First Synthesis of the Dendralene Family of Fundamental Hydrocarbons**

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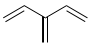
Of all the possible structural classes of conjugated polyene hydrocarbons, the dendralenes have received the least attention.[1] These compounds are typified by an acyclic polyolefinic structure in which both the degree of unsaturation and level of cross conjugation are of the highest order. The simplest member of the group, [3]dendralene (3-methylene-1,4-pentadiene **1**) is a volatile substance which dimerizes readily.[2] [3]Dendralene has been prepared through either low-yielding, classical flow-tube thermolyses of ester derivatives,[3a–d] by Hofmann elimination,[3e] by thermal isomerization of 1,2-hexadien-5-yne followed by partial hydrogenation[3f] and by flash vacuum pyrolysis of 3-vinyl-3-sulfolene.[3g] Polymerization-prone [4]dendralene (3,4-bismethylene-1,5-hexadiene, **2**) has been prepared in low yields by thermolytic isomerization and elimination processes[1] and, more recently, through high-temperature fragmentation of a sulfolane derivative.[4] Surprisingly, none of the higher members of this fundamental class of compounds have been reported, and spectroscopic data for the parent triene **1** and tetraene **2** are still not complete.[5] Herein we report the synthesis and spectroscopic properties of the [*n*]dendralene family ($n = 3-6$) using a unified strategy. We also demonstrate the applicability of this approach for the synthesis of a higher member of the group.



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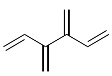

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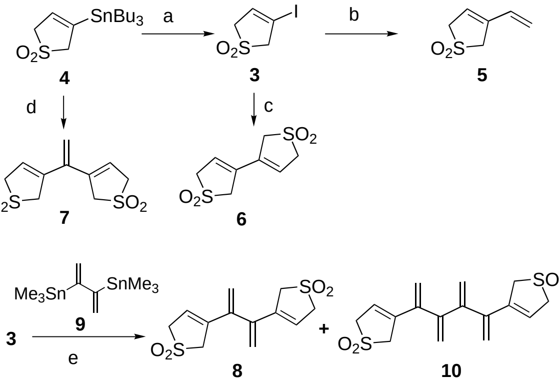
In light of the documented instability of [3]- and [4]dendralene (**1** and **2**, respectively), we formulated a synthetic approach involving the masking of each terminal butadiene residue of the dendralene target as its 3-sulfolene[6] derivative. Assuming that thermolytic cracking of SO_2 from the masked derivatives could be achieved, the problem of [*n*]dendralene synthesis was thus reduced to the construction and union of suitably functionalized ethylene and butadiene building blocks. We targeted Stille cross-coupling[7] for the union of these C_2 and C_4 units, due to the anticipated ease of preparation of the requisite vinylstannane/vinyl iodide precursors and the ease with which the functionalities of the two reacting partners can be interchanged. Moreover, the mildness of the Stille reaction conditions was not expected to cause premature cheletropic elimination of SO_2 from the masked dendralene products and thereby lead to product decomposition.

Synthetic approaches to masked [3]-, [4]-, [5]-, and [6]dendralenes are shown in Scheme 1. The key building block, 3-iodo-3-sulfolene (**3**)[8] was readily prepared by iodinolysis of 3-tributylstannyl-3-sulfolene (**4**).[9] The [3]dendralene precursor, 3-vinyl-3-sulfolene (**5**)[3g] was prepared in high yield by Stille coupling of **3** with vinyltributylstannane. The [4]dendralene precursor **6**[8] was prepared in high yield by coupling equimolar mixtures of **3** and **4**. [5]Dendralene precursor **7**[8] was prepared by twofold Stille coupling of stannane **4** with 1,1-dibromoethylene.[10, 11] The masked [6]dendralene **8**[8] was prepared by twofold cross-coupling of **3** with 2,3-bis(trimethylstannyl)-1,3-butadiene (**9**)[12], a reaction which also furnished [8]dendralene precursor **10**[8] as a by-product.



Scheme 1. The preparation of masked dendralenes. a) I_2, CH_2Cl_2, Ar, 1 h, 80%; b) $Bu_3Sn{-}CH{=}CH_2$ (1.2 equiv), $[PdCl_2(CH_3CN)_2]$ (0.05 equiv), DMF, RT, Ar, 2 h, 92%; c) **4** (1.0 equiv), $[PdCl_2(CH_3CN)_2]$ (0.05 equiv), DMF, RT, Ar, 18 h, 95%; d) $CH_2{=}CBr_2$ (0.5 equiv), $[PdCl_2(CH_3CN)_2]$ (0.05 equiv), DMF, 40°C, Ar, 36 h, 11%; e) **9** (1.0 equiv) $[PdCl_2(CH_3CN)_2]$ (0.10 equiv), DMF, 60°C, Ar, 72 h, 43% of **8** and 30% of **10**.

Masked [*n*]dendralenes **5**–**8** and **10** are white crystalline solids that are stable for extended periods of time (> 1 month) under nitrogen at ambient temperature. Whilst their insolubility precludes solution-phase thermolysis, each of the compounds **5**–**8** undergoes smooth cheletropic elimination of SO_2 upon heating to 450°C at atmospheric pressure under argon to afford a spectroscopically homogeneous sample of the dendralene (Scheme 2). [8]Dendralene was prepared from **10** by thermolyis in vacuo. In each case the hydrocarbon was collected in a trap cooled to liquid N_2 temperature and, after warming to room temperature, the colorless oil was quickly rinsed into an NMR tube with $CDCl_3$. The dendralenes polymerize only slowly in dilute solution in $CDCl_3$ and

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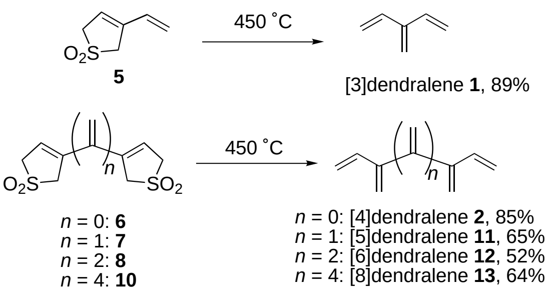

Scheme 2. Unmasking the dendralenes.

full spectral data for each compound was readily obtained (Table 1).

All members of the family exhibited excellent thermal stability: traces from GC/EI-MS analyses consisted of a single peak, from which a molecular ion formulating for the expected species was obtained. Dendralene fragmentation under EI conditions is characterized by a successive loss of methylene groups.

Table 1. Selected spectroscopic data for the dendralenes.

[3]dendralene **1**: $R_f = 0.60$ (SiO_2, hexane); IR ($CDCl_3$ solution): $\tilde{\nu}_{max} =$ 3092, 3009, 2978, 1601, 1585, 990 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta =$ 6.47 (dd, $^3J = 17.6$, 11.2 Hz, 2H), 5.42 (dd, $^3J = 17.6$, $^2J = 1.5$ Hz, 2H), 5.17 (br. d, $^3J = 11.2$ Hz, 2H), 5.17 (br. s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) $\delta =$ 144.5 (quaternary C), 135.7 (CH), 115.6 (CH_2), 115.4 (CH_2); UV/Vis (0.4% $CDCl_3$ in EtOH): λ_{max} (ε) = 232.2 nm (8200); GCMS (EI, 70 eV): m/z (%): 80 (71) [M^+], 79 (100) [$M^+ - H$]; HR-MS (EI, 70 eV): calcd for C_6H_8: 80.0626; found: 80.0630.

[4]dendralene **2**: $R_f = 0.60$ (SiO_2, hexane); IR ($CDCl_3$ solution): $\tilde{\nu}_{max} =$ 3092, 3009, 2974, 1583, 990 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 6.44$ (dd, $^3J = 17.4$, 10.6 Hz, 2H), 5.25 (m, 2H), 5.19 (br. d, $^3J = 17.4$ Hz, 2H), 5.11 (br. d, $^3J = 10.6$ Hz, 2H), 5.07 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) $\delta = 146.4$ (quaternary C), 137.4 (CH), 117.7 (CH_2), 116.5 (CH_2); UV/Vis (0.4% $CDCl_3$ in EtOH): λ_{max} (ε) = 222.8 nm (13500); GC-MS (EI, 70 eV): m/z (%): 106 (35) [M^+], 105 (45) [$M^+ - H$], 91 (100) [$M^+ - CH_3$]; HR-MS (EI, 70 eV): calcd for C_8H_{10}: 106.0782; found: 106.0779.

[5]dendralene **11**: $R_f = 0.48$ (SiO_2, hexane); IR ($CDCl_3$ solution): $\tilde{\nu}_{max} =$ 3092, 1580, 1131, 991 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 6.44$ (dd, $^3J =$ 17.4, 10.6 Hz, 2H), 5.34 (dd, $^3J = 17.4$; $^2J = 1.5$ Hz, 2H), 5.26 (s, 2H), 5.23 (m, 2H), 5.14 (br. d, $^3J = 10.6$ Hz, 2H), 5.12 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) $\delta = 146.9$ (quaternary C), 146.5 (quaternary C), 136.9 (CH), 116.8 (CH_2), 116.4 (CH_2), 116.2 (CH_2); UV/Vis (0.4% $CDCl_3$ in EtOH): λ_{max} (ε) = 219.8 nm (22000); GC-MS (EI, 70 eV): m/z (%):132(13) [M^+], 131(48) [$M^+ - H$], 117(100) [$M^+ - CH_3$]; HR-MS (EI, 70 eV): calcd for $C_{10}H_{12}$: 132.0939; found: 132.0914.

[6]dendralene **12**: $R_f = 0.49$ (SiO_2, hexane); IR ($CDCl_3$ solution): $\tilde{\nu}_{max} =$ 3092, 2978, 2875, 1581, 1113, 989 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta =$ 6.46 (ddd, $^3J = 17.4$, 10.5; $^4J = 0.9$ Hz, 2H), 5.29 (br d, $^3J = 17.4$ Hz, 2H), 5.28 (m, 2H), 5.26 (m, 2H), 5.13 (dm, $^3J = 10.5$ Hz, 2H), 5.09 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) $\delta = 147.3$ (quaternary C), 146.4 (quaternary C), 137.8 (CH), 117.7 (CH_2), 117.4 (CH_2), 116.2 (CH_2); UV/Vis (0.4% $CDCl_3$ in EtOH): λ_{max} (ε) = 220.0 nm (25000); GC-MS (EI, 70 eV): m/z (%): 158 (16) [M^+], 157 (53) [$M^+ - H$], 143 (56) [$M^+ - CH_3$], 129 (100) [$M^+ - C_2H_5$]; HR-MS (EI, 70 eV): calcd for $C_{12}H_{14}$: 158.1095; found: 158.1090.

[8]dendralene **13**: $R_f = 0.40$ (SiO_2, hexane); IR ($CDCl_3$ solution): $\tilde{\nu}_{max} =$ 3093, 3008, 2930, 1577, 1319, 1131, 990 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 6.46$ (dd, $^3J = 17.4$, 10.5 Hz, 2H), 5.36–5.25 (m, 8H), 5.12 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) $\delta = 147.5$ (quaternary C), 147.3 (quaternary C), 146.9 (quaternary C), 137.7 (CH), 117.8 (CH_2), 117.5 (CH_2), 117.2 (CH_2), 116.2 (CH_2); UV/Vis (0.4% $CDCl_3$ in EtOH): λ_{max} (ε) = 220.6 nm (25000); GCMS (EI, 70 eV): m/z (%): 210 (10) [M^+], 209 (31) [$M^+ - H$], 195(100) [$M^+ - CH_3$]; HR-MS (EI, 70 eV): calcd for $C_{16}H_{18}$: 210.1409; found: 210.1405.

The ^1H NMR spectra[13] contain the expected ABX system of a monosubstituted alkene, with the C2 methine proton appearing furthest downfield ($\delta = 6.44$–6.47) as an isolated doublet of doublets ($^3J = 17.4$–17.6, 10.5–11.2 Hz). The remaining signals ($\delta = 5.09$–5.42) are well resolved and first-order at 270 MHz for [3]dendralene but increase in complexity with higher members of the family. The ^{13}C NMR spectra of the dendralenes[13] are particularly informative, with signals appearing in three distinct regions: $\delta = 115.4$–117.7 (methylene C atoms), 135.7–137.8 (methine C atoms), and 144.5–147.3 (quaternary C atoms).

The dendralenes display a single absorption maximum in the UV/Vis region[13] at $\lambda_{max} = 219.8$–232.2 nm (0.4% $CDCl_3$ in ethanol), confirming the nonplanar, nonconjugated arrangement of s-*trans*-1,3-butadiene and ethylene units in these molecules.[14] Indeed, there is an approximate correlation between the extinction coefficient of each dendralene and the number of 1,3-butadiene moieties that makes up its structure.

In summary, the first four members of the dendralene family have been prepared by a modular strategy in which the more exposed terminal 1,3-butadiene residues are masked as 3-sulfolene derivatives. The applicability of this approach for the synthesis of higher family members has been demonstrated by the synthesis of [8]dendralene. Access to this fundamental (yet neglected[1]) class of cross-conjugated hydrocarbons sets the scene for studies into their structure, reactivity, and properties.[15, 16]

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[1] H. Hopf, *Angew. Chem.* **1984**, *96*, 947–958; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 947–959.

[2] W. S. Trahanovsky, K. A. Koeplinger, *J. Org. Chem.* **1992**, *57*, 4711–4716.

[3] a) A. T.Bloomquist, J. A. Verdol, *J. Am. Chem. Soc.* **1955**, *77*, 81–83; b) W. J. Bailey, J. Economy, *J. Am. Chem. Soc.* **1955**, *77*, 1133–1136; c) A. T. Bloomquist, J. A. Verdol *J. Am. Chem. Soc.* **1955**, *77*, 1806–1809; d) W. J. Bailey, C. H. Cunov, L. Nicholas, *J. Am. Chem. Soc.* **1955**, *77*, 2787–2790; e) H.-D. Martin, M. Eckert-Macsic, B. Mayer, *Angew. Chem.* **1980**, *92*, 833; H.-D. Martin, M. Eckert-Macsic, B. Mayer, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 807–809; f) H. Priebe, H. Hopf, *Angew. Chem.* **1982**, *94*, 299–300; H. Priebe, H. Hopf, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 286–287; g) J. I. G. Cadogan, S. Cradock, S. Gillam, I. Gosney, *J. Chem. Soc. Chem. Commun.* **1991**, 114–115.

[4] P. T. Brain, B. A. Smart, H. E. Robertson, M. J. Davis, D. W. H. Rankin, W. J. Henry, I. Gosney, *J. Org. Chem.* **1997**, *62*, 2767–2773.

[5] There is some confusion over the ^{13}C NMR spectrum of **1** (see footnote [26] in ref. [2]), the ^{13}C NMR data reported for **2** is incomplete[4] and no mass spectrometric data for **2** has thus far been reported.

[6] T. Chou, H.-H. Tso, *Org. Prep. Proced. Int.* **1989**, *21*, 257–296.

[7] V. Farina, V. Krishnamurthy, W. J. Scott, *Organic React.* **1997**, *50*, 1–652.

[8] All new compounds were characterized by ^1H and ^{13}C NMR, IR, and UV/Vis spectroscopy, mass spectrometry, and combustion analyses and/or high-resolution mass spectrometric analysis.

[9] a) S. P. Bew, J. B. Sweeney, *Synthesis* **1994**, 698; b) S. P. Bew, J. B. Sweeney, *Synlett* **1997**, 1273–1274.

[10] E. N. Jacobsen, R. G. Bergman, *J. Am. Chem. Soc.* **1985**, *107*, 2023–2032.

[11] This reaction also produces a significant quantity of 3-sulfolene, the product of protiodestannylation. No improvement in yield was obtained with [$Pd_2(dba)_3$]/Ph_3As/NMP (V. Farina, B. Krishnan, *J. Am. Chem. Soc.* **1991**, *113*, 9585–9595; dba = dibenzylideneacetone, NMP = *N*-methylpyrrolidine) or $Pd(OAc)_2/PPh_3$/MeCN (S. Torii, H.

Okumoto, T. Tadokoro, A. Nishimura, M. Rashid, *Tetrahedron Lett.* **1993**, *34*, 2139–2142). An alternative route would involve the coupling of iodide **3** with a 1,1-bis(trialkylstannyl)ethylene. Thus far we have been unable to prepare 1,1-bis(trimethylstannyl)ethylene (T. N. Mitchell, A. Amamria, *J. Organomet. Chem.* **1983**, *252*, 47–56).

[12] H. J. Reich, I. L. Reich, K. E. Yelm, J. E. Holladay, D. Gschneidner, *J. Am. Chem. Soc.* **1993**, *115*, 6625–6635.

[13] The Supporting Information contains ^{1}H NMR, ^{13}C NMR, and UV/Vis spectra of the [*n*]dendralenes.

[14] Gas phase electron diffraction measurements indicate that [3]dendralene adopts a conformation consisting of a planar *s-trans*-1,3-butadiene with the 2-vinyl group skewed 40° out of plane: A. Almenningen, A. Gatail, D. S. B. Grace, H. Hopf, P. Klaeboe, F. Lehrich, C. J. Nielsen, D. L. Powell, M. Tratteberg, *Acta Chem. Scand.* **1988**, *A42*, 634–650. [4]Dendralene behaves similarly, adopting an *s-trans, s-trans,* skew conformation.[2]

[15] Potential applications of dendralenes in molecular electronic and ferromagnetic devices: a) M. R. Bryce, M. A. Coffin, P. J. Skabara, A. J. Moore, A. S. Batsanov, J. A. K. Howard, *Chem. Eur. J.* **2000**, *6*, 1955–1962; b) N. Tyutyulkov, *Pure Appl. Chem.* **1996**, *68*, 345–352.

[16] "Expanded dendralenes", in which ethynyl units are inserted between each "etheno"[1] group have been reported: a) A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 779–796; b) Y. Zhao, R. R. Tykwinski, *J. Am. Chem. Soc.* **1999**, *121*, 458–459; c) Y. Zhao, R. McDonald, R. R. Tykwinski, *Chem. Commun.* **2000**, 77–78.

The Hexaazidogermanate(IV) Ion: Syntheses, Structures, and Reactions**

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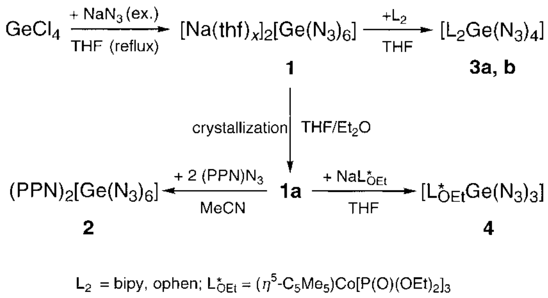
*Dedicated to Professor Herbert Schumann
on the occasion of his 65th birthday*

The synthesis, isolation, and structural characterization of high-energy compounds is an experimental challenge.[1] Binary azides of the main Group IV elements belong to this class of compounds, however, very little is known about their structure and reactivity.[2] To date only the ions $[C(N_3)_3]^+$[2d] and $[E(N_3)_6]^{2-}$ (E = Sn, Pb),[2g,h] as well as α-$Pb(N_3)_2$[2f] have been structurally characterized; in comparison there is no structural information for the analogous silicium and germanium compounds. We recently reported the syntheses, structures, and oxidation reactions of Ge^{II} azides with HN_3;[3] hypercoordinate triazidogermane compounds of the type $[L_3Ge(N_3)_3]$ ($L_3 = [CpCo\{P(O)(OEt)_2\}_3]$, $HB(pz^*)_3$; $Cp = C_5H_5$; pz^* = 3,5-dimethylpyrazol-1-yl) could be prepared and structurally characterized.[4] As an extension to this work on germanium compounds with a high nitrogen content[5] we report herein the formation, structure, and first reactions of the hexaazidogermanate(IV) ion to give derivatives of $Ge(N_3)_4$.

The reaction of $GeCl_4$ with excess NaN_3 in boiling THF leads selectively to disodium hexaazidogermanate(IV) **1**, which, after workup and crystallization, was isolated as colorless, hydrolysis-sensitive, single crystals of composition $[Na_2(thf)_3(Et_2O)][Ge(N_3)_6]$ (**1a**; Scheme 1).[6] The crystal lattice of **1a** is composed of distorted octahedral $[Ge(N_3)_6]^{2-}$ ions of C_1 symmetry and two symmetry independent sodium ions, of which one is solvated by two THF molecules (Na1–O1 2.327(4), Na1–O2 2.287(5) Å) and the other by one THF and one Et_2O molecule (Na2–O3 2.265(5), Na2–O4 2.304(11) Å; Figure 1).[7] The Na–O bond lengths are in the range reported for other Na–THF/Et_2O complexes.[8] Short Na–N contacts exist between the Na^+ ions and the N_α and N_γ atoms of the azide groups of the $[Ge(N_3)_6]^{2-}$ ions. These contacts link each $[Ge(N_3)_6]^{2-}$ ion with two Na1 and Na2 cations and each sodium cation with two $[Ge(N_3)_6]$ anions to give a layer structure. This arrangement results in a strongly distorted octahedral coordination geometry of the Na1 cations and a coordination polyhedron for the pentacoordinate Na2 cations that can be rationalized using the Kepert model for chelate complexes.[9] The Na–N distances (2.410(5)–2.636(6) Å) are in the range found for Na–N coordinate bonds[10] and increase as the coordination number of the Na^+ ions and of the azide nitrogen atoms increases. The short interionic Na–N contacts in **1a** have only a slight influence on the average bonding parameters of the $[Ge(N_3)_6]^{2-}$ ion. This point is shown by a comparison with the crystal structure of the salt $(PPN)_2[Ge(N_3)_6]$ **2** ($(PPN)^+ = [N(PPh_3)_2]^+$), which contains less-polarizing cations (Table 1). Compound **2** is formed in the reaction of **1a** with $(PPN)N_3$ in MeCN (Scheme 1) and was fully characterized. It was isolated in 55% yield as a colorless microcrystalline powder that is very soluble in CH_2Cl_2 but insoluble in THF. In the solid state **2** is air stable for a short time, whereas in solution it is rapidly hydrolyzed releasing HN_3 and $(PPN)N_3$. IR spectroscopy of **2** in MeCN at



Scheme 1. Synthesis of $Ge(N_3)_4$ derivatives starting from $GeCl_4$.

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