ORGANIC LETTERS

2003
Vol. 5, No. 8
1325−1327

Perthio- and Perseleno-1,3-butadienes, -but-1-ene-3-ynes, and -[3]-cumulenes: One-Step Syntheses from 1,4-Dilithio-1,3-butadiyne

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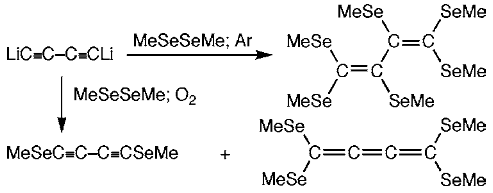
Received February 13, 2003

ABSTRACT



Treatment of 1,4-dilithio-1,3-butadiyne (1) with dichalcogenides RSSR or RSeSeR affords dithio- and diseleno-1,3-butadiynes (2, 3), perthio- and perseleno-[3]-cumulenes (4, 5), perthio- and perseleno-1,3-butadienes (6, 7), and/or perthio- and perseleno-but-1-ene-3-ynes (8, 9). The products can be controlled by stoichiometry and temperature, by the presence or absence of oxygen, and by choice of the "R" group. By X-ray crystallography, hexa(methylthio)-1,3-butadiene is highly twisted, with a torsion angle [Φ(CCCC)] of 84.7° and an elongated C(2)–C(3) distance of 1.484(3) Å.

Perchalcogenohydrocarbons [$(RX)_mC_n$ (X = S or Se)] are of interest as novel electron-accepting materials, host compounds, and reagents.[1] We report simple, one-step syntheses of little known members of this family of compounds, namely perthio- and perseleno-1,3-butadienes (**6**, **7**),[2] perthio- and perseleno-[3]-cumulenes (**4**, **5**), and perthio- and perseleno-but-1-ene-3-ynes (**8**, **9**; Scheme 1).[3] Compounds **4**−**9** are formed by way of dithio- and diseleno-1,3-butadiynes (**2**, **3**), in turn generated in situ from reaction of 1,4-dilithio-1,3-butadiyne (**1**) with dichalcogenides RSSR or RSeSeR. Our synthesis avoids the use of perchloro-1,3-butadiene and related toxic compounds employed in the only previous syntheses of **4** and **8**.[3] The nature of the products can be controlled by the stoichiometry and temperature, by the presence or absence of oxygen, and by the choice of the dichalcogenide "XR" group.

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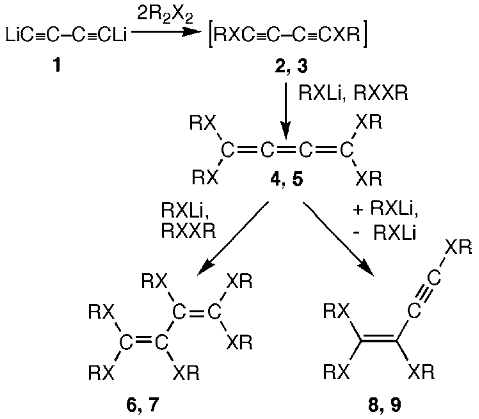
(1) (a) Examples of perchalcogenohydrocarbons include perthio- and perselenomethane,[1b,c] ethane,[1b,c] arenes (e.g. perthio- and perselenobenzenes,[1d] -naphthalenes,[1e,f] anthracenes[1g] and coronenes[1d]), ethene,[1b,c] ethyne,[1h] 1,2-propadiene,[1i] and 1,3-butadiyne.[1j] Many of these compounds display unusual properties and reactivities. (b) $(RS)_4C$, $(RS)_4C_2$, $(RS)_6C_2$: Seebach, D. *Chem. Ber.* **1972**, *105*, 487−510. (c) $(RSe)_4C$, $(RSe)_4C_2$, $(RSe)_6C_2$: Haas, A.; Moeller, G. *Chem. Ber.* **1996**, *129*, 1383−1388. (d) $(RS)_6C_6$, $(RSe)_6C_6$, $(RS)_{12}C_{24}$: Tucker, J. H. R.; Gingras, M.; Brand, H.; Lehn, J.-M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1303−1307. (e) $(RS)_8C_{10}$: Downing, G. A.; Frampton, C. S.; Gall, J. H.; MacNicol, D. D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1547−1549. (f) $(RSe)_8C_{10}$: MacNicol, D. D.; Mallinson, P. R.; Robertson, C. D. *Acta Crystallogr.* **1992**, *C48*, 1557−1558. (g) $(RS)_{10}C_{14}$: Frampton, C. S.; McGregor, W. M.; MacNicol, D. D.; Mallinson, P. R.; Plevey, R. G.; Rowan, S. J. *Supramol. Chem.* **1994**, *3*, 223−226. (h) RSC_2SR: Verkruijsse, H. D.; Brandsma, L. *Synthesis* **1991**, 818. $RSeC_2SeR$: Martynov, A. V.; Le Guillanton, G. *Bull. Soc. Chim. France* **1997**, *134*, 823−831. (i) $(RS)_4C_3$: Hartke, K.; Rettberg, N. *Tetrahedron Lett.* **1991**, *32*, 4679−4682. (j) RSC_4SR: Block, E.; Guo, C.; Thiruvazhi, M.; Toscano, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 9403−4. Arens, J. F.; Volger, H. C.; Doornbos, T.; Bonnema, J.; Greidanus, J. W.; van den Hende, J. H. *Recl. Trav. Chim.* **1956**, *75* 1459−72. Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1990**, *112*, 6437−8.

(2) Hexa(phenylthio)-1,3-butadiene (**6f**), isolated as a minor byproduct in a synthesis of bis(phenylthio)ethyne, was characterized by X-ray crystallography: Mathiesen, R. H.; Sundset, R.; Hauback, B. C.; Mo, F.; Kjosen, H.; Haugan, J. A.; Mørkved, E. H. *Z. Kristallogr.* **1999**, *214*, 475−479.

10.1021/ol034258g CCC: $25.00

Scheme 1[a]



[a] In **2**, **4**, **6**, and **8,** X = S; in **3**, **5**, **7**, and **9**, X = Se; in **2**−**9**, R = Me (a), Et (b), *n*Pr (c), *i*Pr (d), *n*Bu (e), Ph (f), and *t*Bu (g).

The reaction of **1**, prepared from 1,4-dichloro-2-butyne,[4] with dialkyl disulfides was examined as a possible route to 1,4-bis(alkylthio)-substituted 1,3-butadiynes (**2**), key intermediates in our hydrostannylation approach to substituted 1,2-dithiins **10** (Scheme 2).[1j] We previously prepared **2** via Glaser coupling of alkylthioethynes. Reaction of **1** with dimethyl disulfide afforded either 1,1,4,4-tetra(methylthio)-[3]-cumulene (**4a**; 81%) or 1,1,2,3,4,4-hexa(methylthio)-1,3-butadiene (**6a**; 73%), depending on stoichiometry and reaction conditions (Scheme 1). Presumably, nucleophilic addition of methanethiolate to diyne **2a** is followed by capture of the resultant anion by disulfide to give cumulene **4a**; with excess disulfide at higher temperatures, the major product is **6a**. With various disulfides, good yields are obtained of sulfur-substituted [3]-cumulenes **4** and 1,3-butadienes **6**, along with lesser amounts of but-1-ene-3-ynes (**8**; Table 1). Of the disulfides used, only di-*tert*-butyl disulfide failed to react. With the exception of **6f**,[2] all compounds in Table 1 have not been previously reported.

Scheme 2

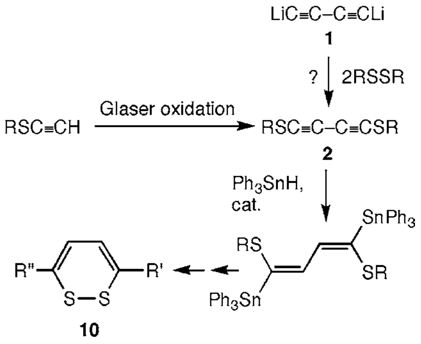


Table 1. Perchalcogeno 1,3-Butadienes (**6**, **7**), 1,3-Butadiynes (**3**), But-1-ene-3-ynes (**8**, **9**), and [3]-Cumulenes (**4**, **5**) Synthesized

product	compd	cond[a]	% yield
$\mathrm{(MeS)_2C{=}C{=}C{=}C(SMe)_2}$	**4a**	A	81
$\mathrm{(EtS)_2C{=}C{=}C{=}C(SEt)_2}$	**4b**	A	78
$\mathrm{(\mathit{n}PrS)_2C{=}C{=}C{=}C(S\mathit{n}Pr)_2}$	**4c**	B	91
$\mathrm{(\mathit{i}PrS)_2C{=}C{=}C{=}C(S\mathit{i}Pr)_2}$	**4d**	A	67
and $\mathrm{(\mathit{i}PrS)_2C{=}C(S\mathit{i}Pr)C{\equiv}CS\mathit{i}Pr}$	**8d**	A	17
$\mathrm{(\mathit{n}BuS)_2C{=}C{=}C{=}C(S\mathit{n}Bu)_2}$	**4e**	B	67
$\mathrm{(MeS)_2C{=}C(SMe)C(SMe){=}C(SMe)_2}$	**6a**	B	73
$\mathrm{(EtS)_2C{=}C(SEt)C(SEt){=}C(SEt)_2}$	**6b**	B	61
$\mathrm{(PhS)_2C{=}C(SPh)C(SPh){=}C(SPh)_2}$[b]	**6f**	B	42
and $\mathrm{(PhS)_2C{=}C(SPh)C{\equiv}CSPh}$	**8f**	B	4
$\mathrm{MeSeC{\equiv}CC{\equiv}CSeMe}$	**3a**	D	25
and $\mathrm{(MeSe)_2C{=}C{=}C{=}C(SeMe)_2}$	**5a**	D	42
$\mathrm{(MeSe)_2C{=}C(SeMe)C(SeMe){=}C(SeMe)_2}$	**7a**	C	87
$\mathrm{(EtSe)_2C{=}C(SeEt)C(SeEt){=}C(SeEt)_2}$	**7b**	B	63
$\mathrm{(\mathit{n}PrSe)_2C{=}C(Se\mathit{n}Pr)C(Se\mathit{n}Pr){=}C(Se\mathit{n}Pr)_2}$	**7c**	B	62
$\mathrm{(\mathit{i}PrSe)_2C{=}C(Se\mathit{i}Pr)C{\equiv}CSe\mathit{i}Pr}$	**9c**	B	74
$\mathrm{(PhSe)_2C{=}C(SePh)C(SePh){=}C(SePh)_2}$	**7f**	B	34
and $\mathrm{(PhSe)_2C{=}C(SePh)C{\equiv}CSePh}$	**9f**	B	11
$\mathrm{\mathit{t}BuSeC{\equiv}CC{\equiv}CSe\mathit{t}Bu}$	**3g**	B	61

[a] Conditions: A, 2 equiv of RXXR; B, 3 equiv of RXXR; C, 4 equiv of RXXR; D, 2 equiv of MeSeSeMe + O_2. [b] Previously reported.[2]

When dimethyl, diethyl, and di-*n*-propyl diselenides are reacted as above *under argon*, the corresponding deeply colored 1,1,2,3,4,4-hexa(alkylseleno)-1,3-butadienes **7a**−**c** are the only products isolated. The high nucleophilicity of selenolate favors its addition to the central bond in the intermediate 1,1,4,4-tetra(alkylchalcogeno)-[3]-cumulene (**5a**−**c**). With the more hindered isopropyl and di-*tert*-butyl diselenides,[5] the reactions take a different course, affording 1,1,2,4-tetra(isopropylseleno)but-1-ene-3-yne (**9d**) and 1,4-bis(*tert*-butylseleno)-1,3-butadiyne (**3g**), respectively (Table 1). Diphenyl diselenide gives a mixture of **5f**, **7f**, and **9f**. When **1** reacts with MeSeSeMe in dry air, the reaction instead affords 1,4-bis(methylseleno)-1,3-butadiyne (**3a**) and 1,1,4,4-tetra(methylseleno)-[3]-cumulene (**5a**) as the main products. Oxidation of MeSeLi to MeSeSeMe is likely more rapid than addition of MeSeLi to **5a** but not so fast as addition of MeSeLi to **3a**. By regulating the O_2 level, the nature of the products from diselenides can be controlled. Attempts to extend the above reactions with MeTeTeMe or LiC≡CC≡CC≡CLi did not succeed.

While the effect of variation in the 1,3-butadiene C1−C2−C3−C4 torsion angle [Φ(CCCC)] on the C1−C2 and C2−C3 bond lengths is relevant to considerations of bonding in this compound, only a few accurate structural determina-

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(3) (a) 1,1,4,4-Tetra(organothio)-[3]-cumulene and 1,1,2,4-tetra(organothio)but-1-ene-3-ynes from perchlorobutenyne: Roedig, A.; Zaby, G.; Scharf, W. *Chem. Ber.* **1977**, *110*, 1484−91. Roedig, A.; Zaby, G. *Liebigs Ann. Chem.* **1979**, 1606−13. Roedig, A.; Ibis, C.; Zaby, G. *Chem. Ber.* **1981**, *114*, 684−698. Ibis, C. *Liebigs Ann. Chem.* **1987**, 1009−1011. (b) Ethenediylidene-2,2′-bis(1,3-dithiole) and butatriene-1,4-ethenediylidene-2,2′-bis(1,3-dithiole), [3]- and [5]-cumulenes (not isolable): Awaji, H.; Sugimoto, T.; Yoshida, Z. *J. Phys. Org. Chem.* **1988**, *1*, 47−51.

(4) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 1988.

(5) Korchevin, N. A.; Podkuiko, P. A.; Stankevich, V. K.; Deryagina, E. N.; Voronkov, M. G. *Zhur. Obsh. Khim.* **1989**, *59*, 1788−1790.

tions have been reported for twisted acyclic 1,3-butadienes. We find that several perchalcogeno-1,3-butadienes, whose structures were determined by X-ray crystallography, show torsion angles varying from 70° to 85°. Table 2 compares experimental and calculated values for 1,3-butadiene (**11**)[6] and perchloro-1,3-butadiene[7](**12**) with data for **6a** and **6f**. As the torsion angle increases from 70.6° for **6f** to 84.7° for **6a**, the double bonds become slightly shorter while the central C(2)−C(3) bond becomes slightly longer, paralleling the trend calculated for 1,3-butadiene[6] and quite similar to the case of **12**, where the torsion angle is 89 ± 3°.[7] The cumulenes, dienes, diynes, and ene-ynes can be distinguished by IR (C≡C, 2032−2148 cm^{-1}; C=C=C, 2029−2035 and 1560−1563 cm^{-1}; C=C, 1653−1688 cm^{-1}) and ^{13}C and ^{77}Se NMR (^{13}C data: [3]-cumulenes, δ 146−151 (sp-C)[3a,8] and 92−110 (sp^2-C)[3a,8] ppm; dienes, δ 115−130 and 139−142 ppm; C≡C in ene-ynes, δ 80−88 and 95−113; C≡C in diynes, δ 67 and 90), among other methods.[9]

Table 2. Comparison of Structural Features of **6a**, **6f**, 1,3-Butadiene (**11**), and Hexachloro-1,3-butadiene (**12**)

compd	C(1)−C(2), Å	C(3)−C(4), Å	C(2)−C(3), Å	Φ(CCCC), deg
6a	1.338(3)	1.329(4)	1.484(3)	84.7
6f[a]	1.345(5)	1.344(5)	1.479(5)	70.6
11[b]	1.337		1.467	180
11[c]	1.345		1.460	180
11[d]	1.344		1.472	39.9
11[e]	1.341		1.486	102.1
12[f]	1.341(5)		1.485(9)	89

[a] Also see ref 2. [b] By microwave spectroscopy.[6b] [c] Calculated, s-trans.[6a] [d] Calculated, gauche.[6a] [e] Calculated, transition state.[6a] [f] By electron diffraction.[7]

Acknowledgment. This work was supported by NSF (CHE-9906566), the NRI Competitive Grants Program/USDA (Award No. 92-375008086), and the Petroleum Research Fund, administered by the American Chemical Society.

Supporting Information Available: Elemental analyses for **4c**, **6a**, **7a**, and **9c**, full characterization of **3g**, **4a**, **4b**, **4d**, **4e**, **6b**, **6f**, **7b**, **7c**, **7f**, **8d**, **8f**, and **9f**, and X-ray diffraction data for **6a** and **6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) (a) Calculated: Gong, X.; Xiao, H. *Int. J. Quantum Chem.* **1998**, *69*, 659−667; MP2/6−311** calculations. (b) Experimental: Caminati, W.; Grassi, G.; Bauder, A. *Chem. Phys. Lett.* **1988**, *148*, 13−16.

(7) Gundersen, G.; Nielsen, C. J.; Thomassen, H. G.; Becher, G. *J. Mol. Struct.* **1988**, *176*, 33−60.

(8) For ^{13}C NMR chemical shifts of [*n*]-cumulenes, see: Van Dongen, J. P. C. M.; De Bie, M. J. A.; Steur, R. *Tetrahedron Lett.* **1973**, 1371−1374.

(9) **1**: *Caution: neat 1,3-butadiyne is potentially explosive on warming! It should be generated in small quantities at low temperatures and used immediately.* 1,4-Dichloro-2-butyne (6.84 mL, 70 mmol) is added dropwise during 30 min to a stirred mixture of DMSO (16 mL) and aq KOH (52 g/80 mL water) at 70−75 °C while argon is bubbled through the solution and then through a series of two gas washing bottles, containing dilute aqueous KOH, and two $CaCl_2$ drying tubes into a −78 °C cooling trap.[4] In this manner, colorless crystals of 1,3-butadiyne (3.27 g, 65 mmol, 93%, by rapid weighing while still cold) are collected at −78 °C and under argon immediately diluted with pre-cooled THF (6 mL/mmol of 1,3-butadiyne), and treated at −78 °C with 2 equiv of *n*BuLi (1.6 M in hexane) giving a white suspension of **1**. Immediately, under argon, disulfide or diselenide was added dropwise to a freshly prepared, stirred suspension of **1** in THF at −78 °C. The mixture was warmed to 25 °C, stirred for 3 h, poured into water, and extracted four times with ether. The combined extracts were washed with brine, dried, and concentrated in vacuo. Chromatography on a column (20:1 hexane:ethyl acetate with 1% Et_3N) and/or with a Chromatotron (hexane, 1% Et_3N) gave the pure products. **3a/5a**: With 2 equiv of MeSeSeMe in the presence of O_2, after chromatography **3a** (25%) and **5a** (42%) were isolated as yellow oils incompletely separated from each other. **3a**: ^1H NMR (300 MHz) δ 2.29 (s, 6 H); ^{13}C NMR (75 MHz) δ 9.7, 65.2, 84.8; ^{77}Se NMR (57 MHz) δ 352; FT-IR (KBr) ν 2065, 2122, 2176 cm^{-1}; GC-MS (70 eV) *m/z* 237 (M^+). **5a**: ^1H NMR (300 MHz) δ 2.36 (s, 6 H); ^{13}C NMR (75 MHz) δ 10.5, 91.7, 151.2; ^{77}Se NMR (57 MHz) δ 337; FT-IR (KBr) ν 1606, 2015 cm^{-1}; LC-MS (70 eV) *m/z* 427 (M^+); UV (hexane) λ_{max} 228, 234, 268, 280, 298, 388 nm (ϵ 398, 393, 971, 928, 904, 737, respectively). **4c**: With 3 equiv of *n*PrSSPr*n*, a yellow oil (91%); ^1H NMR (300 MHz) δ 0.97 (t, 12 H, $^3J = 7.2$ Hz), 1.65 (sextet, 8 H, $^3J = 7.2$ Hz), 2.82 (t, 8 H, $^3J = 7.2$ Hz); ^{13}C NMR (75 MHz) δ 13.2, 22.5, 36.7, 107.7, 146.7; GC-MS (70 eV) *m/z* 348 [M^+]; UV (hexane) λ_{max} 232, 282, 352, 388 nm; FT-IR (KBr) ν 1563, 2030 cm^{-1}. **6a**: With 3 equiv of MeSSMe, after refluxing for 12 h, recrystallization (hexanes−ether) of the solid residue gave **6a** as light yellow crystals (73%); mp 66 °C; ^1H NMR (300 MHz) δ 2.18 (s, 6 H), 2.23 (s, 6 H), 2.32 (s, 6 H); ^{13}C NMR (75 MHz) δ 15.5, 16.6, 16.8, 127.7, 139.4; GC-MS (70 eV) *m/z* 330 (M^+), 283 (M − MeS); FT-IR (KBr) ν 1666 cm^{-1}; UV (hexane) λ_{max} 266, 318, 354 nm (ϵ 886, 986, 840). **7a**: With 4 equiv of MeSeSeMe, yellow crystals (87%); mp 62−63 °C; ^1H NMR (300 MHz) δ 2.14 (s, 6 H, $^2J_{HSe} = 13.2$ Hz), 2.20 (s, 6 H, $^2J_{HSe} = 12.6$ Hz), 2.27 (s, 6 H, $^2J_{HSe} = 12.0$ Hz); ^{13}C NMR (75 MHz) δ 8.7, 9.9, 10.2, 117.2, 139.1; ^{77}Se NMR (57 MHz) δ 208, 282, 312; LC-MS (70 eV) *m/z* 612 [M^+ for all ^{80}Se]; UV (hexane) λ_{max} 236, 328 nm (ϵ 3240, 3667); FT-IR (KBr) ν 1658, 1688 cm^{-1} (w, C=C). **9c**: With 3 equiv of *i*PrSeSe*i*Pr, a yellow oil (74%); ^1H NMR (300 MHz) δ 1.39 (d, 12 H, $^3J = 5.7$ Hz), 1.41 (d, 6 H, $^3J = 5.4$ Hz), 1.43 (d, 6 H, $^3J = 6.6$ Hz), 3.42 (sept, 1 H, $^3J = 6.6$ Hz), 3.5−3.7 (m, 3 H); ^{13}C NMR (75 MHz) δ 23.8, 23.9, 24.2, 24.4, 36.0, 36.7, 36.8, 38.1, 80.8, 99.8, 122.9, 126.6; ^{77}Se NMR (57 MHz) δ 297, 474, 502, 535; LC-MS (70 eV) *m/z* 536 [M^+ for all ^{80}Se]; UV (hexane) λ_{max} 236, 274, 316, 366 nm (ϵ 2598, 2504, 2853, 2676); FT-IR (KBr) ν 1558 (C=C), 2117 (C≡C) cm^{-1}.