]. The crystal structure was solved by direct methods and refined by full matrix least squares on F^2 (SHELX-97) in the space group $P2_1/n$ (monoclinic), lattice parameters a = 7.2336(12) Å, b = 19.414(3) Å, α = 10.834(2) Å, β = 96.523(15)°, V = 1511.7(4) Å^3, Z = 4, $d_{calc.}$ = 1.537 g cm^{-3}, F(000) = 720, absorption coefficient = 0.286 mm^{-1} using 2682 independent reflections and 265 parameters. $R1$ = 0.0489, $wR2$ = 0.0995 [I > 2σ(I)], goodness of fit on F^2 = 0.971, residual electron density = 0.203 and –0.267 e Å^{-3}. CCDC 278475 contains supplementary crystallographic data for this paper, obtainable free of charge from www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033; or deposit@ccdc.cam.ac.uk.

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(18) **Experimental Details.**
Melting points were measured on a Büchi 520 apparatus and were uncorrected. ^{1}H NMR, ^{13}C NMR, ^{14}N NMR, and ^{15}N NMR spectra were obtained on a Bruker Avance with 400 MHz proton frequency, ^{15}N NMR were measured in inverse 2D mode (gs-HMBC). ^{1}H NMR spectra in $CDCl_3$ were referenced to tetramethylsilane (TMS) at δ = 0.0 ppm; ^{13}C NMR spectra refer to the solvent signal center at δ = 77.0 ppm. Other solvents as follows: DMSO-d_6: 2.50 ppm (^{1}H), 39.70 ppm (^{13}C); $(CD_3)_2CO$: 2.04 ppm (^{1}H), 29.8 ppm (^{13}C), C_6D_6: 7.20 ppm (^{1}H), 128.0 ppm (^{13}C). N NMR spectra were externally referenced to nitromethane at δ = 0.0 ppm. IR spectra were obtained on a Bruker 'Vector 22' FT IR as KBr IR. Mass spectra were recorded on a Hewlett Packard system '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 Varian MAT 311 A spectrometer with pre-selected molecular ion peak matching at R >> 10000 to be within ± 2 ppm of the exact masses. Elemental analyses were performed by Institut für Pharmazeutische Chemie, TU Braunschweig. TLC was carried out on Merck plates coated with silica gel (60 F 254). Silica gel 60 was also used for column chromatography.
(*Z*)-1,1,4-Trichloro-2,4-dinitro-1,3-butadiene (1).[3]
Yellow solid, mp 70–71 °C. ^{1}H NMR ($CDCl_3$): δ = 8.12 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 142.6 (C-4), 141.5 (C-2), 135.7 (C-1), 118.1 (C-3). ^{15}N NMR ($CDCl_3$): δ = –20.5, –21.4.
4-Chloro-5-(2,2-dichloro-1-nitrovinyl)-1-methyl-4-nitrocyclohex-1-ene (7a) and 5-Chloro-4-(2,2-dichloro-1-nitrovinyl)-2-methyl-5-nitrocyclohex-1-ene (6b).
An ampule was charged with 0.50 g (2.00 mmol) dinitrodiene **1**, 0.68 g (10.0 mmol) isoprene (**3**), and 10 mg (0.1 mmol) hydroquinone and sealed. The mixture was stirred under N_2 atmosphere for 60 h at 80–85 °C. After extraction thrice with PE–Et_2O (3:1) and separation of polymeric by-product, the solvent and residual volatiles were evaporated in vacuo. The crude product was purified by column chromatography with PE as the eluent. Yield 0.16 g (25%) of **6a**,**b**, mp 118–119 °C. Isomeric ratio **6a**/**6b** = 3:1. IR (KBr): 2937, 2915, 1618 (C=C), 1566 (NO_2), 1543 (NO_2), 1442, 1430, 1364 (NO_2), 1350 (NO_2), 1054, 1021, 978, 935, 843, 774, 706, 643, 588 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ (major isomer) = 1.73 (s, 3 H, CH_3), 2.52 (m, 1 H, CH_2), 2.70 (m, 1 H, CH_2), 2.92 (m, 1 H, CH_2), 3.27 (m, 1 H, CH_2), 4.48 (dd, ^3J = 8.5, 6.0 Hz, 1 H, H-5), 5.31 (m, 1 H, -CH=); δ (minor isomer) = 1.72 (s, 3 H, CH_3), 2.42 (m, 1 H, CH_2),

2.65 (m, 1 H, CH_2), 2.85 (m, 1 H, CH_2), 3.35 (m, 1 H, CH_2), 4.39 (dd, ^3J = 8.3, 5.8 Hz, 1 H, H-4), 5.43 (m, 1 H, -CH=). ^{13}C NMR ($CDCl_3$): δ (major isomer) = 22.59 (CH_3), 32.58 (CH_2), 40.73 (CH_2), 44.26 (-CH-), 102.42 [$C(NO_2)Cl$], 115.84 (CH=), 127.84 (=CCl_2), 132.54 (=*C*-Me), 146.73 [=$C(NO_2)$]; δ (minor isomer) = 22.47 (CH_3), 27.98 (CH_2), 43.88 (CH), 44.80 (CH_2), 102.67 [$C(NO_2)Cl$], 118.45 (CH=), 127.81 (=CCl_2), 129.74 (=C–Me), 146.77 [=$C(NO_2)$]. MS (GC-MS, EI): *m/z* (%) = 314 (3) [M^+], 297 (2), 267 (7), 250 (14), 221 (17), 185 (45), 149 (60), 125 (35), 115 (100). Anal. Calcd for $C_9H_9Cl_3N_2O_4$ (315.54): C, 34.26; H, 2.87; N, 8.88. Found: C, 34.49; H, 2.91; N, 8.49.

4-Chloro-5-(2,2-dichloro-1-nitrovinyl)-1,2-dimethyl-4-nitrocyclohex-1-ene (7).

Preparation as described for **6a**,**b**, except for reaction conditions: 65–70 °C, 40 h. Yield 37%, mp 84–85 °C. IR (KBr): 2922, 1619 (C=C), 1562 (NO_2), 1541 (NO_2), 1433, 1368 (NO_2), 1352 (NO_2), 1252, 1061, 953, 852, 810, 778, 637 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.65 (br s, 6 H, 2 CH_3), 2.46 (dd, ^2J = 17.8 Hz, ^3J = 5.8 Hz, 1 H, H-6), 2.64 (dd, ^2J = 17.8 Hz, ^3J = 8.1 Hz, 1 H, H-6), 2.80 (d, ^2J = 17.6 Hz, 1 H, H-3), 3.27 (d, ^2J = 17.6 Hz, 1 H, H-3), 4.44 (dd, ^3J = 8.1, 5.8 Hz, 1 H, H-5). ^{13}C NMR ($CDCl_3$): δ = 18.2 (CH_3), 18.3 (CH_3), 33.6 (C-6), 44.3 (C-5), 45.6 (C-3), 102.6 (C-4), 121.7 (=*C*–Me), 124.0 (=C–Me), 127.7 (=CCl_2), 146.8 [=$C(NO_2)$]. MS (direct inlet): *m/z* (%) = 328 (2) [M^+], 313 (1), 298 (2), 281 (9), 264 (8), 246 (6), 235 (27), 199 (33), 164 (34), 139 (19), 129 (41), 105 (36), 43 (100). Anal. Calcd for $C_{10}H_{11}Cl_3N_2O_4$ (329.57): C, 36.44; H, 3.36; N, 8.50. Found: C, 36.60; H, 3.33; N, 8.22.

2-*exo*-Chloro-3-*exo*-(2,2-dichloro-1-nitrovinyl)-2-*endo*-nitrobicyclo[2.2.1]hept-5-ene (8).

Procedure: 0.50 g (2.0 mmol) dinitrodiene **1** and 1.32 g (20 mmol) cyclopentadiene (**5**) were stirred for 4 d at r.t. Subsequently, the mixture was cooled down to 0 °C. The precipitated crude product was filtered off and recrystallized from PE–Et_2O (1:1). Yield 0.38 g (60%), mp 119–120 °C. IR (KBr): 3082, 3013, 2975, 2888, 1608, 1575 (NO_2), 1535 (NO_2), 1458, 1360 (NO_2), 1338 (NO_2), 1254, 1172, 1065, 987, 971, 950, 888, 808, 767, 703, 676, 645, 591, 544 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.93 (s, 2 H, CH_2), 3.38 (s, 1 H, H-4), 3.60 (s, 1 H, H-1), 4.31 (s, 1 H, H-3), 6.07 (br s, 1 H, H-6), 6.56 (br s, 1 H, H-5). ^{1}H NMR (C_6D_6): δ = 1.25 (d, ^2J = 10.7 Hz, 1 H, H-7_{syn},), 1.70 (d, ^2J = 10.7 Hz, 1 H, H-7_{anti}), 2.79 (m, 1 H, H-4), 3.10 (br s, 1 H, H-1), 3.98 (d, ^3J = 2.1 Hz, 1 H, H-3), 5.50 (dd, ^3J = 5.5, 3.2 Hz, 1 H, H-6), 5.71 (dd, ^3J = 5.5, 3.2 Hz, 1 H, H-5). ^{13}C NMR ($CDCl_3$): δ = 46.6 (C-3), 47.2 (CH_2), 50.8 (C-4), 56.6 (C-1), 108.4 (C-2), 128.8 (=CCl_2), 134.5 (C-6), 141.3 (C-5), 148.1 [=$C(NO_2)$]. MS (GC-MS): *m/z* (%) = 266 (2) [M – NO_2^+], 219 (13), 183 (38), 149 (73), 136 (21), 115 (34), 66 (100). HRMS (EI) [M^+]: *m/z* calcd for $C_9H_7Cl_3N_2O_4$: 311.9471.

2-*exo*-{(3-*exo*-Chloro-3-nitrobicyclo[2.2.1]hept-5-en-2-yl)nitromethyl}benzoxazole (9).

To a suspension of 0.40 g (1.28 mmol) bicycloheptene **8** in 10 mL MeOH was added a solution of 0.46 g (4.23 mmol) *o*-aminophenol in 20 mL MeOH at 0 °C within 10 min. The mixture was kept at 0–10 °C for 1 h, then 4 h at r.t. After addition of 10 drops of concd HCl and 1 h at r.t., the mixture was cooled down to 0 °C. The precipitate was sucked off, washed thrice with H_2O and once with 10 mL of cold MeOH. Drying in vacuo yielded 0.38 g (85%) of benzoxazole **9**, mp 165–167 °C. IR (KBr): 3018, 1611, 1568 (NO_2), 1557 (NO_2), 1481, 1451, 1353 (NO_2), 1232, 1173, 1067, 1003, 977, 950, 912, 879, 805, 784, 760, 749, 732, 687, 574, 513 cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 1.92 (ddd, *J* = 10.3, 4.2, 2.1 Hz, 1 H, H-7_{syn}), 2.43 (d, 1 H, H-7_{anti}, ^2J = 10.3 Hz), 2.88 (m, 1 H, H-1), 3.70 (m, 1 H, H-4), 4.35 (dd, *J* = 11.5, 2.1 Hz, 1 H, H-2), 6.09 (dd, *J* = 5.6, 3.1 Hz, 1 H, H-5), 6.48 [d, *J* = 11.5 Hz, 1 H, -$CH(NO_2)$], 6.66 (dd, *J* = 5.6, 3.1 Hz, 1 H, H-6), 7.50 (ddd, *J* = 7.8, 7.5, 1.2 Hz, 1 H, H_{aryl},), 7.56 (ddd, *J* = 8.1, 7.5, 1.4 Hz, 1 H, H_{aryl}), 7.78 (ddd, *J* = 8.1, 1.2, 0.7 Hz, 1 H, H_{aryl}), 7.86 (ddd, *J* = 7.8, 1.4, 0.7 Hz, 1 H, H_{aryl}). ^{13}C NMR (CD_3COCD_3): δ = 46.9 (C-1), 47.6 (C-7), 50.4 (C-2), 60.1 (C-4), 85.8 [-$CH(NO_2)$], 109.7 (C-3), 112.2 (C_{aryl}), 121.8 (C_{aryl}), 126.4 (C_{aryl}), 128.0 (C_{aryl}), 133.4 (C-5), 141.2 ($C_{quat.,aryl}$), 142.9 (C-6), 151.7 ($C_{quat.,aryl}$), 158.2 (C=N). MS: *m/z* (%) = 304 (2) [M – NO_2^+], 273 (32), 256 (10), 238 (100), 220 (58), 204 (47), 191 (50). HRMS (EI) [M^+]: *m/z* calcd for $C_{15}H_{12}ClN_3O_5$: 349.0465.[15]

2-*exo*-{(3-*exo*-Chloro-3-nitrobicyclo[2.2.1]hept-5-en-2-yl)nitromethyl}-1*H*-benzimidazole (10).

Prepared in analogy to compound **9** from bicycloheptene **8** and *o*-phenylenediamine (ratio 1:2.2), yield 80%, mp 105–107 °C. IR (KBr): 3385, 2998, 1621 (C=C), 1561 (NO_2), 1456, 1430, 1346 (NO_2), 1231, 1149, 1061, 958, 906, 840, 784, 749, 616, 578, 439 cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 1.85 (dd, *J* = 10.2, 2.1 Hz, 1 H, H-7_{syn}), 2.34 (d, ^2J = 10.2 Hz, 1 H, H-7_{anti}), 2.64 (m, 1 H, H-1), 3.66 (m, 1 H, H-4), 4.49 (m, 1 H, H-2), 6.06 (dd, *J* = 5.6, 3.0 Hz, 1 H, H-5), 6.39 [d, *J* = 11.6 Hz, 1 H, -$CH(NO_2)$], 6.62 (dd, *J* = 5.6, 3.0 Hz, 1 H, H-6), 7.36 (m, 2 H, H_{aryl}), 7.72 (m, 2 H, H_{aryl}). ^{13}C NMR (CD_3COCD_3): δ = 47.0 (C-1), 47.7 (CH_2), 50.6 (C-2), 60.1 (C-4), 86.0 [-*C*H(NO_2)], 110.1 (C-3), 116.8 (2 C, C_{aryl}), 124.8 (2 C, C_{aryl}), 133.2 (C-5), 138.4 (2 C, $C_{quat.,aryl}$), 143.0 (C-6), 146.1 (C=N). MS: *m/z* (%) = 348 (2) [M^+], 302 (34), 287 (12), 272 (35), 255 (15), 237 (100), 219 (92). HRMS (EI) [M^+]: *m/z* calcd for $C_{15}H_{13}ClN_4O_4$: 348.0625.