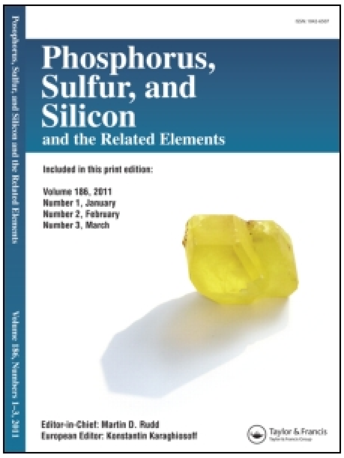

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Novel Germaheterocycles Using Low-Coordinated Germanium Species

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To cite this Article Matsumoto, Tsuyoshi , Kishikawa, Kuniyuki , Tokitoh, Norihiro and Okazaki, Renji(1994) 'Synthesis of Novel Germaheterocycles Using Low-Coordinated Germanium Species', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 177 — 180

To link to this Article: DOI: 10.1080/10426509408021810

URL: http://dx.doi.org/10.1080/10426509408021810

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 177-180
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SYNTHESIS OF NOVEL GERMAHETEROCYCLES USING LOW-COORDINATED GERMANIUM SPECIES

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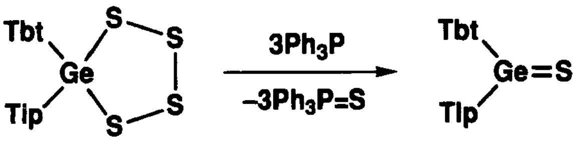
Abstract Some novel four-, five-, and six-membered germaheterocycles are synthesized using low-coordinated germanium species such as Tbt(Tip)Ge, Tbt(Tip)Ge=X(X=O, S, Se, Te)(Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip=2,4,6-triisopropylphenyl).

INTRODUCTION

Low-coordinated compounds of carbon, such as carbenes and ketones (and its congeners $R^1R^2C=X$, X=S, Se, Te) are useful building blocks of carbocyclic compounds. Heavy congeners of these species, i.e., R^1R^2M: and $R^1R^2M=X$ are also considered to be good building blocks for the synthesis of inorganic rings containing Si, Ge, Sn and Pb. We present here utility of germylene R^1R^2Ge: and germaketone congeners $R^1R^2Ge=X$(X=O, S, Se, Te) in the synthesis of germanium containing heterocycles.

SYNTHESIS OF GERMAHETEROCYCLES USING GERMANETHIONE 1

We recently reported the synthesis of the first stable germanethione **1**[1] by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt), developed in our group. Although **1** is thermally quite stable, it reacts readily with 2,3-dimethyl-1,3-butadiene, mesitonitrile oxide, phenyl isothiocyanate, carbon disulfide to give germaheterocycles **2-5**, respectively.



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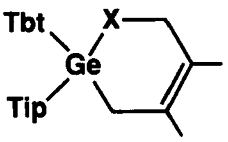
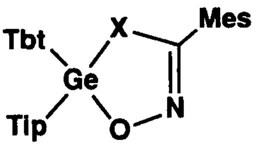
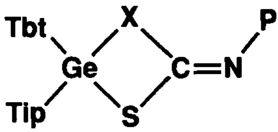
Germanethione **1** was also synthesized by sulfurization of germylene Tbt(Tip)Ge: with styrene episulfide and converted to **2**-**4** by cycloaddition reactions similar to the above.



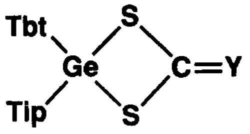
2: X=S
8: X=Se



3: X=S
9: X=Se
15: X=Te
20: X=O



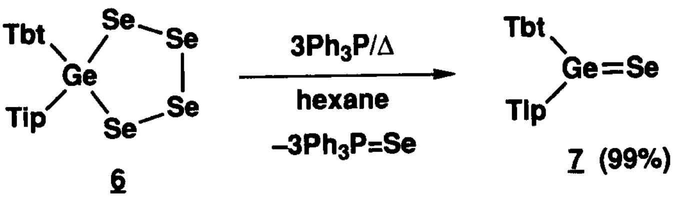
4: X=S
10: X=Se



5: Y=S
17: Y=O

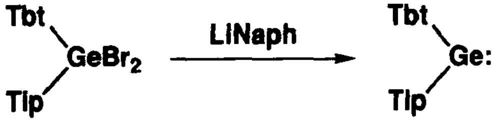
SYNTHESIS OF GERMAHETEROCYCLES USING GERMANESELONE 7

Germaneselone **7** was similarly synthesized by deselenation of tetraselenagermolane **6** as stable red crystals [λ_{max}(hexane) 530 nm (ε 40); δ_{Se} 940.6].[2] The structure of 7 was determined by X-ray crystallographic analysis to be of trigonal planar geometry with Ge=Se bond being 2.180 Å(Figure 1). Germaneselone 7 underwent [4+2], [3+2], and [2+2] cycloadditions with dimethylbutadiene, mesitonitrile oxide, and phenyl isothiocyanate to give **8** (84 %), **9** (100 %) and **10** (61 %), respectively.

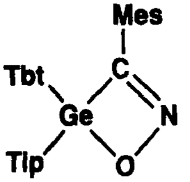


SYNTHESIS OF GERMAHETEROCYCLES USING GERMYLENE 12

Reductive debromination of dibromogermane **11** with lithium naphthalenide gave a deep blue solution of germylene **12**, which was allowed to react with mesitonitrile oxide and phenyl isothiocyanate to afford four memberd rings **13** and **5**, respectively. The formation of **5** is explained in terms of the initial formation of germanethione **1** followed by its cycloaddtion with another molecule of PhNCS. The structure of **13** was established by X-ray crystallography.



11 12



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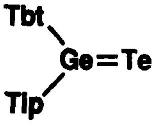
SYNTHESIS OF GERMAHETEROCYCLES USING GERMANETELLONE 14

Germylene **12** prepared in situ from **11** reacted with one equivalent of tellurium to give germanetellone **14**, the formation of which was evidenced by trapping with mesitonitrile oxide giving a [3+2] adduct **15** (37 %). We have found that germylene **12** generated from **11** reacts with diphenylacetylene to give germirene **16**, which acts as an excellent precursor of germylene **12**. For example, reaction **16** with an excess of phenyl isothiocyanate and carbon disulfide afforded four-membered ring compounds **4** and **17** respectively. The formation of **17** is most likely explained by the initial formation of three-membered **18** followed by oxidation during work up.

Reaction of **16** with 1 equiv of tellurium proceeded very cleanly to give germanetellone **14** quantitatively as judged by ^{1}H and ^{125}Te NMR spectroscopy.



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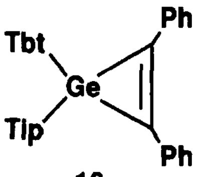

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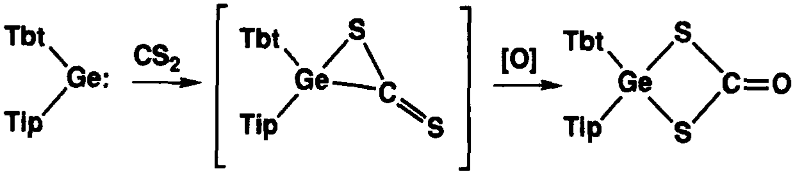
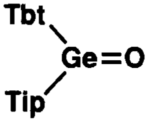


12 18 17

The ^{125}Te chemical shift of **14** was considerably low, i.e. 1143 ppm, characteristic of low-coordinated tellurium compounds, and λ_{max} was 623 nm.

SYNTHESIS OF A GERMAHETEROCYCLE USING GERMANONE

Germylene **12** generated from dibromogermane **11** was allowed to react with tribenzylamine *N*-oxide to produce germanone **19**, the formation of which was evidenced by trapping with mesitonitrile oxide giving [3+2] cycloadduct **20** (76 %).



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