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Stereospecific Synthesis of 1,2-Difunctionalized Buta-1,3-Dienes via Tandem [3,3]–[3,3] Sigmatropic Rearrangements[1]

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Dedicated to Professor Wolfgang Kirmse on the occasion of his 70th birthday

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Abstract—Thermolysis of bis-thiocarbamates derived from but-3-yne-1,2-diols resulted in the formation of buta-1,3-dienes with carbamoylthio groups in positions 1 and 2 with good to excellent yields. The stereochemistry of the products is controlled by substituents at C-1 of the starting material and can be explained by chair-like reacting conformations.

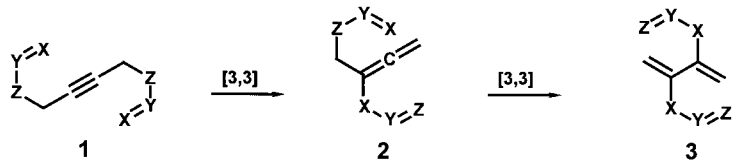
Introduction

Tandem [3,3]–[3,3] sigmatropic rearrangements like the well-known reaction **1** → **2** → **3**, for instance with XYZ=C–C=C (Cope rearrangement),[2] C–CO_2R (ortho-ester Claisen rearrangement),[3] NCO,[4] NCS,[5] NCSe,[6] N_3,[7] $SCONMe_2$,[8] SCN,[9] can be utilized to convert the but-2-yne-1,4-diyl starting materials **1** into the 2,3-difunctionalized buta-1,3-dienes **3** (Scheme 1). The synthesis of similar products proceeds analogously via two consecutive [2,3] sigmatropic isomerizations, for example in the reaction of phosphinites to phosphane oxides,[10] phosphites to phosphonates,[11] sulfinates to sulfones,[12] or sulfenates to sulfoxides.[12,13]

Recently, we described the first tandem sigmatropic rearrangements that provide a convenient approach to 1,2-difunctionalized buta-1,3-dienes.[14] Thus, a sequence of [3,3] migrations such as **4** → **5** → **6** as well as [2,3] shifts **7** → **8** → **9** could be used to direct both functional groups into vinylic positions (Scheme 2). The [2,3] isomerizations afforded the parent compounds of type **9** like sulfones (XY=Ts), sulfoxides (XY=S(O)Ar), or phosphane oxides (XY=$P(O)Ph_2$) with exclusive *E* configuration.[14] On the other hand, parent compounds of type **6** such as trichloroacetamides (XYZ=$NHCOCCl_3$), thioesters (XYZ=S-COPh), thiocarbamates (XYZ=$SCONMe_2$), thiocarbonates (XYZ=SCO_2Ar), or dithiocarbonates (XYZ=SC(O)SMe), which resulted from [3,3] sigmatropic rearrangements, were formed as mixtures of separable *E*/*Z* isomers. We describe here that the tandem reaction **4** → **5** → **6** proved to be completely stereospecific if a substituent is introduced at C-1 of **4**. This substituent controls both the stereochemistry at the C-1/C-2 double bond and that at the C-3/C-4 double bond of **6**.

Results and Discussion

Starting with a 1:2 mixture of *meso*-**10a** and *rac*-**10a**, we prepared a mixture of *meso*-**11a** and *rac*-**11a** (1:2, 89% yield), since separation of these thiocarbamates by simple crystallization from diethyl ether was much more convenient than isolation of the diastereomeric diols[15] (Scheme 3). Pure *meso*-**10a**[16] analogously yielded only *meso*-**11a** as shown in a control experiment. A mixture of *syn*-**10b** and *anti*-**10b** (1.9:1) was synthesized by dihydroxylation of pent-2-en-4-yne[17] (*cis*/*trans*=1.9:1), however, we did not use the known procedure[18] with H_2O_2/HCO_2H due to low yields. Instead, epoxidation of



Scheme 1.

Keywords: alkynes; thiocarbamates; dienes; rearrangements; diastereoselection.

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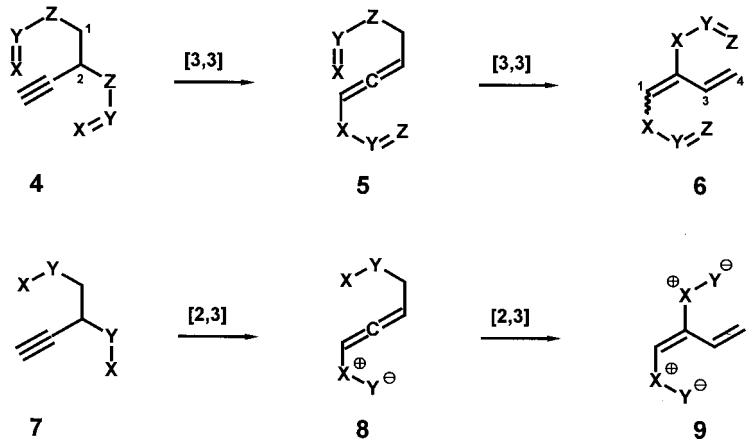
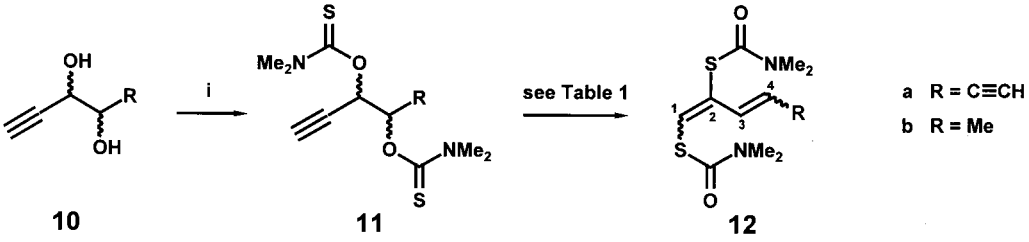


Scheme 2.



Scheme 3. *Reagents and conditions:* (i) NaH, THF, 20°C, 20–24 h (and 35–40°C, 9 h in the case of **10a**) and then $Me_2NC(S)Cl$, 20°C, 16–24 h, 77–89%.

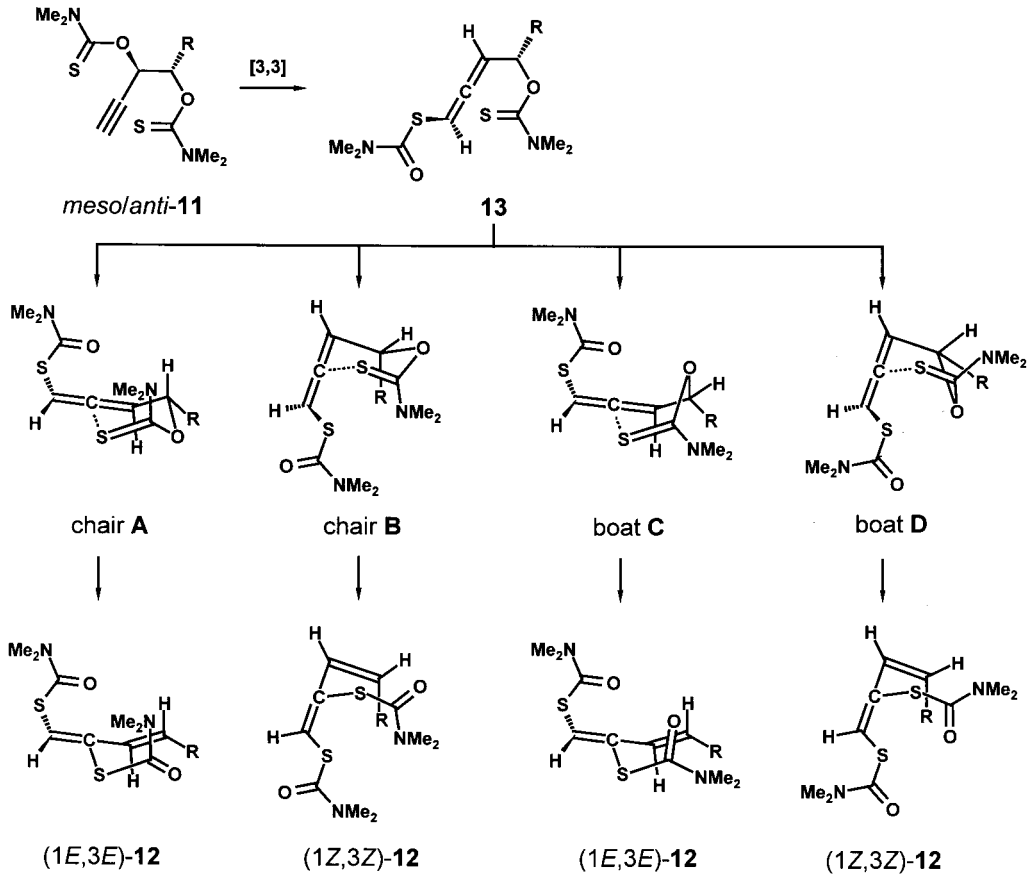
the enyne with 3-chloroperbenzoic acid (48% yield) followed by hydrolysis (H_2O, 100°C, 2 days, 87%) gave **10b**, which was transformed into **11b** (77% yield, *syn*/*anti*=1.9:1). These diastereomeric compounds could be separated by HPLC. Alternatively, *anti*-**11b** was synthesized and purified by crystallization from diethyl ether starting with **10b** (*syn*/*anti*=1:7), which was prepared from the reaction of 2-bromopropanal[19] and ethynylmagnesium bromide (29%, *syn*/*anti*=1:7) followed by ring closure of the bromohydrins by treatment with potassium hydroxide (87%, *cis*/*trans*=1:7) and hydrolysis of the resulting oxiranes (87%). Furthermore, the starting material *syn*-**10b** could selectively be generated in analogy to the method of R. W. Friesen.[20] Thus, *syn*-4-iodopent-4-ene-2,3-diol[21] was available from penta-3,4-dien-2-ol[22] and was then transformed to *syn*-**10b**, however, the yields and their reproducibility were very low.

The tandem rearrangement of **11** was performed by thermolysis in toluene (Table 1). While *meso*-**11a** furnished mainly (1*E*,3*E*)-**12a** and the minor product (1*Z*,3*E*)-**12a**, *rac*-**11a** gave the major product (1*Z*,3*E*)-**12a** and a small amount of (1*E*,3*Z*)-**12a**. The isomerization of **11b** was also completely stereospecific, however, in this case each of the two rearrangement reactions afforded only one product: (1*E*,3*E*)-**12b** from *anti*-**11b** and (1*Z*,3*E*)-**12b** from *syn*-**11b**. The configuration of the C-3/C-4 double bond of **12** was easily established by the vicinal coupling constants of the ^1H NMR spectra, whereas the stereochemistry at the C-1/C-2 double bond was determined with the help of NOE difference spectra. Thus, saturating the proton H-1 led to an enhancement of the signal of H-3, which was in the range of 11–15% in the case of (1*Z*,3*Z*)-**12a**, (1*Z*,3*E*)-**12a**, and (1*Z*,3*E*)-**12b**, while no effect was observed in the case of (1*E*,3*E*)-**12a**, (1*E*,3*Z*)-**12a**, and (1*E*,3*E*)-**12b**.

The stereochemical outcome of the transformation **11→12** could be explained by chair-like transition states such as **A** and **B** as well as boat-like reacting conformations such as **C** and **D** derived from the intermediate **13** (Scheme 4). For example, starting with *meso*-**11** or *anti*-**11**, (1*E*,3*E*)-**12** and (1*Z*,3*Z*)-**12** prove to be the only 1,3-dienes, which could result from tandem [3,3]–[3,3] sigmatropic rearrangements via chair-like or boat-like transition states. Upon similar consideration, *rac*-**11** or *syn*-**11** should be converted solely into (1*E*,3*Z*)-**12** and (1*Z*,3*E*)-**12**. However, the fact that

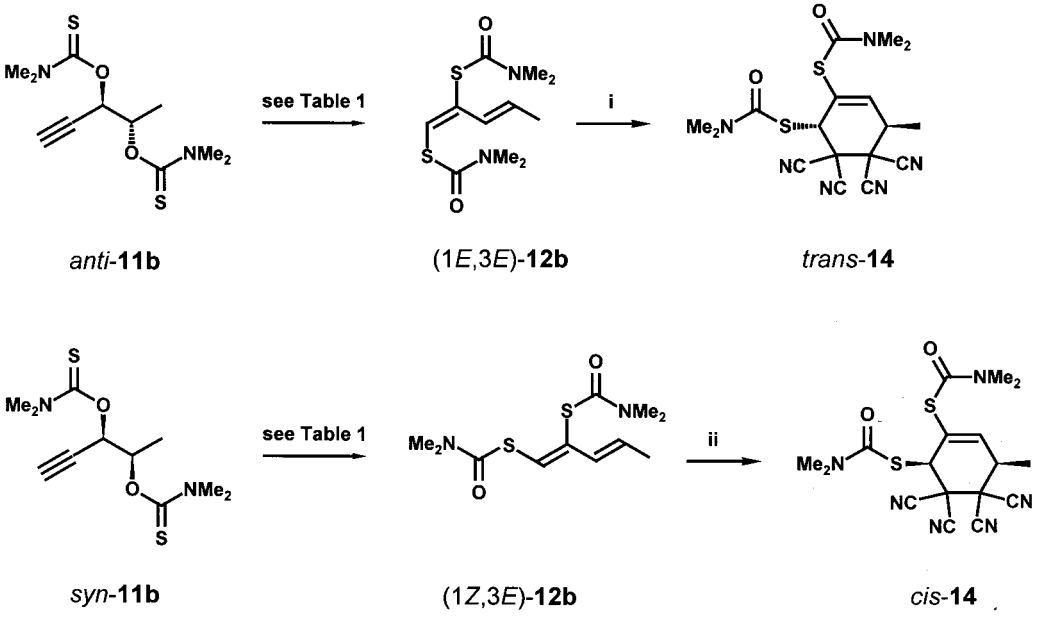
Table 1. Thermolysis of **11** in toluene

Starting material	Temperature (°C)	Time (h)	Yield (%)			
			(1*E*,3*E*)-**12**	(1*E*,3*Z*)-**12**	(1*Z*,3*E*)-**12**	(1*Z*,3*Z*)-**12**
meso-**11a**	110	1.5	66	–	–	9
rac-**11a**	110	2	–	9	68	–
anti-**11b**	100	8	100	–	–	–
syn-**11b**	100	8	–	–	100	–



Scheme 4.

(1*E*,3*E*)-**12** is the main product and (1*Z*,3*Z*)-**12** the by-product and that (1*Z*,3*E*)-**12** is favored as compared to (1*E*,3*Z*)-**12**, could only be rationalized by chair-like instead of boat-like reacting conformations. For instance, the substituent R lies axial in chair **B**. Thus, this conformation should be disfavored compared with chair **A** due to the interaction of R and NMe_2. The analogous unfavorable steric effect is to be expected for boat **C** in comparison to boat **D**. Nevertheless, (1*E*,3*E*)-**12**, which may result from advantageous chair **A** or unfavorable boat **C**, is found to be the preferred product. When the small ethynyl group of **11a** is replaced by the more bulky[23] methyl group of **11b**, chair



Scheme 5. *Reagents and conditions:* (i): TCNE, THF, 40°C, 12 days, 50%; (ii) TCNE, THF, 20°C, 8 h, 41%.

B is completely disfavored as compared to chair **A**. Therefore, thermolysis of *anti*-**11b** produced solely (1*E*,3*E*)-**12b**, and the exclusive formation of (1*Z*,3*E*)-**12b** from *syn*-**11b** could be explained similarly (Scheme 5).

Double functionalized dienes of type **6** and **9** may find use as synthetic building blocks.[14] For example, [4+2] cycloadducts **14** were prepared from **12b** and TCNE (tetracyanoethylene). The Diels–Alder reaction of (1*Z*,3*E*)-**12b** was distinctly more rapid than that of (1*E*,3*E*)-**12b**. Obviously, a *cisoid* conformation of the buta-1,3-diene unit, which is necessary for [4+2] cycloaddition, is more difficult to attain for (1*E*,3*E*)-**12b** due to steric factors. During the sequence **11b** → **12b** → **14**, the stereochemical information of the relative configurations at two stereogenic centers is first transferred to that of different configurations at C=C bonds and then retransformed into that of two stereogenic centers again.

Conclusion

In summary, we have demonstrated that the stereochemistry of the formation of 1,2-difunctionalized buta-1,3-dienes such as **12** is controlled by substituents at C-1 of the starting materials of type **11**. A plausible explanation including chair-like reacting conformations is presented. Work is in progress in our laboratory in order to develop further examples of stereospecific tandem rearrangements in analogy to **4** → **5** → **6** or **7** → **8** → **9** using other [3,3] or [2,3] sigmatropic reactions.

Experimental

General

Melting points (uncorrected): Electrothermal IA 9100. Elemental analyses: Vario EL Elementar Analysensysteme GmbH (Hanau). IR: Bruker IFS 28. ^{1}H NMR: Varian Gemini 300 (300 MHz), internal standard TMS (δ=0) or solvent signals, recalculated relative to TMS. ^{13}C NMR: Varian Gemini 300 (75 MHz); internal standard TMS (δ=0) or solvent signals, recalculated relative to TMS. The multiplicities were determined by the aid of *gated* spectra and/or DEPT 135 experiments. HPLC: Knauer HPLC Pump 64, Knauer UV detector (λ=254 nm), column LiChrospher Si 60 (5 μm), 2 cm ∅×20 cm. Flash column chromatography was performed with silica gel, 32–63 μm.

Hexa-1,5-diyne-3,4-diol bis[(*N*,*N*-dimethyl)thiocarbamate] (11a). To a suspension of crystalline NaH (340 mg, 14.2 mmol) in dry THF (10 ml) under argon at room temperature, a solution of **10a**[15] (580 mg, 5.27 mmol, *meso*/*rac*=1:2) in dry THF (15 ml) was added dropwise. The mixture was stirred for 20 h at room temperature and then for 9 h at 35–40°C. Thereafter, a solution of *N*,*N*-dimethylthiocarbamoyl chloride (1.37 g, 11.1 mmol) in dry THF (5 ml) was added dropwise. The resulting mixture was stirred for 24 h at room temperature, diluted with THF/Et_2O (1:2, 50 ml), washed three times with water (3×10 ml), and dried with $MgSO_4$. Removal of the solvent in vacuo gave a mixture of *meso*- and *rac*-**11a** (1:2, 1.33 g, 89%), which was treated with a small amount of dry Et_2O. The resulting precipitate was collected by suction filtration to afford *meso*-**11a** (380 mg). The filtrate was passed through a short column of silica gel using Et_2O as eluting agent. Removal of the solvent in vacuo yielded *rac*-**11a** (800 mg). Compound *meso*-**11a**: mp=134°C (Et_2O). ^{1}H NMR ($CDCl_3$): δ 2.60 (dd, *J*=1.4, 0.8 Hz, 2H, C≡CH), 3.18 (s, 3H, NMe), 3.38 (s, 3H, NMe), 6.43 (dd, *J*=1.4, 0.8 Hz, 2H, CH–CH). ^{13}C NMR ($CDCl_3$): δ 38.13 (q, NMe), 43.20 (q, NMe), 70.79 (d), 75.85 (d), 77.07 (s), 185.90 (s, C=S). IR ($CDCl_3$): 3306 (C≡CH), 2939, 1539, 1399, 1287, 1186, 1151, 1037 cm^{-1}. Elemental analysis: $C_{12}H_{16}N_2O_2S_2$; calcd: C, 50.68; H, 5.67; N, 9.85; S, 22.55; found: C, 50.58; H, 5.70; N, 9.47; S, 21.94. Compound *rac*-**11a**: mp=89–90°C (Et_2O/hexane). ^{1}H NMR ($CDCl_3$): δ 2.61 (dd, *J*=1.4, 0.8 Hz, 2H, C≡CH), 3.18 (s, 3H, NMe) 3.38 (s, 3H, NMe), 6.48 (dd, *J*=1.4, 0.8 Hz, 2H, CH–CH). ^{13}C NMR ($CDCl_3$): δ 38.15 (q, NMe), 43.18 (q, NMe), 69.87 (d), 75.86 (d), 77.39 (s), 185.75 (s, C=S). IR ($CDCl_3$): 3306 (C≡CH), 2942, 1538, 1399, 1287, 1178, 1148, 1039 cm^{-1}. Elemental analysis: $C_{12}H_{16}N_2O_2S_2$; calcd: C, 50.68; H, 5.67; N, 9.85; S, 22.55; found: C, 50.67; H, 5.79; N, 9.77; S, 22.62. Pure *meso*-**10a**[16] was analogously treated with NaH in THF and *N*,*N*-dimethylthiocarbamoyl chloride to give *meso*-**11a** without the diastereomeric isomer.

Pent-4-yne-2,3-diol bis[(*N*,*N*-dimethyl)thiocarbamate] (11b) from pent-2-en-4-yne. To a solution of pent-2-en-4-yne[17] (2.2 g, 33 mmol, *cis*/*trans*=1.9:1) in CH_2Cl_2 at 0°C, a solution of 3-chloroperbenzoic acid (40%, 24 g, 56 mmol) in CH_2Cl_2 (180 ml) was added in portions. The mixture was stirred for 15 min at 0°C and then for 16 h at room temperature. Thereafter, it was washed repeatedly with cold aqueous Na_2SO_3 solution, with aqueous $NaHCO_3$ solution, and with water. The organic layer was dried with $MgSO_4$ and concentrated by distillation. Recondensation of the residue at 0.001 Torr and distillation led to the epoxides (1.3 g, 48%, *cis*/*trans*=1.9:1) as a colorless liquid, bp 68–70°C. The ^{1}H NMR spectra of the products were similar to those of the oxiranes synthesized by another method.[24] NMR data of *cis-1-ethynyl-2-methyloxirane*: ^{1}H NMR ($CDCl_3$): δ 1.44 (d, ^3J=5.3 Hz, 3H, Me), 2.36 (d, ^4J=1.8 Hz, 1H, C≡CH), 3.17 (qd, ^3J=5.3, 4.0 Hz, 1H, H-2), 3.41 (dd, ^3J=4.0 Hz, ^4J=1.8 Hz, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 14.21 (q, Me), 45.00 (d), 53.75 (d), 73.55 (d), 78.83 (s). NMR data of *trans-1-ethynyl-2-methyloxirane:* ^{1}H NMR ($CDCl_3$): δ 1.34 (d, ^3J=5.3 Hz, 3H, Me), 2.31 (d, ^4J=1.6 Hz, 1H, C≡CH), 3.06 (t, $J\approx$2.0 Hz, 1H, H-1), 3.17 (qd, ^3J=5.3, 2.2 Hz, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 17.28 (q, Me), 45.71 (d), 56.39 (d), 71.73 (d), 80.35 (s). The assignments of the configurations of the epoxides are based on vicinal coupling constants observed in the ^{1}H NMR spectra and γ effects detected in the ^{13}C NMR spectra.

The mixture of oxiranes and an eightfold molar excess of water were heated for 2 days at 100°C in a sealed glass ampoule. After removal of the excess water in vacuo, the residue was recondensed at 50°C/0.001 Torr to give **10b** (87%, *syn*/*anti*=1.9:1) as a colorless oil. The ^{1}H NMR spectra of the products were nearly identical to those of **10b** synthesized by another method.[25] NMR data of *syn*-**10b**: ^{1}H NMR ($CDCl_3$): δ 1.29 (d, ^3J=6.5 Hz, 3H, Me), 2.47

(br. s, 2H, OH), 2.52 (d, ^4J=2.2 Hz, 1H, H-5), 3.85 (br. quint, $^3J\approx$6.5 Hz, 1H, H-2), 4.11 (dd, ^3J=6.8 Hz, ^4J=2.2 Hz, 1H, H-3). ^{13}C NMR ($CDCl_3$): δ 18.21 (q, Me), 66.15 (d), 69.18 (d), 75.19 (d), 84.38 (s, C-4). NMR data of *anti*-**10b**: ^{1}H NMR ($CDCl_3$): δ 1.29 (d, ^3J=6.5 Hz, 3H, Me), 2.47 (br. s, 2H, OH), 2.52 (d, ^4J=2.2 Hz, 1H, H-5), 3.92 (qd, ^3J=6.4, 3.5 Hz, 1H, H-2), 4.31 (dd, ^3J=3.5, ^4J=2.2 Hz, 1H, H-3). ^{13}C NMR ($CDCl_3$): δ 18.49 (q, Me), 65.87 (d), 69.35 (d), 74.87 (d), 84.79 (s, C-4).

The mixture of diols **10b** was treated with NaH in THF (20°C, 24 h) and *N*,*N*-dimethylcarbamoyl chloride (20°C, 16 h) as described in the case of **10a**. The crude product was filtered through silica gel eluting with ethyl acetate/hexane, 1:3 to give **11b** (77%, *syn*/*anti*=1.9:1). These diastereomeric compounds could be separated by HPLC using LiChrospher Si 60, 5 μm, 2 cm ∅×20 cm, ethyl acetate/hexane, 1:3, order of elution: *syn*-**11b** (41 min), *anti*-**11b** (49 min). Compound *anti*-**11b**: Colorless solid, mp=69.5–71°C. ^{1}H NMR ($CDCl_3$): δ 1.47 (d, ^3J=6.6 Hz, 3H, Me), 2.55 (d, ^4J=2.3 Hz, 1H, C≡CH), 3.11 (s, 3H, NMe), 3.14 (s, 3H, NMe), 3.35 (s, 3H, NMe), 3.37 (s, 3H, NMe), 5.87 (qd, ^3J=6.6, 3.2 Hz, 1H, C*H*Me), 6.27 (dd, ^3J=3.2, ^4J=2.2 Hz, 1H, CH–C≡C). ^{13}C NMR ($CDCl_3$): δ 15.50 (q, Me), 37.68 (q, NMe), 37.98 (q, NMe), 42.54 (q, NMe), 42.96 (q, NMe), 72.20 (d), 75.44 (d), 76.88 (d), 77.79 (s), 186.00 (s, C=S), 186.61 (s, C=S). IR ($CDCl_3$): 3306 (C≡CH), 2941, 1536, 1400, 1289, 1199, 1050 cm^{-1}. Elemental analysis: $C_{11}H_{18}N_2O_2S_2$; calcd: C, 48.15; H, 6.61; N, 10.21; S, 23.37; found: C, 48.16; H, 6.51; N, 10.18; S, 23.75. Compound *syn*-**11b**: Colorless oil: ^{1}H NMR ($CDCl_3$): δ 1.47 (d, ^3J=6.6 Hz, 3H, Me), 2.53 (d, ^4J=2.2 Hz, 1H, C≡CH), 3.11 (s, 3H, NMe), 3.14 (s, 3H, NMe), 3.35 (s, 3H, NMe), 3.37 (s, 3H, NMe), 5.86 (quint, ^3J=6.5 Hz, 1H, C*H*Me), 6.28 (dd, ^3J=6.5, ^4J=2.2 Hz, 1H, CH–C≡C). ^{13}C NMR ($CDCl_3$): δ 15.77 (q, Me), 37.85 (q, NMe), 37.06 (q, NMe), 42.74 (q, NMe), 43.15 (q, NMe), 72.46 (d), 75.50 (d), 77.10 (d), 78.02 (s), 186.22 (s, C=S), 186.85 (s, C=S). Elemental analysis: $C_{11}H_{18}N_2O_2S_2$; calcd: C, 48.15; H, 6.61; N, 10.21; S, 23.37; found: C, 48.08; H, 6.59; N, 10.10; S, 23.38.

Pent-4-yne-2,3-diol bis[(*N*,*N*-dimethyl)thiocarbamate] (11b) from 2-bromopropanal. To a saturated solution of acetylene in dry THF at 0°C, a solution of ethylmagnesium bromide in THF prepared from EtBr (33.0 g, 303 mmol) and magnesium (6.10 g, 251 mmol) was added dropwise while further acetylene was introduced into the reaction mixture. To this solution of ethynylmagnesium bromide cooled to −15°C, a solution of 2-bromopropanal[19] (24 g, 175 mmol) in THF was added dropwise. The mixture was stirred at room temperature for 16 h. Thereafter, saturated aqueous NH_4Cl solution was added with cooling. The organic layer was separated, and the aqueous layer was extracted repeatedly with Et_2O. The combined organic extracts were washed repeatedly with water and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was distilled to give the bromohydrins as a light-yellow liquid (8.17 g, 29%, *syn*/*anti*=1:7), bp 34–35°C/0.01 Torr. After 2 days at −20°C, the *anti* isomer crystallized as a colorless solid, which could be separated by suction filtration and purified by washing with cold pentane. However, it was not possible to isolate the pure *syn* isomer. Data of *anti-4-bromopent-1-yn-3-ol*: mp 44°C (Et_2O). ^{1}H NMR ($CDCl_3$): δ 1.75 (d, ^3J=6.8 Hz, 3H, Me), 2.56 (d, ^4J=2.2 Hz, 1H, H-1), 2.60 (br. s, 1H, OH), 4.27 (qd, ^3J=6.8, 3.6 Hz, 1H, H-4), 4.43 (dd, ^3J=3.6 Hz, ^4J=2.2 Hz, 1H, H-3). ^{13}C NMR ($CDCl_3$): δ 20.92 (q, Me), 54.14 (d), 66.62 (d), 74.81 (d), 80.58 (s, C-1). IR ($CDCl_3$): 3359 (OH), 3306 (C≡CH), 1238, 1196, 1118, 1050 cm^{-1}. Elemental analysis: C_5H_7BrO; calcd: C, 36.84; H, 4.33; found: C, 36.45; H, 4.40. NMR data of *syn-4-bromopent-1-yn-3-ol*: ^{1}H NMR ($CDCl_3$): δ 1.70 (d, ^3J=6.8 Hz, 3H, Me), 2.56 (d, ^4J=2.2 Hz, 1H, H-1), 2.60 (br. s, 1H, OH), 4.19 (qd, ^3J=6.8, 5.4 Hz, 1H, H-4), 4.40 (dd, ^3J=5.4 Hz, ^4J=2.2 Hz, 1H, H-3). ^{13}C NMR ($CDCl_3$): δ 21.52 (q, Me), 53.31 (d), 66.87 (d), 74.65 (d), 80.90 (s, C-1).

To a suspension of powdered potassium hydroxide (3.43 g, 61.1 mmol) in Et_2O (50 ml), a solution of the bromohydrins (8.17 g, 50.1 mmol, *syn*/*anti*=1:7) in Et_2O was added dropwise. The reaction mixture was stirred at room temperature for 16 h. After separation of the precipitate, distillation of the resulting solution led to the epoxides (3.57 g, 87%, *cis*/*trans*=1:7) as a colorless liquid, bp 65°C. The NMR data of the products were identical to those of 1-ethynyl-2-methyloxiranes obtained from pent-2-en-4-yne.

A mixture of 1-ethynyl-2-methyloxiranes (*cis*/*trans*=1:7) was hydrolyzed as described above (water, 100°C, 2 days, 87% yield), and the resulting **10b** (*syn*/*anti*=1:7) was treated with NaH in THF and then with *N*,*N*-dimethylcarbamoyl chloride as depicted before. In this case, the obtained mixture of *syn*-**11b** and *anti*-**11b** led to the pure *anti* compound by multiple crystallization from Et_2O.

Conversion of 11a,b into 12a,b. Solutions of **11a,b** in dry toluene (0.05–0.07 M) were thermolyzed as described in Table 1. Thereafter, the solvent was removed in vacuo. In the case of *meso*-**11a** and *rac*-**11a**, the residue was treated with THF/hexane (2:1) or dry Et_2O, respectively, and filtrated. Then the filtrate was concentrated in vacuo to yield the products, which were analyzed by ^{1}H NMR spectroscopy. In the case of (1*E*,3*E*)-**12b** and (1*Z*,3*E*)-**12b**, which were formed nearly quantitatively, purification was performed by flash chromatography (Et_2O) or by crystallization from CH_2Cl_2/hexane, respectively. Compound (1*E*,3*E*)-**12a**: ^{1}H NMR ($CDCl_3$): δ 3.00 (br. s, 12H, 4×NMe), 3.14 (d, ^4J=2.45 Hz, 1H, H-6), 6.03 (dd, $^3J_{trans}$=15.4, ^4J=2.45 Hz, 1H, H-4), 7.01 (d, $^3J_{trans}$=15.4 Hz, 1H, H-3), 7.46 (s, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 36.98 (br. q, 4×NMe), 81.76 (d, C-6), 82.58 (s, C-5), 111.27 (d, C-4), 122.32 (s, C-2), 135.86 (d, C-1), 138.97 (d, C-3), 162.18 (s, C=O), 165.32 (s, C=O). Assignments were based on heteronuclear shift correlation. Compound (1*E*,3*Z*)-**12a**: ^{1}H NMR ($CDCl_3$): δ 3.00 (br. s, 13H, 4×NMe and H-6), 5.61 (ddd, $^3J_{cis}$=11.7, ^4J=2.7 Hz, J=0.9 Hz, 1H, H-4), 6.58 (dd, $^3J_{cis}$=11.7, J=0.9 Hz, 1H, H-3), 7.41 (t, J=0.9 Hz, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 36.51 (br., 4×NMe), 80.68 (C-6), 82.53 (C-5), 109.53 (C-4), 121.89 (C-2), 135.72 (C-1), 137.67 (C-3), 162.62 (C=O), 166.57 (C=O). Compound (1*Z*,3*E*)-**12a**: ^{1}H NMR ($CDCl_3$): δ 3.00 (br. s, 12H, 4×NMe), 3.03 (d, ^4J=2.5 Hz, 1H, H-6), 5.81 (dd, $^3J_{trans}$=15.4, ^4J=2.5 Hz, 1H, H-4), 6.89 (d, $^3J_{\text{trans}}$=15.4 Hz, 1H, H-3), 7.74 (s, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 36.78 (br. q, 2×NMe), 37.01 (br. q, 2×NMe), 80.49 (d, C-6), 82.47 (s, C-5), 107.55 (d, C-4),

123.84 (s, C-2), 140.62 (d), 142.46 (d), 162.42 (s, C═O), 162.58 (s, C═O). IR ($CDCl_3$): 3306 (C≡CH), 1673 (C═O), 1367, 1260, 1102 cm^{-1}. Elemental analysis: $C_{12}H_{16}N_2O_2S_2$; calcd: C, 50.68; H, 5.67; N, 9.85; S, 22.55; found: C, 50.13; H, 5.63; N, 9.47; S, 22.59. Compound (1*Z*,3*Z*)-**12a**: ^1H NMR ($CDCl_3$): δ 3.00 (br. s, 12H, 4×NMe), 3.37 (d, ^4J=2.7 Hz, 1H, H-6), 5.50 (dd, $^3J_{cis}$=11.8, ^4J=2.7 Hz, 1H, H-4), 6.36 (d, $^3J_{cis}$=11.8 Hz, 1H, H-3), 8.40 (s, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 36.87 (br. q, 4×NMe), 80.92 (d, C-6), 85.11 (s, C-5), 105.25 (d, C-4), 121.91 (s, C-2), 139.78 (d), 140.41 (d), 162.85 (s, C═O), 163.84 (s, C═O). Compound (1*E*,3*E*)-**12b**: mp=70.5–71.5°C. ^1H NMR ($CDCl_3$): δ 1.78 (ddd, ^3J=6.7, J=1.6, 0.7 Hz, 3H, Me), 2.98 (br. s, 12H, 4×NMe), 6.08 (dqd, $^3J_{trans}$=14.8, ^3J=6.7, J=0.7 Hz, 1H, H-4), 6.29 (dqd, $^3J_{trans}$=14.8, J=1.6, 0.7 Hz, 1H, H-3), 7.12 (s, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 18.00 (q, Me), 36.66 (q, 2×NMe), 36.83 (q, 2×NMe), 123.42 (s, C-2), 127.61 (d), 129.65 (d), 130.78 (d), 162.90 (s, C═O), 166.05 (s, C═O). IR ($CDCl_3$): 2935, 1666 (C═O), 1441, 1408, 1365, 1260, 1194, 1111, 1050, 954, 813 cm^{-1}. Elemental analysis: $C_{11}H_{18}N_2O_2S_2$; calcd: C, 48.15; H, 6.61; N, 10.21; S, 23.37; found: C, 48.12; H, 6.62; N, 10.22; S, 23.70. Compound (1*Z*,3*E*)-**12b**: Colorless solid, mp=117.5–118.5°C (CH_2Cl_2/hexane). ^1H NMR ($CDCl_3$): δ 1.74 (ddd, ^3J=6.7, J=1.6, 0.7 Hz, 3H, Me), 2.96 (br. s, 12H, 4×NMe), 5.89 (dqd, $^3J_{trans}$=14.8, ^3J=6.7, J=0.7 Hz, 1H, H-4), 6.27 (dqd, $^3J_{trans}$=14.8, J=1.6, 0.7 Hz, 1H, H-3), 7.42 (s, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 17.61 (q, Me), 36.23 (q, 2×NMe), 36.65 (q, 2×NMe), 125.10 (s, C-2), 126.70 (d), 130.90 (d), 134.12 (d), 163.47 (s, C═O), 163.65 (s, C═O). IR ($CDCl_3$): 2935, 1666 (C═O), 1440, 1408, 1367, 1261, 1100, 956, 841 cm^{-1}. Elemental analysis: $C_{11}H_{18}N_2O_2S_2$; calcd: C, 48.15; H, 6.61; N, 10.21; S, 23.37; found: C, 47.70; H, 6.53; N, 10.04; S, 23.39.

Diels–Alder reaction of 12b with TCNE. A solution of (1*E*,3*E*)-**12b** or (1*Z*,3*E*)-**12b** (150 mg, 0.55 mmol) and tetracyanoethylene (TCNE, 100 mg, 0.78 mmol) in dry THF (5 ml) was stirred for 12 days at 40°C or for 8 h at 20°C, respectively (see Scheme 5). Thereafter, the mixture was concentrated in vacuo, and the residue was purified by flash chromatography (Et_2O) to give *trans*-**14** (110 mg, 50%) or *cis*-**14** (90 mg, 41%). Compound *trans*-**14**: Colorless solid, mp=137.5–138.5°C (Et_2O). ^1H NMR ($CDCl_3$): δ 1.63 (d, ^3J=7.1 Hz, 3H, Me), 2.98 (s, 6H, 2×NMe), 3.09 (s, 6H, 2×NMe), 3.48 (m, 1H, C*H*Me), 5.48 (dd, J=2.4, 1.0 Hz, 1H, CHS), 6.19 ('t', J=2.2 Hz, 1H, C═CH). ^{13}C NMR ($CDCl_3$): δ 16.69 (q, Me), 36.48 (q, NMe), 36.87 (q, NMe), 37.17 (q, NMe), 37.77 (q, NMe), 38.31 (d, *C*HMe), 45.56 (s), 47.41 (s), 50.80 (d, CHS), 107.95 (s, CN), 109.50 (s, CN), 109.96 (s, CN), 110.53 (s, CN), 126.96 (s, SC═C), 140.34 (d, *C*H═C), 162.10 (s, C═O), 164.14 (s, C═O). Assignments were based on heteronuclear shift correlation. Elemental analysis: $C_{17}H_{18}N_6O_2S_2$; calcd: C, 50.73; H, 4.51; N, 20.88; S, 15.93; found: C, 50.58; H, 4.49; N, 20.92; S, 16.05. Compound *cis*-**14**: Colorless solid, mp=140.5–141.5°C (Et_2O). ^1H NMR ($CDCl_3$): δ 1.61 (d, ^3J=7.1 Hz, 3H, Me), 2.97 (s, 3H, NMe), 3.00 (s, 3H, NMe), 3.04 (s, 3H, NMe), 3.10 (s, 3H, NMe), 3.48 (m, 1H, C*H*Me), 5.60 (dd, J=2.4, 1.0 Hz, 1H, CHS), 6.18 ('t', J=2.2 Hz, 1H, C═CH). ^{13}C NMR ($CDCl_3$): δ 16.74 (q, Me), 36.57 (q, NMe), 36.77 (q, NMe), 37.05 (q, NMe), 37.75 (q, NMe), 38.29 (d, *C*HMe), 42.25 (s), 45.18 (s), 49.08 (d, CHS), 108.15 (s, CN), 109.35 (s, CN), 109.75 (s, CN), 111.03 (s, CN), 126.71 (s, SC═C), 139.43 (d, *C*H═C), 163.06 (s, C═O), 164.34 (s, C═O). IR ($CDCl_3$): 2978, 2878, 1677 (C═O), 1444, 1409, 1368, 1259, 1111, 833 cm^{-1}. Elemental analysis: $C_{17}H_{18}N_6O_2S_2$; calcd: C, 50.73; H, 4.51; N, 20.88; S, 15.93; found: C, 51.08; H, 4.90; N, 19.12; S, 15.13.

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