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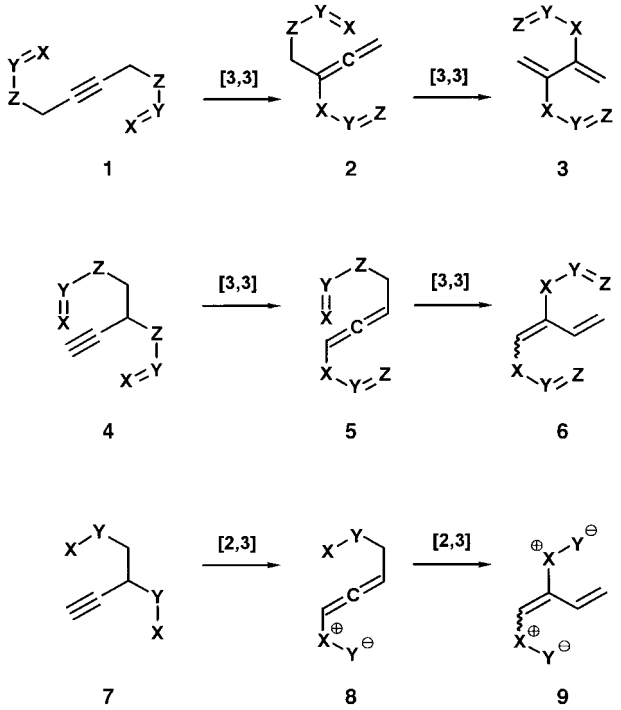
Synthesis of 1,2-Difunctionalized 1,3-Butadienes through a Sequence of Sigmatropic Rearrangements**

Klaus Banert,* Wolfgang Fendel, and Jana Schlott

Dedicated to Professor Günter Marx on the occasion of his 60th birthday

Sequential [3,3] sigmatropic rearrangements such as the well-known reaction **1**→**2**→**3**, for example where XYZ = NCO,[1] NCS,[2] NCSe,[3] N_3,[4] $SCONMe_2$,[5] SCN,[6] C–CO_2R[7] (orthoester Claisen rearrangement), C–C=C[8] (Cope rearrangement), can be used to transform the 2-butyne-1,4-diyl precursors **1** into the 2,3-difunctionalized 1,3-butadienes **3** (Scheme 1). The synthesis of similar products proceeds analogously through two consecutive [2,3] sigmatropic isomerizations, for instance in the reaction of phosphinites to phosphane oxides,[9] phosphites to phosphonates,[10] sulfinates to sulfones,[11] or sulfenates to sulfoxides.[11, 12] To the best of our knowledge, however, sigmatropic rearrangements have not been employed to prepare 1,2-difunctionalized 1,3-butadienes. We describe here a sequence of sigmatropic isomerizations that provide a convenient approach to these target compounds. In this connection [3,3] migrations such as **4**→**5**→**6** as well as [2,3] shifts **7**→**8**→**9** are used to direct both functional groups into vinylic positions.



Scheme 1. Synthesis of doubly functionalized 1,3-butadienes by two consecutive sigmatropic rearrangements.

The hydroxyl groups of the readily available diols **10**[13] can be easily transformed into isomerizable functional groups (Scheme 2). The subsequent gas-phase thermolysis (flash vacuum pyrolysis)[14] of the imidate **11a** and the heating of the thiono carboxylates/carbamates/carbonates **13a,d** or sulfinates **17a,c** in solution lead to the 1,2-difunctionalized 1,3-butadienes **12a**, **14a,d**, and **18a,c**, respectively. The reactions of **10** to give **15a** or **16a – d** require no warming and succeed in one-pot procedures. The products **12a** and **14a**, which result from [3,3] sigmatropic rearrangements, are formed as mixtures of separable *E*/*Z* isomers. However, the [2,3] isomerizations afford the dienes **15a**, **16a – d**, and **18a,c** with exclusive *E* configuration. The sulfoxides **16a – d** are obtained as mixtures of *like*/*unlike* diastereomers as a consequence of the stereocenters at the sulfur atoms.[15] A subsequent isomerization of the C-C double bond is not observed on thermolysis in solution. For example, a constant ratio of 1:1 is detected for the distribution of products with *E* and *Z* configuration when the transformation **13a**γ→**14a**γ is investigated both immediately after low conversion and after very long reaction times (about 50 half-life periods of **13a**γ). In the case of **13d**β the sequences of [3,3] sigmatropic migrations prove to be stereospecific. Thus, *meso*-**13d**β furnishes nearly exclusively (*E*)-**14d**β, while *rac*-**13d**β leads almost solely to (*Z*)-**14d**β.

The bis(sulfenate) derived from *meso*-**10d** can give rise not only to **16d**α but also to a hexa-1,2,4,5-tetraene compound by

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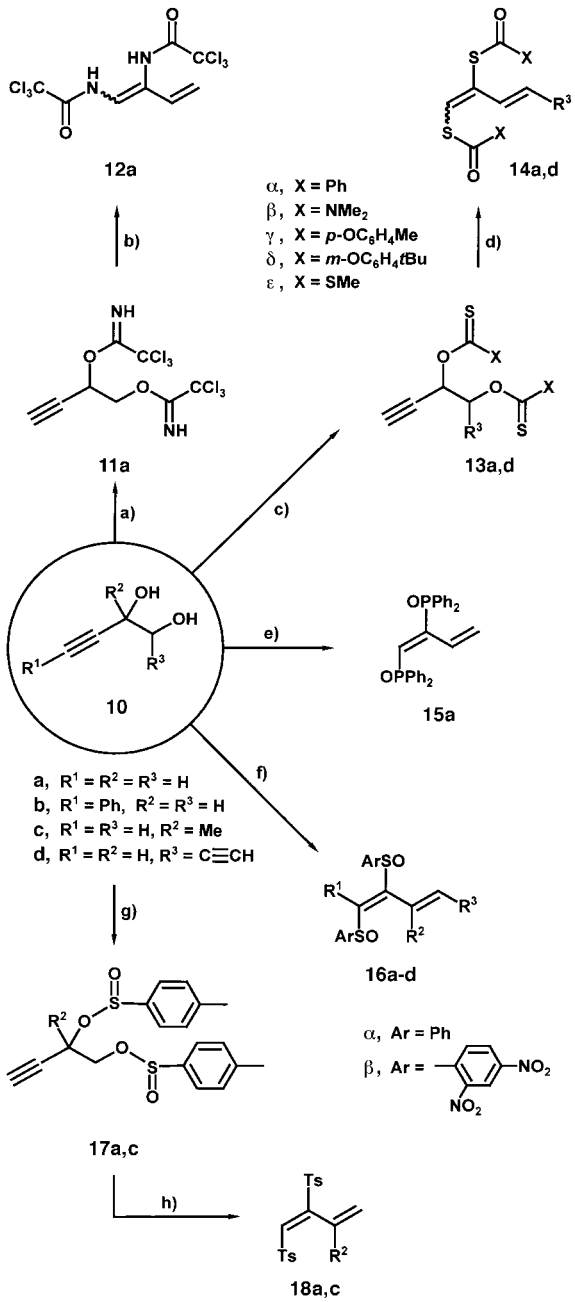
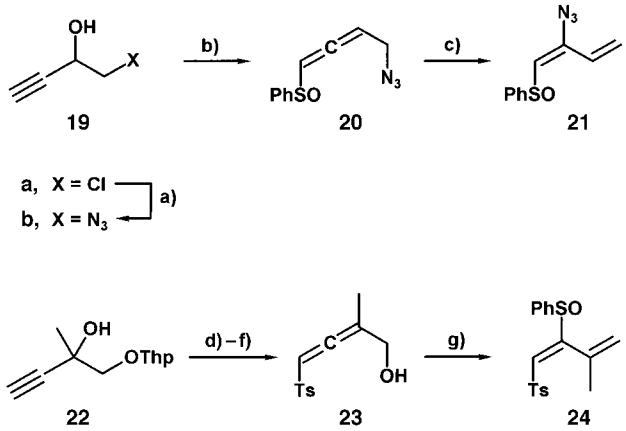


Scheme 2. Transformation of the 3-butyne-1,2-diols **10** into the 1,2-difunctionalized 1,3-butadienes **12**, **14**, **15**, **16**, and **18**. a) DBU, CH_2Cl_2, Cl_3CCN, $-40 \rightarrow 20\,^{\circ}C$, 97%; b) gas-phase thermolysis at $400\,^{\circ}C/10^{-5}$ Torr, 40%, $E:Z = 1:4$; c) Py, THF, PhCSCl,[16] $0 \rightarrow 20\,^{\circ}C/5$ h, 69% **13a**α; NaH, THF, $0 \rightarrow 20\,^{\circ}C/16$ h, then Me_2NCSCl/THF, $-15\,^{\circ}C/1$ h $\rightarrow 20\,^{\circ}C/16$ h, 60% **13a**β; Py, THF, 4-MeC_6H_4CSCl, $-10\,^{\circ}C/1$ h $\rightarrow 20\,^{\circ}C/4$ h, 80% **13a**γ; Py, THF, 3-tBuC_6H_4CSCl, 69% **13a**δ; acetone, KOH, then CS_2, $-15\,^{\circ}C/35$ min, then MeI, $-15 \rightarrow 20\,^{\circ}C$, 32% **13a**$\varepsilon$; NaH, THF, $20 \rightarrow 35\,^{\circ}C/25$ h, then Me_2NCSCl/THF, $20\,^{\circ}C/6-16$ h, 62% *meso*-**13d**β; 71% *rac*-**13d**β; d) toluene, $110\,^{\circ}C/1.5-4$ h; approximately 100% **14a**α, $E:Z = 1:1$; 65% **14a**β, $E:Z = 1.4:1$; approximately 100% **14a**γ, $E:Z = 1:1$; 97% **14a**δ, $E:Z = 1.1:1$; 80% **14a**ε, $E:Z = 1.2:1$; 75% (*E*)-**14d**β (from *meso*-**13d**β); 75% (*Z*)-**14d**β (from *rac*-**13d**β); e) THF, BuLi, $-78\,^{\circ}C/45$ min, then addition to Ph_2PCl/THF, $-78\,^{\circ}C/1$ h $\rightarrow 20\,^{\circ}C$, 25%; f) THF, NEt_3, PhSCl,[17] approximately $-20 \rightarrow 0\,^{\circ}C$; 66% **16a**$\alpha$, diastereomers 1:1.2; 58% **16b**α, *like*:*unlike* = 1:1.5; 40% **16c**α, diastereomers 1:1.3; 65% **16d**α, diastereomers 1:1.3; THF, NEt_3, 2,4-$(O_2N)_2C_6H_3SCl$, $-25 \rightarrow 0\,^{\circ}C$, 46% **16a**$\beta$, diastereomers 1:1.4; g) 4-$MeC_6H_4S(O)Cl$,[18] NEt_3, THF or CH_2Cl_2, $0\,^{\circ}C/3$ h; h) PhCl, Li_2CO_3, $130\,^{\circ}C/27$ h, 55% **18a**, 40% **18c** (based on **10a** and **10c**, respectively). DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, Ts = *p*-toluenesulfonyl.

two independent [2,3] rearrangements. However, such a product has not been found. Evidently, the [2,3] migrations in the **7** $\rightarrow$ **8** $\rightarrow$ **9** direction are favored.

There are two methods to prepare 1,3-butadienes with two different functional groups in positions 1 and 2 by the aid of a sequence of sigmatropic isomerizations (Scheme 3): 1. The



Scheme 3. Synthesis of 1,3-butadienes with different functional groups at C-1 and C-2. a) NaN_3, H_2O, $60\,^{\circ}C/5$ h, 77%; b) CH_2Cl_2, NEt_3, PhSCl, $-15 \rightarrow 20\,^{\circ}C/24$ h; c) $CHCl_3$, $50\,^{\circ}C/17$ h, 48% based on **19b**; d) CH_2Cl_2, NEt_3, 4-$MeC_6H_4S(O)Cl$, $0\,^{\circ}C/3$ h; e) PhCl, Li_2CO_3, $130\,^{\circ}C/4$ h; f) MeOH, H_2SO_4, $20\,^{\circ}C/16$ h, 86% based on **22**; g) CH_2Cl_2, NEt_3, PhSCl, $0\,^{\circ}C/2$ h, 42%. Thp = tetrahydropyranyl.

two quite distinct, isomerizable groups, the azide[19] and the sulfenate function, are selectively introduced into the precursor **19a**[13a] so that regioisomer **21** results exclusively. The structure of this product is proved not only by spectroscopic data (Table 1), but also by its photochemical transformation into 3-ethenyl-2-phenylsulfinyl-2*H*-azirine. 2. Two relatively similar groups such as sulfinate and sulfenate functions are used selectively to synthesize the 1,3-butadiene **24** from the half-protected diol **22**[20] via **23**.[21]

Derivatives of the alcohol **25a**[22] can also be used as starting materials to prepare functionalized 1,3-butadienes on a sequence of sigmatropic isomerizations (Scheme 4). In this case, a Cope rearrangement is performed in the last step. The transformations **25a** $\rightarrow$ **25b** $\rightarrow$ **26**, **25a** $\rightarrow$ **27** $\rightarrow$ **28**, **25a** $\rightarrow$ **25c** $\rightarrow$ **29**, and **25a** $\rightarrow$ **25d** $\rightarrow$ **25e** $\rightarrow$ **30** $\rightarrow$ **31** lead to trichloroacetamides, thiocarbonates, sulfones, and isothiocyanates. Whereas flash vacuum pyrolysis of the thiocyanate **25e** at $400\,^{\circ}C$ generates (*E*)-**31** exclusively (80% yield), pyrolysis in the range of $320-260\,^{\circ}C$ gives a mixture of (*E*)-**31**/(*Z*)-**31** = 1.5:1 and allene **30** in 40–64% yield. A renewed thermolysis of this mixture at $400\,^{\circ}C$ gives the only product (*E*)-**31**. Apparently the Cope rearrangement **30** $\rightarrow$ **31** at least is reversible at higher temperatures.

Doubly functionalized dienes of type **6** and **9** may find use as synthetic building blocks. Preliminary investigations indicate that [4 + 2] cycloadducts are formed from tetracyanoethylene and **12a** (yield 63%), (*Z*)-**14a**α (28%), **14a**β (44%), (*Z*)-**14a**γ (64%), (*Z*)-**14a**δ (46%), (*Z*)-**14a**ε (71%), **26** (42%), (*E*)-**28** (60%), or (*E*)-**31** (57%). The sulfone **18a** is converted into **32** by regio- and stereoselective Diels–Alder reactions with electron-rich or electron-deficient dienophiles (Scheme 5). The nucleophilic substitution **18a** $\rightarrow$ **33** succeeds

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Table 1. Selected physical data of compounds (*Z*)-**12a**, **14aε**, **15a**, **16bα**, **18a**, **21**, **24**, and **31**.[a]

(*Z*)-**12a**: Colorless oil; ^{1}H NMR: $\delta = 5.26$ (d, $^3J = 10.9$, 1H; H-4), 5.27 (d, $^3J = 17.3$, 1H; H-4), 6.41 (dd, $^3J = 17.3$, 10.9, 1H; H-3), 6.74 (d, ^3J(NH,CH) = 9.4, 1H; H-1), 8.07 (br s, 1H; NH), 9.35 (br d, ^3J(NH,CH) = 9.4, 1H; NH); ^{13}C NMR: $\delta = 91.57$ (CCl_3), 91.75 (CCl_3), 113.94 (C-4), 118.76 (CH), 119.26 (C-2), 131.56 (CH), 159.38 (C=O), 160.68 (C=O).

(*E*)-**14aε**: Brown liquid; ^{1}H NMR: $\delta = 2.39$ (s, 3H; SMe), 2.51 (s, 3 H; SMe), 5.40 (d, $^3J = 10.5$, 1H; H-4), 5.70 (d, $^3J = 16.6$, 1H; H-4), 6.53 (dd, $^3J = 16.6$, $^3J = 10.5$, 1H; H-3), 7.42 (s, 1H; H-1); ^{13}C NMR: $\delta = 13.41$ (SMe), 13.49 (SMe), 120.18 (C-4), 124.67 (C-2), 130.65 (CH), 131.38 (CH), 184.44 (C=O), 188.64 (C=O); IR ($CDCl_3$): $\tilde{\nu} = 2933$, 1727 (C=O), 1652 (C=O), 1422, 1313, 1077, 971, 850, 802.

(*Z*)-**14aε**: ^{1}H NMR: $\delta = 2.41$ (s, 3H; SMe), 2.50 (s, 3H; SMe), 5.25 (d, $^3J = 10.5$, 1H; H-4), 5.54 (d, $^3J = 16.6$, 1H; H-4), 6.60 (dd, $^3J = 16.6$, $^3J = 10.5$, 1H; H-3), 7.65 (s, 1H; H-1); ^{13}C NMR: $\delta = 13.27$ (SMe), 13.38 (SMe), 116.97 (C-4), 125.93 (C-2), 134.83 (CH), 134.92 (CH), 185.48 (C=O), 185.80 (C=O).

15a: Colorless solid, m.p. 142–143 °C; ^{1}H NMR: $\delta = 5.43$ (d, $^3J = 11.4$, 1H; H-4), 5.73 (d, $^3J = 17.6$, 1H; H-4), 6.85 (t, J(P,H) = 23.0, 1H; H-1), ≈7.45 (m, 1H; H-3), 7.40–7.80 (m, 20H; 4 × Ph); ^{13}C NMR (the coupling constants correspond to ^{31}P,^{13}C coupling): $\delta = 126.54$ (dd, $^3J = 6$, $^4J = 1.5$; C-4), 128.64 (d, $^3J = 12.3$; Ph-*m*), 128.67 (d, $^3J = 12.3$; Ph-*m*), 130.53 (dd, $J = 9.5$, $J = 8.5$; C-3), 130.79 (d, $^2J = 9.9$; Ph-*o*), 130.80 (d, $^1J = 103$; Ph-*i*), 131.84 (d, $^3J = 9.9$; Ph-*o*), 131.97 (d, $^4J = 2.8$; Ph-*p*), 132.30 (d, $^4J = 2.8$; Ph-*p*), 132.78 (d, $^1J = 105$; Ph-*i*), 135.77 (dd, $^1J = 87$, $^2J = 6.3$; C-1), 151.98 (dd, $^1J = 81$, $^2J = 2$; C-2); ^{31}P NMR (external standard: 85% H_3PO_4): $\delta = 21.26$ (d, J(P,P) = 49.6), 30.22 (d, J(P,P) = 49.6); correct elemental analysis based on $C_{28}H_{24}O_2P_2$.

16bα (*unlike* isomer): Colorless solid, m.p. 155–157 °C (decomp); ^{1}H NMR: $\delta = 5.78$ (dd, $^3J = 11.6$, $^2J \approx 1.1$, 1H; H-4), 5.97 (dd, $^3J = 17.5$, $^2J \approx 1.1$, 1H; H-4), 6.55 (dd, $^3J = 17.5$, $^3J = 11.6$, 1H; H-3), 6.94 (br d, $J = 6.7$, 2H; Ph), 7.22–7.60 (m, 13H; Ph); ^{13}C NMR: $\delta = 123.91$, 124.59, 124.66, 127.50, 127.73, 127.88, 128.96, 129.10, 129.20, 130.89, 131.26, 131.40, 141.11, 141.83, 149.57, 151.56; (*like* isomer): ^{1}H NMR: $\delta = 5.77$ (d, $^3J = 11.5$, 1H; H-4), 5.82 (d, $^3J = 17.5$, 1H; H-4), 6.69 (dd, $^3J = 17.5$, $^3J = 11.5$, 1H; H-3), 6.83 (br d, $J \approx 6.7$, 2H; Ph), 7.22–7.60 (m, 13H; Ph); ^{13}C NMR: $\delta = 123.58$, 124.74, 127.57, 127.81, 128.02, 128.42, 129.15, 129.27, 129.79, 131.00, 131.14, 131.41, 142.09, 142.61, 148.98, 152.10; correct elemental analysis based on $C_{22}H_{18}O_2S_2$.

18a: Colorless solid, m.p. 95–97 °C; ^{1}H NMR: $\delta = 2.45$ (s, 3H; Me), 2.48 (s, 3H; Me), 5.69 (d, $^3J = 11.9$, 1H; H-4), 6.12 (d, $^3J = 17.9$, 1H; H-4), 7.00 (dd, $^3J = 17.9$, $^3J = 11.9$, 1H; H-3), 7.34 (2H; AA′BB′), 7.39 (2H; AA′BB′), 7.42 (s, 1H; H-1), 7.68 (2H; AA′BB′), 7.80 (2H; AA′BB′); ^{13}C NMR: $\delta = 21.66$ (Me), 21.70 (Me), 123.01 (C-3), 128.01 (CH), 128.37 (C-4), 128.55 (CH), 130.05 (CH), 130.25 (CH), 134.91, 135.51 (C-1), 136.71, 145.62, 145.87, 148.60; correct elemental analysis based on $C_{18}H_{18}O_4S_2$.

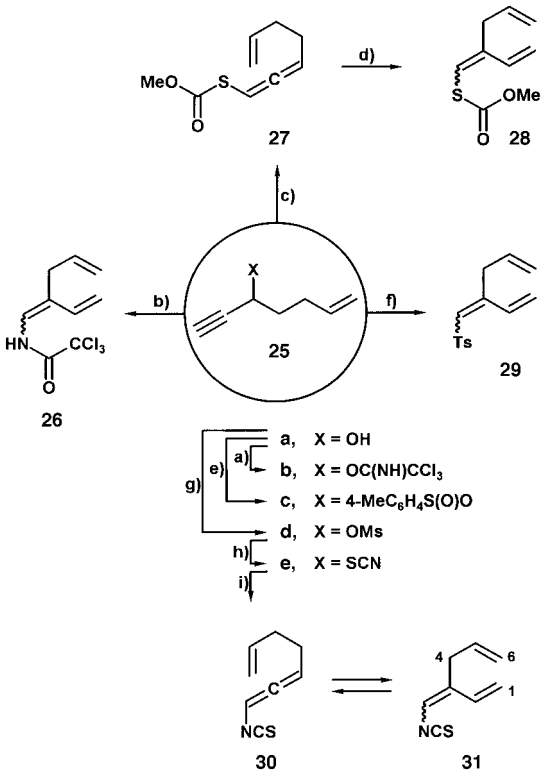
21: Colorless oil; ^{1}H NMR: $\delta = 5.60$ (br d, $^3J = 10.7$, 1H; H-4), 5.95 (d, $^3J = 16.7$, 1H; H-4), 6.00 (br s, 1H; H-1), 7.05 (dd, $^3J = 16.7$, $^3J = 10.7$, 1H; H-3), 7.49–7.67 (m, 5H; Ph); ^{13}C NMR: $\delta = 120.97$, 122.94, 123.87, 126.05, 129.32, 130.81, 144.02, 146.81; IR ($CDCl_3$): $\tilde{\nu} = 3061$, 2935, 2154, 2109, 1543, 1444, 1315, 1245, 1036.

24: Colorless solid, m.p. 119–121 °C; ^{1}H NMR: $\delta = 1.52$ (m, 3H; Me), 2.40 (s, 3H; Ar-Me), 4.83 (m, 1H; H-4), 5.22 (m, 1H; H-4), 6.95 (s, 1H; H-1), 7.31 (2H; AA′BB′), 7.40–7.58 (m, 5H; Ph), 7.75 (2H; AA′BB′); ^{13}C NMR: $\delta = 21.51$, 23.41, 120.10, 125.87, 127.08, 127.58, 129.14, 129.77, 132.16, 134.79, 137.29, 140.24, 144.90, 161.18; correct elemental analysis based on $C_{18}H_{18}O_3S_2$.

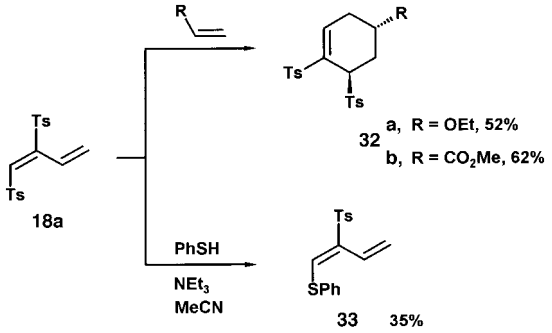
(*E*)-**31**: Colorless liquid; ^{1}H NMR: $\delta = 3.14$ (dt, $^3J = 6.3$, $^4J = 1.6$, 2H; H-4), 5.08 (dq, $^3J = 10.1$, $^2J = {}^4J = 1.6$, 1H; H-6), 5.13 (dq, $^3J = 17.3$, $^2J = {}^4J = 1.6$, 1H; H-6), 5.24 (dt, $^3J = 10.7$, $J \approx 0.6$, 1H; H-1), 5.43 (dt, $^3J = 17.3$, $J \approx 0.6$, 1H; H-1), 5.79 (ddt, $^3J = 17.1$, 10.1, 6.3, 1H; H-5), 6.04 (s, 1H; CHNCS), 6.26 (ddd, $^3J = 17.3$, $^3J = 10.7$, $J \approx 0.6$, 1H; H-2); ^{13}C NMR: $\delta = 30.77$ (C-4), 116.44 (CH–N), 116.61 (=CH_2), 117.23 (=CH_2), 133.90 (CH), 134.04 (CH), 135.61 (NCS), 139.80 (C-3); GC-MS: *m/z* (%): 151 (38) [M^+], 93 (100), 91 (63), 77 (91), 65 (40), 39 (91); IR ($CDCl_3$): $\tilde{\nu} = 2108$ (NCS).

(*Z*)-**31**: Colorless liquid; ^{1}H NMR: $\delta = 2.96$ (dq, $^3J = 6.6$, $^4J = 1.4$, 2H; H-4), 5.12 (dq, $^3J = 17.6$, $^2J = {}^4J = 1.4$, 1H; H-6), 5.12 (dq, $^3J = 10.0$, $^2J = {}^4J = 1.4$, 1H; H-6), 5.35 (d, $^3J = 11.0$, 1H; H-1), 5.46 (d, $^3J = 17.6$, 1H; H-1), 5.80 (ddt, $^3J = 17.6$, $^3J = 10.0$, $^3J = 6.6$, 1H; H-5), 5.89 (s, 1H; CHNCS), 6.81 (dd, $^3J = 17.6$, $^3J = 11.0$, 1H; H-2); ^{13}C NMR: $\delta = 33.65$ (C-4), 113.96 (CH), 117.47 (=CH_2), 118.01 (=CH_2), 130.52 (CH), 134.24 (CH), 136.23 (NCS), 137.77 (C-3).

[a] ^{1}H NMR: $CDCl_3$, 300 MHz, *J* in Hz; ^{13}C NMR: $CDCl_3$, 75 MHz, *J* in Hz, assignments of signals by DEPT experiments (DEPT = *d*istortionless *e*nhancement of *p*olarization *t*ransfer); MS: EI, 70 eV, IR: $\tilde{\nu}$ in cm^{-1}; elemental analysis: C, H, S.



Scheme 4. Synthesis of 2-allyl-1,3-butadienes with a functional group at C-1. a) DBU, Et_2O, Cl_3CCN, −40 °C/1 h → 20 °C/1 h, 97%; b) **25b**, gas-phase thermolysis 390 °C/10^{-3} Torr, 98%, *E*:*Z* = 1:2; c) **25a**, NaH, Et_2O, then dropwise addition to $CSCl_2/Et_2O$, 0 °C/1 h → 20 °C/24 h, then MeOH, 20 °C/16 h, 72%; d) gas-phase thermolysis at 400 °C/10^{-3} Torr, 83%, *E*:*Z* = 1:1.5; e) CH_2Cl_2, NEt_3, 4-$MeC_6H_4S(O)Cl$, 0 °C/3 h; f) **25c**, PhCl, 130 °C/15 h, 63% based on **25a**, *E*:*Z* = 1:1.6; g) $MeSO_2Cl$, NEt_3, 20 °C/24 h, 95%; h) NH_4SCN, MeOH, 60 °C/7 h, 75%; i) gas-phase thermolysis at 260–400 °C/10^{-3} Torr, 94–80% for **30**+**31**. Ms = methanesulfonyl.



Scheme 5. Bis(sulfone) **18a** as a synthetic building block.

with similar selectivity. Nucleophilic addition reactions are also possible.

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[14] For the conditions of the flash vacuum pyrolysis, see Scheme 2 and refs. [2, 3].
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An Iron(III) – Catechol Complex as a Mushroom Pigment**

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Dedicated to Prof. Heinrich Nöth on the occasion of his 70th birthday

Cortinarius violaceus [(L.: Fr.) S. F. Gray][1] is a spectacular mushroom well known for its dark blue-violet color and its cedar-wood-like smell. Fries[2] described this type species of the genus *Cortinarius* as "species nobilissima, pulcherrima". Previous efforts to examine the chemical nature of the violet pigment failed because of its instability and polarity. The dark violet water extracts of fresh or freeze-dried fruit bodies became dark brown within minutes. We were able to suppress this decomposition by exhaustive extraction of the lyophilized mushrooms with methanol prior to the water extraction. After freeze-drying the resulting aqueous solution, the residue was purified by chromatography on a Sephadex LH-20 column with methanol/water (1/1). This procedure enabled us to enrich the highly sensitive pigment. The pigment's NMR spectra were inconclusive due to strong signal broadening by paramagnetic iron, which can be detected both in the extract and the mushrooms. Since the intensity of the violet color correlates with the concentration of iron, the presence of an iron complex as the coloring principle seems obvious.

Energy dispersive X-ray analysis[3] (EDX), atomic absorption spectroscopy[4] (AAS), and the thiocyanate test indicated that *C. violaceus* is capable of accumulating iron in a unique manner. The amount of iron in the mushroom is 4.5 – 7.5 mg g^{-1} (dry weight), which is about 100 times the average value of 0.06 mg g^{-1} determined for other basidiomycetes.[5, 6] The Mössbauer spectra[7] (Figures 1 and 2, Table 1) show that the iron in the pigment is trivalent, and the ESR spectra[8] indicate a high-spin Fe^{III} complex.[9] The spectra of the freeze-dried mushrooms and the water extracts are identical.

After addition of aqueous HCl to the enriched pigment (*R*)-*β*-dopa ((*R*)-**3**) can be identified as the complex ligand.[10] Chromatographic workup of the methanol extracts followed by recrystallization yields the analytically pure amino acid. The (*R*)-*β*-dopa amounts to 2% of the dry weight of the mushroom. *β*-Dopa is a new natural product that has been synthesized only as the racemate before.[11] We obtained

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