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Synthesis, Structure, Reactions, and Photoelectron Spectra of New Mixed Sulfur-, Selenium- or Tellurium and Silicon- or Tin-Containing Heterocycles

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ABSTRACT: *More than 40 new 4- to 12-membered ring heterocycles containing various combinations of Group 14 elements (Si and Sn) and Group 16 elements (S, Se, and Te) have been synthesized and fully characterized. Synthesis of these small-ring as well as medium-ring (mesocyclic) heterocycles from α, ω-dihalides was facilitated by the presence of gem-dialkylsilyl and gem-dialkylstannyl groups in the precursors. Solid-state conformations of the new ring systems have been determined by X-ray crystallography. Oxidation of mixed S(Se, Te)/Si eight-membered ring mesocycles as well as 1,5-dithia-, 1,5-diselena-, and 1,5-ditelluracyclooctane with* $NOPF_6$ *gave dications, which can be characterized by NMR. On treatment with nucleophiles, mesocyclic dications or the corresponding radical cations underwent ring contraction to give five- or six-membered ring heterocycles. The ionization energies of the above conformationally constrained β-disilanyl sulfides and selenides were determined by photoelectron spectroscopy. These ionization energies reflect substantial (0.53–0.75 eV) orbital destabilizations. The basis for these destabilizations was investigated by theoretical calculations, which reveal geometry-dependent interaction between sulfur or selenium lone pair orbitals and σ-orbitals, especially Si—Si σ-orbitals. These results suggest facile redox chemistry for these compounds and significantly extend the concept of σ-stabilization of electron-deficient centers.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:509–515, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20333

INTRODUCTION

Pioneering research by Musker and Furukawa revealed the rich chemistry associated with radical cations and dications formed from dichalcogen mesocycles (medium-sized heterocycles) such as 1,5-dithiocane **4** (Scheme 1), 1,6-dithiecane **5**, and Se- and Te-analogs **15** and **16**, respectively (Fig. 1) [1].

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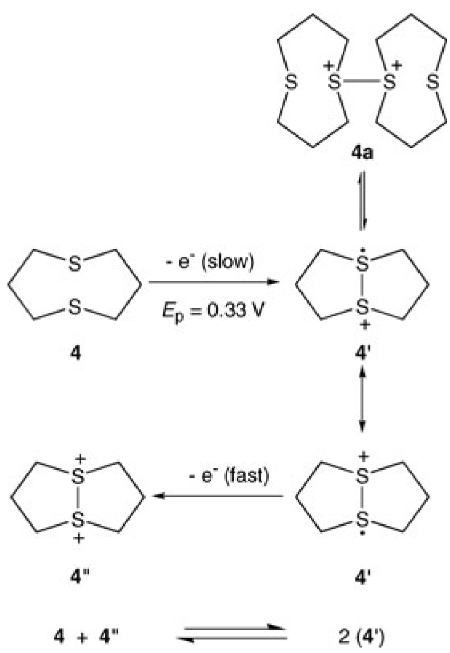


SCHEME 1

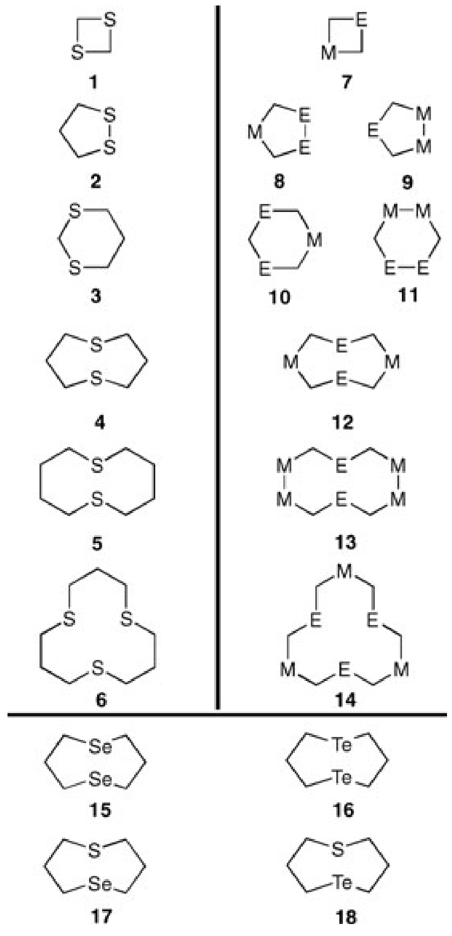


FIGURE 1 New mixed Group 14/16 and mixed S/Se and S/Te heterocycles **7–14** (M = R_2Si or R_2Sn; E = S, Se, Te) and **17, 18**, respectively; known S/Se/Te heterocycles **1–6** and **15, 16**.

Thus, it is known that radical cation **4′** and dication **4″**, formed on sequential one-electron oxidation, are stabilized (e.g. lowered electrochemical oxidation potential for **4**) by transannular bond formation and that dimerization of radical cation **4′** to **4a** is observed. Dichalcogen-containing mesocycles **4, 15**, and **16** show unusual redox chemistry [1,2], catalytic activity [3], and metal coordination abilities [4]. In the present work, we investigate the consequences of inserting one or more ring R_2Si or R_2Sn groups, separated from S/Se/Te by CH_2 groups (e.g. **7–14**, Fig. 1), because it is well known that silicon or tin positioned β to chalcogen atoms also facilitate one-electron ionization when the geometry is appropriate [5]. Compounds of type **7–14** (E = S, Se, or Te) are virtually unknown, despite novel properties that might be anticipated by analogy with those of well-studied systems **1–6**, **15**, and **16** [2].

Exocyclic β-silicon and β-tin groups, e.g. in 2-substituted derivatives of 1,3-dithiane [2f], 1,3-dithioles [6a], and oxiranes and thiiranes [6b], are known to significantly facilitate one-electron oxidation at the chalcogen atom(s) by the β-effect of these elements [5] when the angular relationship of the C—Si or C—Sn orbitals with adjacent chalcogen *p*-type lone-pair orbitals is optimum (eclipsed). The lowering of IE and facilitation of oxidation in **1–6** as well as in **15** and **16** has been evaluated using photoelectron spectroscopy (PES), cyclic voltammetry (CV), MO calculations, and/or more qualitatively by measuring the IE-proportional λ_{max} of their tetracyanoethylene charge-transfer (TCNE-CT) complexes [1a,1f,6]. It has also been reported that β-Si—Si σ-bonds stabilize benzyl [7] and cyclopropyl [8] cations of general structure Si—Si—C^+. This β-effect is ascribed to Si—Si σ-bond hyperconjugation, dramatically illustrated by the lack of such stabilization when the β-Si—Si σ-bond is orthogonal to the leaving group [7a].

We summarize here the syntheses [9b] of previously unknown heterocycles **7–14**, possessing endocyclic or exocyclic C—Si, C—Sn, and Si—Si orbitals (Si—Si orbitals are *exocyclic* when M = $(Me_3Si)_2Si$, e.g. in **7, 10**, and **12**) oriented at various angles to the chalcogen *p*-orbitals, and report on the ease of their one- and two-electron oxidation. We have prepared more than 40 new 4- to 12-membered ring heterocycles including mixed S—Si, S—Sn, Se—Si, Se—Sn, and Te—Si systems. In many cases the solid-state conformations of these new compounds have been determined by X-ray crystallography [9b]. In those new heterocycles containing one or more Si—Si bonds we have examined the stabilization of sulfur and selenium radical cations Si—Si—C—$E^{+\bullet}$ (E = S, Se) by a σ-(Si—Si) bond. These conformationally constrained compounds were investigated by PES because preliminary theoretical calculations indicated that interaction of a sulfide or selenide *p*-orbital with a Si—Si σ-orbital should be geometry dependent [9a].

Radical cations and dications of **12** were generated in solution using stoichiometric $NOPF_6$. In some cases the dications of **12** can be characterized by NMR spectroscopy and undergo novel rearrangements on treatment with nucleophiles. In view of these interesting findings, we reexamined the formation of dications from **15** and **16** and prepared for the first time mesocycles **17** and **18** having two different chalcogen atoms, to examine dications from these systems.

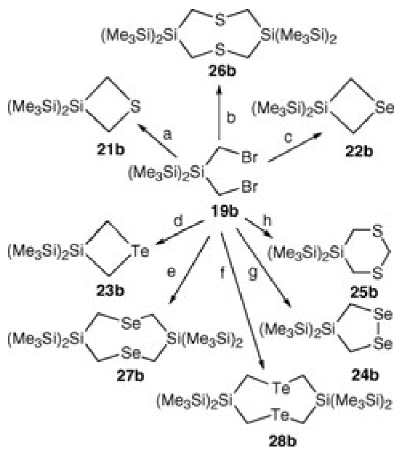
RESULTS AND DISCUSSION

Synthetic Studies

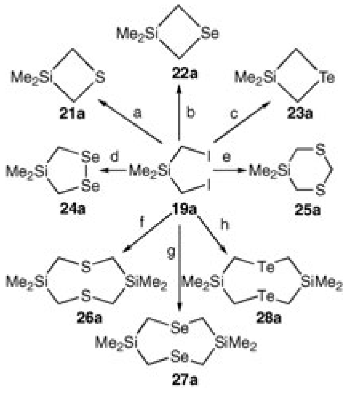
Bis(halomethyl) compounds **19a** ($Me_2Si(CH_2I)_2$; $Me_2Si(CH_2Cl)_2$ and NaI), **19b** ($(Me_3Si)_2Si(CH_2Br)_2$; $(Me_3Si)_2SiCl_2$ and $LiCH_2Br$), **19c** ($Me_2Sn(CH_2I)_2$; Me_2SnCl_2 and ICH_2ZnI), **19d** (t-$BuMeSi(CH_2Br)_2$; t-$BuMeSiCl_2$ and $LiCH_2Br$), and **20** ($BrCH_2SiMe_2SiMe_2CH_2Br$; $ClSiMe_2SiMe_2Cl$ and $LiCH_2Br$) could easily be converted to the four-, five-, six-, eight-, nine-, and ten-membered rings shown in Schemes 2–6, many of which were characterized by X-ray crystallography and PES. The *gem*-dialkyl (Thorpe–Ingold) effect [10] as well as the enhanced S_N2 reactivity of α-halosilanes and α-halostannanes [11] presumably facilitates ring closure in these compounds.

Structural Studies

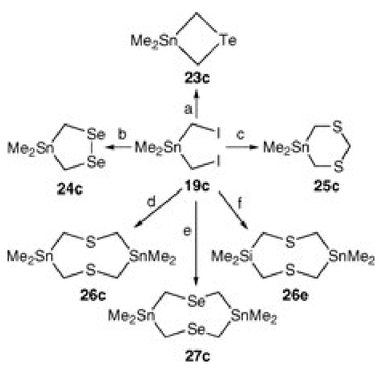
Structural features of the new heterocycles are discussed with reference to a model system R—S—CH_2—$SiMe_2$–$SiMe_2R'$, where the dihedral angle about the RS—CSi bond is θ and the dihedral angle about the SC—SiSi bond is ϕ. In the solid state, the four-membered ring in 3,3-bis(trimethylsilyl)-1,3-thiasiletane (**21b**; Scheme 3) is planar, as determined by X-ray crystallography. Computations show that in the gas phase the four-membered ring is close to planar in its lowest energy conformation with $\theta = 11^\circ$ and $\phi = 100^\circ, 126^\circ$. The amount of destabilization caused by the presence of the Si—Si bond can be judged by comparing the lowest vertical ionization (HOMO) energies for thietane (8.55 [12a,b], 8.65 [12c] eV), 3,3-dimethyl-1,3-thiasiletane (**21a**; Scheme 2) (8.49 eV [13]) and **21b** (7.98 eV). There is only a modest destabilization of



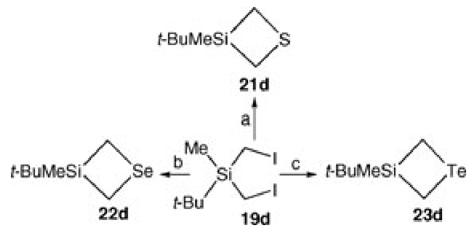
SCHEME 3 Conditions: (a) Li_2S, THF (43%); (b) $(Me_3Si)_2Si(CH_2SAc)_2$, KOH, EtOH (22%); (c) Li_2Se (57%); (d) Na_2Te, EtOH (66%); (e) **24b**, $NaBH_4$, EtOH, THF (76%); (f) $(Me_3Si)_2Si(CH_2TeCN)_2$, $NaBH_4$, EtOH, DMSO (21%) (g) Na_2Se_2, EtOH, 0°C (55%); (h) CS_2, $NaBH_4$, THF (57%).



SCHEME 2 Conditions: (a) KHS, EtOH (55%); (b) Li_2Se (60%); (c) Na_2Te, EtOH; (d) Na_2Se_2, EtOH, 0°C (71%); (e) CS_2, $NaBH_4$, THF (47%); (f) $Me_2Si(CH_2SAc)_2$, KOH, EtOH (34%); (g) **24a**, $NaBH_4$, EtOH, THF (73%); (h) $Me_2Si(CH_2TeCN)_2$, $NaBH_4$, EtOH, DMSO (23%).



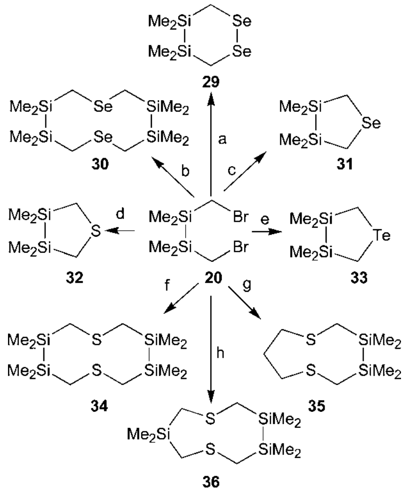
SCHEME 4 Conditions: (a) Na_2Te, EtOH; (b) Na_2Se_2, EtOH, 0°C (89%); (c) KSAc, THF then CH_2I_2, KOH (24%); (d) $Me_2Sn(CH_2SAc)_2$, KOH (42%); (e) **24c**, $NaBH_4$, EtOH, THF (58%); (f) $Me_2Si(CH_2SAc)_2$, KOH, EtOH (34%).



SCHEME 5 Conditions: (a) Li_2S, THF (31%); (b) Li_2Se (47%); (c) Na_2Te, EtOH (68%).

the HOMO (0.06 eV) upon introducing a 3-Me_2Si moiety (i.e. **21a**), but there is substantial destabilization (0.57 eV) on introducing a 3-$(Me_3Si)_2Si$ moiety (i.e. **21b**) into a thietane ring. The vertical ionization energy of 3,3-bis(trimethylsilyl)-1,3-selenasiletane (**22b**; Scheme 3), as expected, is even lower (7.89 eV) than that of **21a**.

Compound **34** (Scheme 6), 3,3,4,4,8,8,9,9-octamethyl-1,6-dithia-3,4,8,9-tetrasilecane, adopts a c,c,c (chair–chair–chair) conformation in the solid state, as shown by X-ray crystallography. Calculations indicate that this conformation is also the most stable in the gas phase. For this conformation, $\theta = 159.6^\circ$, 156.1° and $\phi = 82.1^\circ$, 78.8°. Orbital interactions for **34** with θ about 180° and ϕ about 90° should be comparable to those for **21b**. However, because there are two interacting chalcogen atoms in this system, there is an additional factor important in its analysis. That is, there will be symmetric and antisymmetric orbitals combining both sulfur 3*p* lone pair orbitals. In mesocyclic dithioethers [14], the antisymmetric lone pair combination is the HOMO and the symmetric combination HOMO-1. Comparison of the sulfur lone pair ionization energies for **34** (7.62 and 8.00 eV) with those of 1,6-dithiecane **5** (8.38 and 8.53 eV [12,14]) reveals substantial destabilization in **34** relative to **5**. The destabilization of the ionization from HOMO-1 of **34** relative to **5** (0.53 eV) is comparable to the destabilization of the ionization from the HOMO of **21b** relative to that of thietane (0.57 eV). The IPs of HOMO and HOMO-1 of **30** (Scheme 6), 3,3,4,4,8,8,9,9-octamethyl-1,6-diselena-3,4,8,9-tetrasilecane, as expected, are even lower (7.45 and 7.80 eV) than that of **34**.



SCHEME 6 Conditions: (a) Na_2Se_2, EtOH (40%); (b) **29**, $NaBH_4$, EtOH/THF (41%); (c) Li_2Se (33%); (d) $Na_2S \cdot 9H_2O$ (68%); (e) Na_2Te (74%); (f) $(SiMe_2CH_2SAc)_2$, KOH, EtOH (30%); (g) KSAc, THF then $Br(CH_2)_3Br$, KOH, EtOH, rt; (h) KSAc, THF then **19a**.

While the crystal structure of 3,3,4,4-tetramethyl-1,3,4-thiadisilolane (**32**, Scheme 6) could not be determined, the lowest energy structure found computationally is an envelope conformation where the sulfur atom is out of the plane of the C—Si—Si—C atoms, e.g., there is a C—S—C flap. In this most stable conformation, the C—S—C—Si (θ) and S—C—Si—S (ϕ) dihedral angles are 50° and 30°, respectively, which indicates that the C—Si σ-orbital, the Si—Si σ-orbital, and the sulfur lone pair can interact. The PES shows ionizations of lowest energy at 7.87 and 8.87 eV, which are assigned to the sulfur 3*p* lone pair and Si—Si σ-bond ionizations, respectively. The HOMO for **32** is 0.57 eV lower than that for thiolane (8.64 eV) [12c].

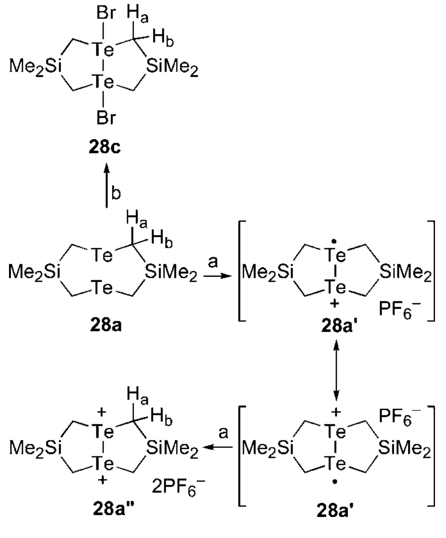
Calculations on 3,3,7,7-tetrakis(trimethylsilyl)-1,5-dithia-3,7-disilocane (**26b**; Scheme 3) show that the twist–twist conformer with a C_2 axis through the ring Si atoms is the most favorable in the gas phase, although a second conformer, which is found in the solid state by X-ray crystallography [9b], is only 0.4 kcal/mol higher in energy. The calculated dihedral angles for the twist–twist and second conformer are approximately $\theta = 119^\circ$, $\phi = 163^\circ$ and 74°, and $\theta = 51^\circ$ and 62°, $\phi = 177^\circ$ and 57°, respectively. The HOMO ionization energy for **26a** is 0.39 eV lower than that for **26b**, which lacks the Si—Si orbitals but is calculated to have a similar ring geometry as **26a** [9a]. In addition, the HOMO ionization for **26a** is 0.70 eV lower than that for 1,5-dithiocane (**4**) [12b,14a]. This is the largest destabilization observed in this study. The ionization energy for 5,5-bis(trimethylsilyl)-1,3,5-dithiasilinane (**25b**) is also substantially (0.64–0.75 eV) lower than that of 1,3-dithiane (**3**), e.g., 7.80 vs 8.55 and 8.44 eV [1f].

The PES that we have measured show that there is a general destabilization of the chalcogen-based ionizations of these mesocyclic molecules, and that the amount of destabilization observed, which can be as large as 0.70–0.75 eV, is dependent upon the geometry of the mesocycles. The experimental results demonstrate the presence of Si—Si σ-orbital destabilization of the sulfur 3*p* lone pair orbital, and also that the amount of this destabilization is geometry dependent. Theoretical calculations using the above described model system R—S—CH_2–$SiMe_2$–$SiMe_2R'$, predict the same ionization energy trends observed experimentally for the geometrically constrained mesocycles **2a, 5–8a**, and **11a** having either exocyclic (**2a, 8a, 11a**) or endocyclic (**5–7a**) Si–Si bonds. Furthermore, these molecular orbital calculations provide insight into the complex geometry-dependent σ- and *p*-orbital interactions that are responsible for the experimentally observed ionization energies. The detailed theoretical studies presented on model compounds and the conformationally constrained compounds provide an understanding of the specific basis for destabilization, which involves mixing not only of Si—Si but other σ-orbitals as well, as determined by energy, overlap, and symmetry.

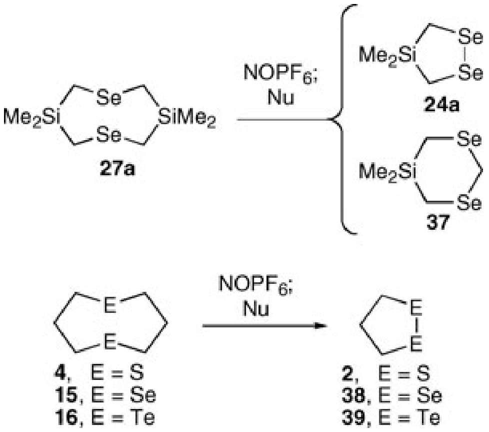
SEQUENTIAL ONE-ELECTRON OXIDATION OF **26a, 27a**, *AND* **28a** *GIVING RADICAL CATIONS AND DICATIONS*

Treatment of 3,3,7,7-tetramethyl-1,5-ditellura-3,7-disilocane (**28a**; Scheme 3) with two equivalents of one-electron oxidant $NOPF_6$ gives the corresponding dication **28a″** (Scheme 7) as indicated by the ^{1}H, ^{13}C, and ^{125}Te NMR spectra. When one equivalent of $NOPF_6$ is added, the mixture turns red, presumably due to formation of a radical cation. After two equivalents of $NOPF_6$ is added, the solution becomes colorless, due to formation of dication **28a″**. Comparison of the NMR data for **28a** (^{1}H:δ 1.67 (s, 8H, CH_2), 0.18 (s, 12H, Me); ^{13}C: δ 0.4 (CH_3), −17.0 (CH_2); ^{125}Te: δ 75.2) and **28a″** (^{1}H: 2.73 (d, $J = 12.8$, 4H), 2.49 (d, $J = 12.8$, 4H), 0.30 (s, 6H), 0.26 (s, 6H); ^{13}C: 15.2 [TeC], 2.19 [CH_3]; ^{125}Te: 1068) shows a notable deshielding at tellurium (δ 75.2 vs 1068 ppm) as well as at all protons and carbon atoms. Both the methyl groups on silicon and the methylene protons in **28a″** are nonequivalent. These NMR results are in good agreement with ^{1}H, ^{13}C, and ^{125}Te NMR data on dication **16″** from 1,5-ditellurocane **16** [2e]. Efforts to characterize the intermediate radical cation **28a′** by ESR under various conditions were unsuccessful. Treatment of **28a** with one equivalent of bromine gives a *cis*-bicyclic dibromide **28c**, whose NMR spectra (^{1}H NMR: δ 2.76 (d, $J = 13.2$ Hz, 4H), 2.62 (d, $J = 13.2$ Hz, 4H), 0.31 (s, 6H), 0.30 (s, 6H); ^{13}C: δ 17.2, [TeC]; ^{13}C: δ 17.2, [TeC] 3.3 [CH_3], 2.7 [CH_3]; ^{125}Te: δ 867) are similar to those of **28a″**. *cis*-Stereochemistry follows from the nonequivalence of both the silicon methyl groups and the ring methylene protons.

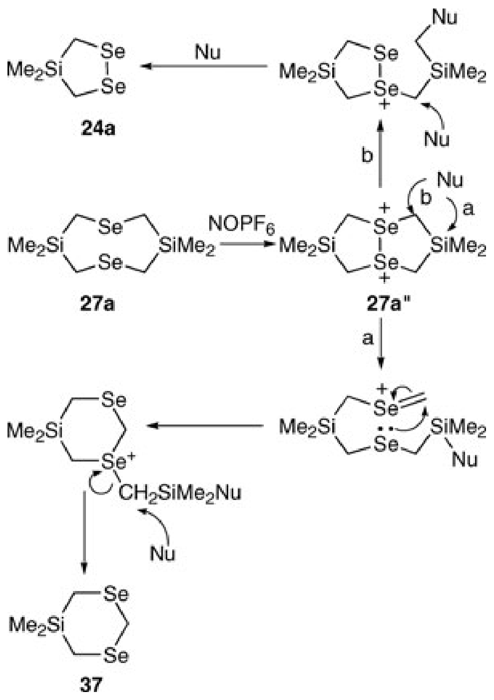
When the orange-red reaction product from addition of one equivalent of $NOPF_6$ to selenium compound **27a** is quenched with ethanethiol, a 1:3:55 mixture of five- and six-membered rings **24a** and **37** and starting material **27a**, respectively, is formed, together with Et_2S_2 (Scheme 8). When the light-yellow product from addition of two equivalents of $NOPF_6$ to selenium compound **27a** is similarly quenched, a 1:5.5 mixture of five- and six-membered rings **24a** and **37** is formed, together with Et_2S_2. In the latter case, starting material is not recovered. Similar results (e.g., 1:8.6 **24a:37**) are obtained with methanol as the quenching agent, and upon quenching the products from addition of one and two equivalents of $NOPF_6$ to mesocycles **4, 15, 16, 26a**, and



SCHEME 7 Conditions: (a) $NOPF_6$, CD_3CN-CD_2Cl_2, −78°C to 25°C; (b) Br_2.



SCHEME 8



SCHEME 9

28a with thiols or alcohols (e.g., from quenching with thiol the yellow-orange products from addition of one equivalent $NOPF_6$ to **4, 15**, and **16**, disulfide was formed along with 2.4:1 **4:2** from **4**, 6.8:1 **15:38** from **15**, and **39** from **16**).

We suggest (Scheme 9, path a) that nucleophilic attack by oxygen or sulfur at the silicon atom in the bicyclic dication results in C—Si bond cleavage and ring fragmentation, giving a selenium-stabilized carbocation, which recyclizes to a six-membered ring, followed by nucleophilic cleavage of the carbon–selenium bond.

Alternatively, nucleophilic attack at carbon (twice) would result in carbon–selenium bond cleavage (path b) giving five-membered ring heterocycle **24a**.

CONCLUSION

We have found that a variety of mixed Group 14/16 heterocycles **7–14** (Fig. 1) with 4- to 12-membered rings can be readily prepared from bis(halomethyl)silanes and bis(halomethyl)stannanes or compounds prepared therefrom. The majority of the compounds represent previously unknown ring systems, including rare examples of four-membered rings containing a single tin or tellurium atom. Solid-state conformations for many of these new ring systems have been established by X-ray crystallography. 1,5-Dichalcogena-3,7-disilocanes, on treatment with $NOPF_6$ give dications characterized by low-temperature NMR methods. On treatment with nucleophiles, these dications rearrange giving mixtures of five-membered ring 1,2-dichalcogenolanes and six-membered ring 1,3,5-dichalcogenasilinanes. Heterocycles with eight-membered rings containing two different chalcogen atoms, e.g. S/Se or S/Te, have been prepared for the first time. Given the ease of one-electron oxidation for many of these heterocycles, based on reactivity toward $NOPF_6$, it can be anticipated that they should be of interest as ligands and catalysts. Additional aspects of the chemistry of these novel heterocycles, including detailed study of their electrochemistry, will be presented elsewhere.

REFERENCES

[1] (a) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryan, M. D.; Musker, W. K. J Am Chem Soc 1979, 101, 1040–1042; (b) Musker, W. K. Acct Chem Res 1980, 13, 200–206; (c) Brown, T. G.; Hirschon, A. S.; Musker, W. K. J Phys Chem 1981, 85, 3767–3771; (d) Fujihara, H.; Furukawa, N. J Mol Struct (Theochem) 1989, 186, 261–272; (e) Fujihara, H.; Ninoi, T.; Akaishi, R.; Erata, T.; Furukawa, N. Tetrahedron Lett 1991, 32, 4537–4540; (f) Glass, R. S.; Radspinner, A. M.; Singh, W. P. J Am Chem Soc 1992, 114, 4921–4923; (g) Fujihara, H.; Furukawa, N. Phosphorus, Sulfur Silicon Rel Elements 1992, 67, 131–134; (h) Fujihara, H.; Takaguchi, Y.; Ninoi, T.; Erata, T.; Furukawa, N. J Chem Soc Perkin Trans 1 1992, 2583–2584; (i) Nakayama, N.; Takahashi, O.; Kikuchi, O.; Furukawa, N. Heteroatom Chem 2000, 11, 31–41; (j) Nenajdenko, V. G.; Shevchenko, N. E.; Balenkova, E. S.; Alabugin, I. V. Chem Rev 2003, 103, 229–282; (k) Detty, M. R.; Logan, M. E. Adv Phys Org Chem 2004, 39, 79–145; (l) Clennan, E. L.; Hightower, S. E.; Greer, A. J Am Chem Soc 2005, 127, 11819–11826.

[2] Comprehensive Heterocyclic Chemistry, 2nd ed.; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. (Eds.); Pergamon Press: Oxford, 1996.

[3] (a) Kataoka, T.; Iwama, T.; Tsujiyama, S.; Iwamura, T.; Watanabe S. Tetrahedron 1998, 54, 11813–11824; (b) Takaguchi, Y.; Hosokawa, A.; Yamada, S.; Motoyoshiya, J.; Aoyama, H. J Chem Soc Perkin Trans 1 1998, 3147–3149.

[4] (a) Stein, C. A.; Taube, H. J Am Chem Soc 1978, 100, 1635–1637; (b) Blake, A. J.; Schröder, M. Adv Inorg Chem 1990, 35, 1–80; (c) Cooper, S. R. In Crown Compounds: Toward Future Applications; Cooper, S. R. (Ed.); VCH: New York, 1992; pp 285–302; (d) Musker, W. K. Coord Chem Rev 1992, 117, 133–157; (e) Adams, R. D.; McBride, K. T.; Rogers, R. D. Organometallics 1997, 16, 3895–3901; (f) Davies, M. K.; Durrant, M. C.; Levason, W.; Reid, G.; Richards, R. L. J Chem Soc Dalton Trans 1999, 1077–1083; (g) Hill, N. J.; Levason, W.; Patel, R.; Reid, G.; Webster, M. Dalton Trans 2004, 980–981.

[5] (a) Lambert, J. B.; Wang, G.; Teramura, D. H. J Org Chem 1988, 53, 5422–5428; (b) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. Acct Chem Res 1999, 32, 183–190; (c) Jouikov, V.; Fattahova, D. Electrochim Acta 1998, 43, 1811–1819; (d) Jouikov, V.; Fattahova, D. J. Organomet Chem 2000, 613, 220–230; (e) Fu, Y.; Liu, L.; Guo, Q.-X. THEOCHEM 2005, 725, 1–4; (f) Müller, T.; Juhasz, M.; Reed, C. A. Angew Chem, Int Ed 2004, 43, 1654–1546; (g) Müller, T.; Margraf, D.; Syha, Y. J Am Chem Soc 2005, 127, 10852–10860.

[6] (a) Li, H.; Nishiwaki, K.; Itami, K.; Yoshida, J. Bull Chem Soc Jpn 2001, 74, 1717–1725; (b) Block, E.; Yencha, A. J.; Aslam, M.; Eswarakrishnan, V.; Luo, J.; Sano, A. J Am Chem Soc 1988, 110, 4748–4753.

[7] (a) Shimizu, N.; Kinoshita, C.; Osajima, E.; Hayakawa, F.; Tsuno, Y. Bull Chem Soc Jpn 1991, 64, 3280–3288; (b) Shimizu, N.; Watanabe, S.; Hayakawa, F.; Yasuhara, S.; Tsuno, Y.; Inazu, T. Bull Chem Soc Jpn 1994, 67, 500–504.

[8] Shimizu, N.; Hayakawa, F.; Tsuno, Y. Bull Chem Soc Jpn 1992, 65, 959–964.

[9] (a) Glass, R. S.; Block, E.; Lorance, E.; Zakai, U. I.; Gruhn, N. E.; Jin, J.; Zhang, S.-Z. J Am Chem Soc 2006, 128, 12685–12692; (b) Block, E.; Dikarev, E. V.; Glass, R. S.; Jin, J.; Li, B.; Li, X; Zhang, S.-Z. J Am Chem Soc 2006, 128, 14949–14961.

[10] (a) Jung, M. E.; Gervay, J. J Am Chem Soc 1991, 113, 224–232; (b) Jung, M. E.; Piizzi, G. Chem Rev 2005, 105, 1735–1766.

[11] (a) Fleming, I. In Comprehensive Organic Chemistry; Barton, D. H. R.; Ollis, W. D. (Eds.); Pergamon Press: Oxford, 1979; Vol. 3, pp. 541–686; (b) Bassindale, A. R.; Taylor, P. G. In The Chemistry of Organic Silicon Compounds; Patai, S.; Rappoport, Z. (Eds.); John Wiley & Sons: New York, 1989; Vol. 2, pp. 893–963. (c) Shimizu, M.; Hata, T.; Hiyama, T. Tetrahedron Lett 1997, 38, 4591–4594.

[12] (a) Mollere, P. D.; Houk, K. N. J Am Chem Soc 1977, 99, 3226–3233; (b) Glass, R. S.; Wilson, G. S.; Coleman, B. R.; Setzer, W. N.; Prabhu, U. D. G. Adv Chem Ser 1982, 201, 417–441; (c) Trofimov, B. A.; Mel'dev, U. Kh.; Pikver, R. I.; Vyalykh, E. P. Theor Exp Chem (Engl.) 1975, 11, 129–135.

[13] Traven, V. F.; Rokitskaya, V. T.; Rodin, O. G.; Shvets, V. F.; Redchenko, V. V.; Voronkov, M. G.; Kirpichenko, S. V.; Suslova, E. N. Dokl Akad Nauk 1986, 288, 1160–1163.

[14] (a) Setzer, W. N.; Coleman, B. R.; Wilson, G. S.; Glass, R. S. Tetrahedron 1981, 37, 2743–2747; (b) Setzer, W. N.; Glass, R. S. In Conformational Analysis of Medium-Sized Sulfur-containing Heterocycles; Glass, R. S. (Ed.); VCH: Weinheim, 1988; pp. 151–179.