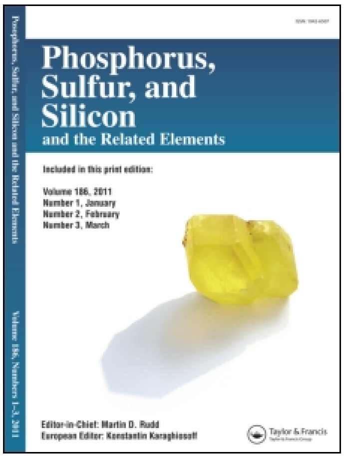

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Chemistry of Higher Group 14 Homologues of Thioketones $R^1R^2M=S$ (M=Si, Ge, Sn, Pb)

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CHEMISTRY OF HIGHER GROUP 14 HOMOLOGUES OF THIOKETONES $R^1R^2M=S$ (M=Si, Ge, Sn, Pb)

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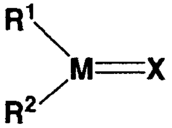
The title compounds are synthesized by desulfurization of tetrathiametallolanes. Among these silanethione and germanethione have been analysed by X-ray crystallography to have a trigonal planar geometry as that of the ketone.

Key words thioketone homologues, group 14 metals, low-coordinated compounds

INTRODUCTION

Although ketones (and aldehydes) have been extensively studied and play a central role in organic chemistry, very little is known for their corresponding higher homologues $R^1R^2M=X$ (**1**), because of their extremely high reactivity and unavailability of appropriate synthetic methodology. We describe in this paper the synthesis of the first examples of heavier group 14 homologues of ketones, $R^1R^2M=X$, for which we coin "heavy ketones", with emphasis on their thiohomologues $R^1R^2M=S$ (M=Si, Ge, Sn, Pb).

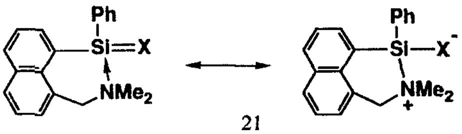


M: Si, Ge, Sn, Pb
X: O, S, Se, Te

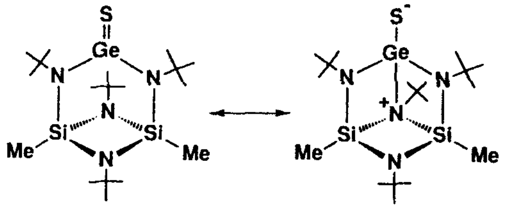
1

Heavy Ketone

There have been some scattered examples of transient heavy ketones in the literature,[1] but only the following three compounds **2-4** have been so far isolated as stable species.[2,3]



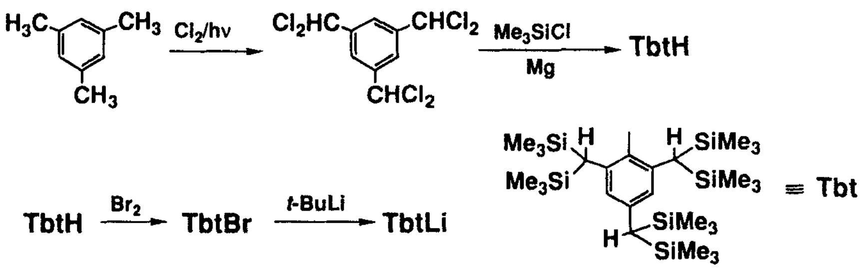
2: X = S
3: X = Se



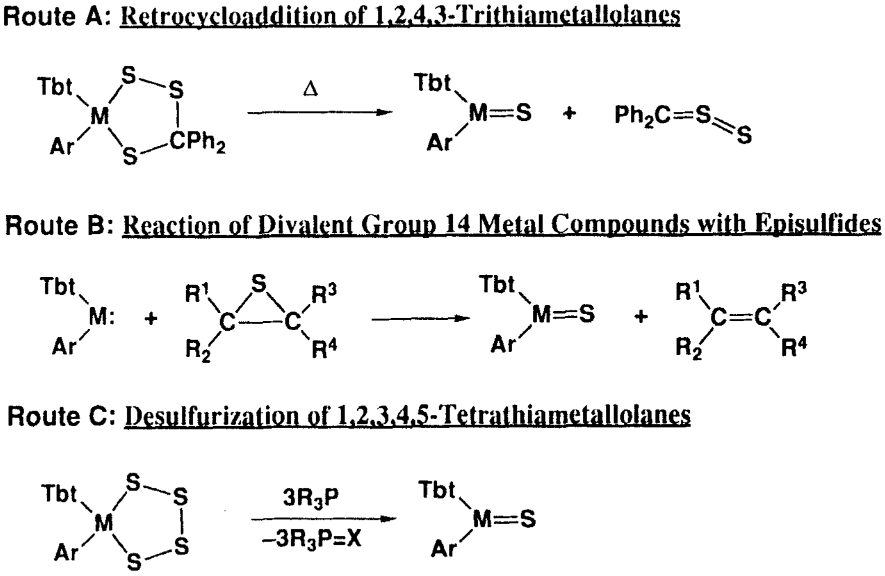
4

However, the X-ray structural analyses of these compounds clearly indicate that they are tetracoordinate species involving intramolecular coordination by a nitrogen lone pair and cannot be regarded as heavy ketones (*vide infra*).

We undertook our investigation on heavy ketones by taking advantage of kinetic stabilization by an extremely bulky and efficient steric protection group



Scheme 1



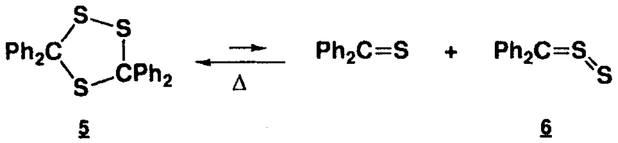
Scheme 2

developed by us,[4] i. e., 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (designated as Tbt), because "heavy ketones" are considered to be highly reactive, especially toward oligomerization. This protection group can be easily prepared in a large scale starting from mesitylene, and a variety of functionalization is possible by using TbtLi obtained from TbtBr (Scheme 1).

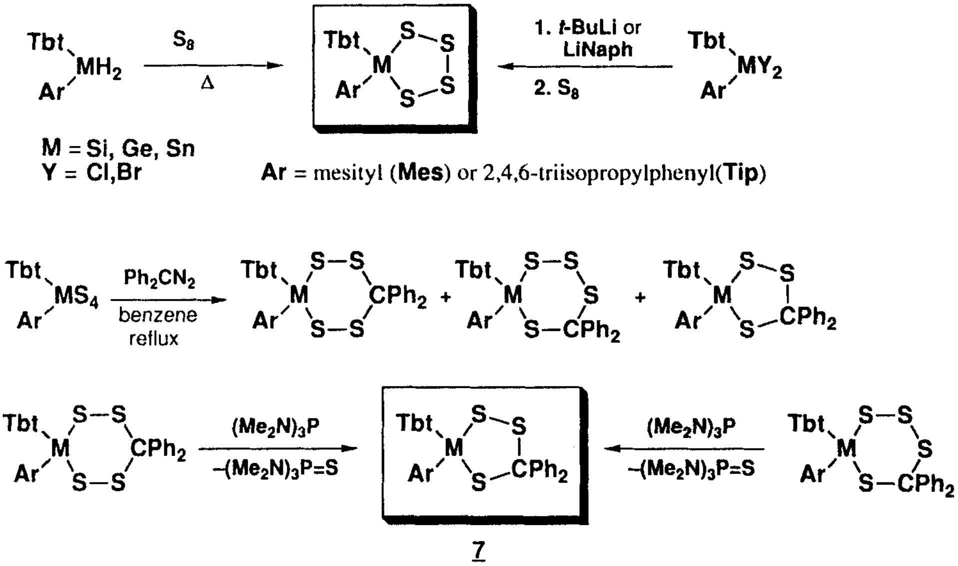
In the present study we used three synthetic approaches to heavy ketones as shown in Scheme 2.

RETROCYCLOADDITION OF 1,2,3,4-TRITHIAMETALLOLANES

Huisgen and Raap reported that thermal cycloreversion of 1,2,4-trithiolane **5** led to the formation of thiobenzophenone and transient thioxothioketone **6**.[5]

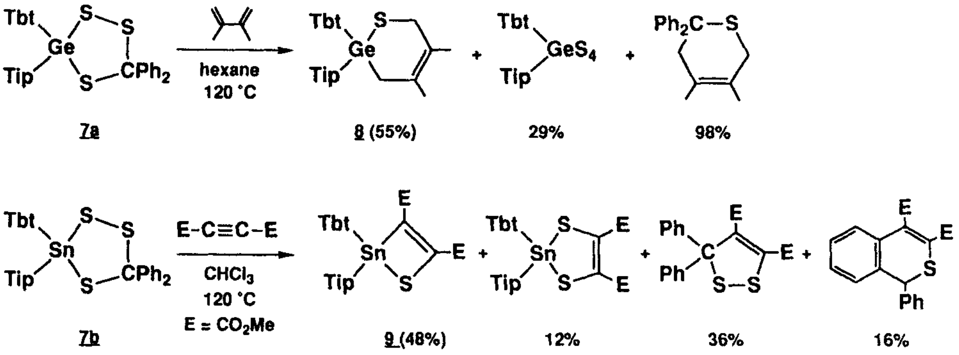


We anticipated that a similar reaction of trithiametallolanes would lead to the formation of heavy ketones (Scheme 2, Route A). The starting metallolanes 7 were prepared as shown in Scheme 3.[6]

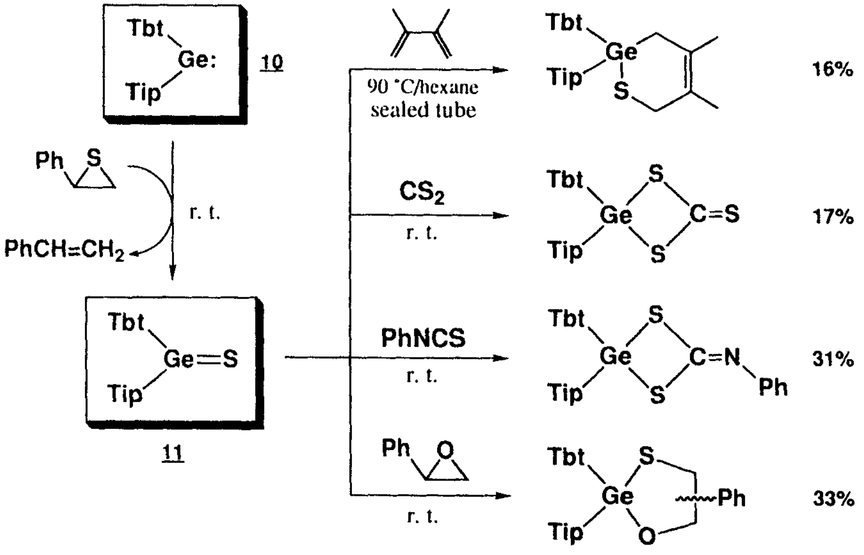


Scheme 3

Thermolysis of trithiagermolane **7a** (M=Ge, Ar=Tip) and trithiastannolane **7b** (M=Sn, Ar=Tip) in the presence of 2,3-dimethyl-1,3-butadiene and dimethyl acetylenedicarboxylate gave [4+2] adduct **8** of germanethione Tbt(Tip)Ge=S and [2+2] adduct **9** of stannanethione Tbt(Tip)Sn=S, respectively, suggesting these metallolanes can be precursors of heavy ketones (Scheme 4).[7] These reactions, however, were found not to be a good approach to heavy ketones because of the complexity of the reaction products as shown in Scheme 4.



Scheme 4



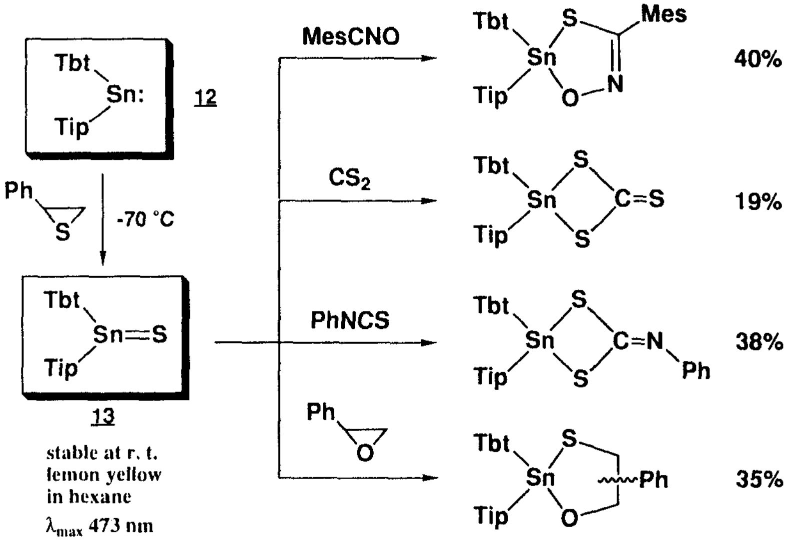
Scheme 5

REACTION OF DIVALENT GROUP 14 METAL COMPOUNDS WITH EPISULFIDES

In the second approach divalent species such as germylene, stannylene, and silylene were used as starting compounds.

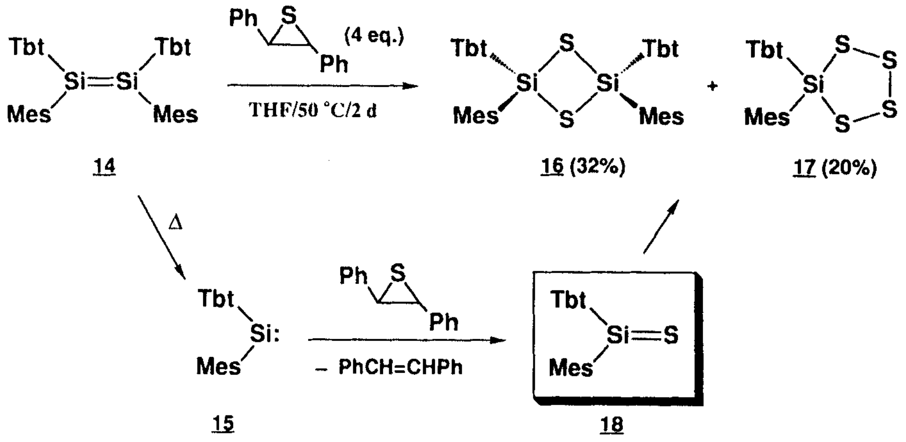
Diarylgermylene **10** can be prepared by the reaction of diiodogermylene with TbtLi and TipLi[8] and is the first diarylgermylene stable in solution. Reaction of **10** with styrene episulfide afforded germanethione **11**, the formation of which was substantiated by some trapping reactions as shown in Scheme 5.

Diarylstannylene **12** stable in solution is prepared in a similar way and converted to stannanethione **13** which is stable in solution at room temperature and shows it absorption maximum at 493 nm. The formation of stannylene **13** was again substantiated by some trapping reactions as shown in Scheme 6.[9]



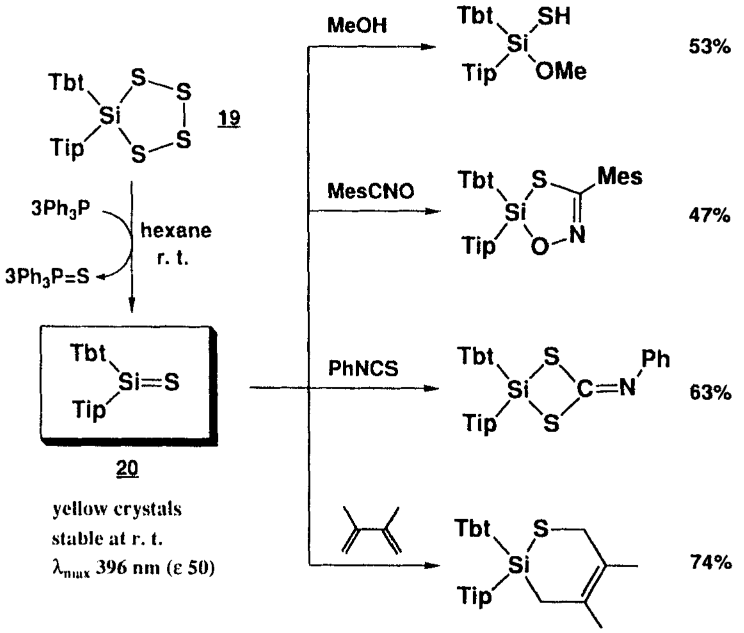
Scheme 6

Since dihalosilylenes are not available, an approach to a diarylsilylene by a route used for diarylgermylene **10** and diarylstannylene **12** is impossible. However, we recently succeeded in the synthesis of highly crowded disilene **14** and found that it underwent a facile thermal dissociation to silylene **15**.[10] When **14** was heated in the presence of *trans*-stilbene episulfide, dithiadisiletane **16** and tetrathiasilolane **17** were formed. This suggests that silanethione **18** was formed by the reaction of **15** with the episulfide but it underwent facile dimerization to give **16** or further sulfurization by the episulfide to afford **17** (Scheme 7).



Scheme 7

It is clear from these facts that divalent group 14 metals can produce heavy ketones by the reaction with episulfides. However, it has turned out that this approach is a multi-step reaction and not suitable for the synthesis of pure heavy ketones which have extremely high reactivity.



Scheme 8

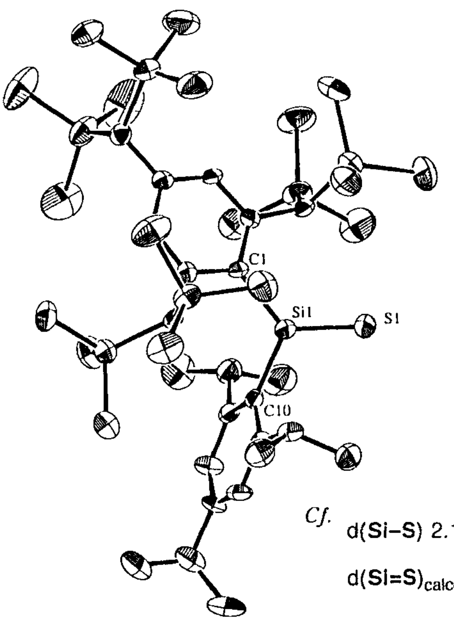
DESULFURIZATION OF 1,2,3,4,5-TETRATHIAMETALLOLANES

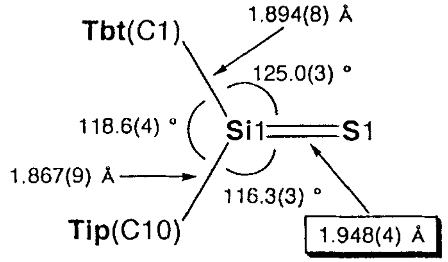
The third approach, i.e., desulfurization of 1,2,3,4,5-tetrathiametallolanes, was found to be the best method for the synthesis of heavy ketones.

Treatment of tetrathiosilolane **19** with three equivalents of triphenylphosphine in hexane at room temperature resulted in the formation of silanethione **20** (Scheme 8). It is yellow crystals having its λ_{max} of 396 nm (ε 50) and quite stable in the absence of water and oxygen. It readily undergoes reactions with methanol, mesitonitrile oxide or phenyl isothiocyanate to give the corresponding adducts, indicating a high reactivity of the silathiocarbonyl unit.

The structure of **20** was established by X-ray crystallographic analysis (Figure 1). The bond distance of Si=S is 1.948 Å, which is about 9 % shorter than typical Si-S single bond lengths, indicating a double bond nature of the Si-S bond. Another important structural feature is its trigonal planar geometry with the sum of the bond angles around Si being 359.9°.

When a similar desulfurization was carried out for mesityl substituted tetrasulfide **17**, there was obtained a yellow solution of silanethione **18**, the formation of which was evidenced by quenching with methanol, mesitonitrile oxide, phenyl isothiocyanate, and 2,3-dimethyl-1,3-butadiene as in the case of Tip-substituted silanethione **20**. However, the isolation of **18** was impossible because of ready





Sum of the bond angles
around Si1 = 359.9 °

Cf. d(Si–S) 2.13–2.15 Å

d(Si=S)$_{calcd}$ 1.936 Å

crystal data

Formula	$C_{42}H_{84}Si_7S$
Crystal Size (mm)	0.4x0.5x0.7
Crystal System	monoclinic
Lattice Parameters	
a/Å	21.33(1)
b/Å	13.82(1)
c/Å	36.13(2)
b/deg	92.50(5)
V/Å^3	10639(12)
Space Group	$P2_1/n$
Z	8
R	0.061
R_w	0.051

FIGURE 1 ORTEP drawing of Tbt(Tip)Si=S (**20**).

dimerization giving dithiadisiletane **16** at room temperature, indicating the importance of steric protection in the isolation of a monomeric silanethione.

With kinetically stabilized, genuine silanethione **20** in hand, it is interesting to compare the properties of **20** with those of the Corriu's silanethione **2**. The ^{29}Si chemical shift of **20** is 166.56 ppm characteristic of sp^2 Si, while that of **2** is 22.3 ppm, indicating a higher sp^3 nature of the central silicon in **2**. The bond length of Si=S in **2** is also suggestive of its tetracoordinated structure due to the intramolecular nitrogen coordination; the Si-S bond length of **2** is about 0.07 Å longer than that of **20**.

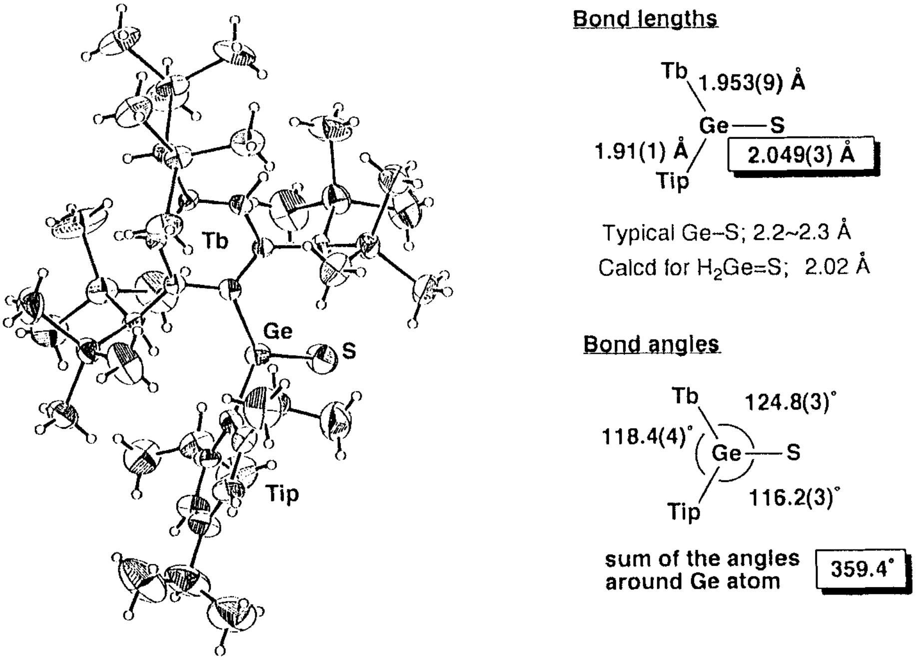
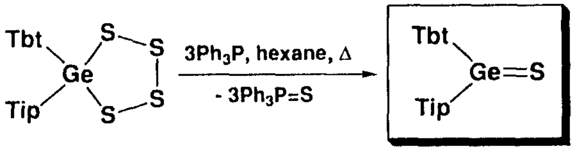


FIGURE 2 ORTEP drawing of Tbt(Tip)Ge=S (**11**).

The present desulfurization methodology was also successful in the synthesis of a stable germanethione. Desulfurization of **21** with triphenylphosphin gave a quantitative yield of germanethione **11**, which was orange yellow crystals with λ_{max} of 450 nm (ε 100).[11] The structure of **11** was determined by X-ray structure analysis (Figure 2). As in the case of silanethione **20**, **11** has a complete trigonal planar structure and the Ge=S bond is about 9 % shorter than typical single bonds of Ge-S. The X-ray crystallographic analysis of silanethione **20** and germanethione **11** is the first experimental demonstration that the heavy ketone has a trigonal planar geometry similar to that of the ketone.

Here again, the bulkiness of substituents on the central metal was found to be a key factor to decide the stability of heavy ketones. Desulfurization of mesityl- **22** and 2,6-diethylphenyl-substituted tetrasulfides **23** resulted in the formation of the dimers of intermediary germanethiones Tbt(Ar)Ge=S [Ar=Mes, Dep(2,6-diethylphenyl)], although, in the case of Tbt(Dep)Ge=S, yellow color (λ_{max} = 450 nm) due to the germathiocarbonyl group was observed in the reaction solution at the initial stage of the reaction.

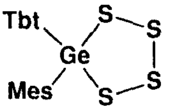
Germanethione **11** is thermally quite stable. Heating of its hexane solution in a sealed tube at 160 °C for 3 days resulted in a complete recovery of **11**. This is in sharp contrast to the instability of dimethyl germanethione Me_2Ge=S which is reportedly stable only below 40 K.[12]



21

11 (quant.)

orange yellow crystals
mp 163–165 °C
UV(hexane): λ_{max} 450 nm (ε 100)
Raman: 521 cm^{-1} ($\nu_{Ge=S}$)



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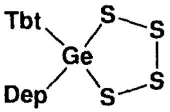
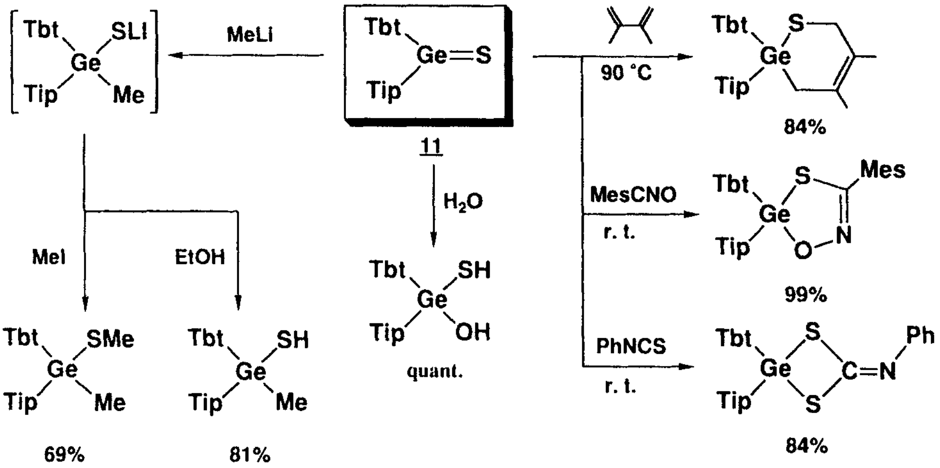


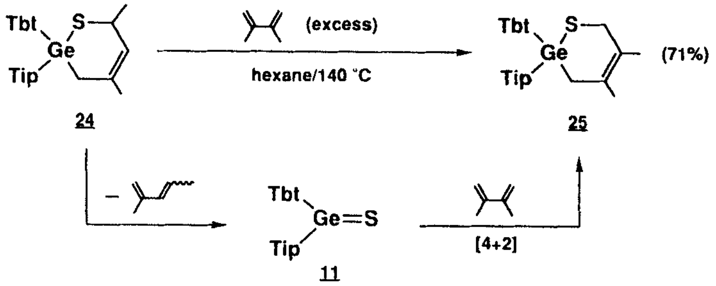
23

In spite of its high thermal stability, **11** is very reactive. It reacts with water instantaneously to give a hydrated product Tbt(Tip)Ge(OH)SH. Some other reactions are shown in Scheme 9. Of particular note are reactions with 1,3-dienes leading to Diels-Alder adducts, which are indicative of a high dienophilic nature of **11** in spite of severe steric congestion around the Ge=S bond. When an adduct **24** with 4-methyl-2,4-pentadiene was heated in the presence of an excess of 2,3-dimethyl-1,3-butadiene at 140 °C, an adduct **25** with the latter diene was formed, suggesting that **24** underwent a retro Diels-Alder reaction giving germanethione **11**, which then reacted with dimethylbutadiene to afford **25** (Scheme 10). This shows that Diels-Alder adducts such as **24** and **25** can be good, stable precursors of germanethiones.

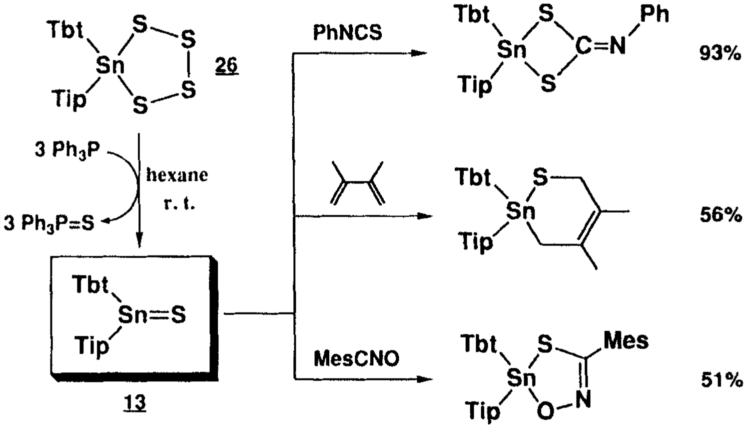
Treatment of tetrathiastannolane **26** with triphenylphosphine proceeded smoothly at room temperature to give stannanethione **13**, the formation of which was evidenced by trapping reactions as shown in Scheme 11. Crystalline **13** suitable for X-ray structure analysis has not been obtained so far. As was observed in the cases of silanethione and germanethione, the use of a mesityl group, a smaller substituent,



Scheme 9



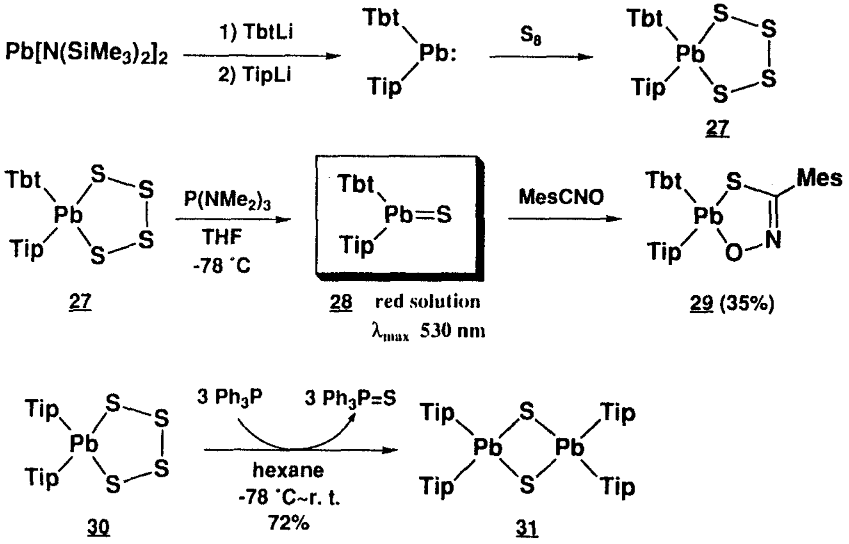
Scheme 10



Scheme 11

on the tin atom resulted in the formation of dithiadistannetane, the dimer of intermediary stannanethione Tbt(Mes)Sn=S.

The desulfurization methodology was also applicable to the heaviest congener, plumbanethione. Tetrathiaplumbolane **27**, prepared by the reaction of the cooresponding plumbylene Tbt(Tip)Pb with sulfur, was subjected to desulfurization with $P(NMe_2)_3$ at -78 °C to result in the formation of a red solution of plumbanethione **28** (λ_{max} = 530 nm) (Scheme 12). Since addition of mesitonitrile oxide to the solution thus formed gave [2+3] cycloadduct **29**, plumbanethione **28** was found to be stable at least in solution. Here again, the use of tetrathiaplumbolane **30** having smaller substituents than **27** gave a dimer **31** most likely via intremediary plumbanethione $(Tip)_2Pb{=}S$.



Scheme 12

ELECTRONIC SPECTRA OF HEAVY KETONES

The synthesis of silanethione **20**, germanethione **11**, and stannanethione **13** has enabled us to compare the electronic spectra (n→π*) of a series of $R^1R^2M{=}S$ (M=C, Si, Ge, Sn) compounds. In Table 1 are listed observed spectra of these compounds along with calculated spectra of $H_2M{=}S$(M=C, Si, Ge, Sn) at the CIS[13]/DZ+d level[14] using the Gaussian 92/DFT program. One can see a very interesting change in the observed λ_{max} depending on the difference in group 14 elements; λ_{max} is much blue-shifted on going from thione **32** to silanethione **20**, whereas λ_{max}'s for **20**, germanethione **11**, and stannanethione **13** are red-shifted with increasing the atomic number of the group 14 elements. This trend is also found in calculated values for $H_2M=S$(M=C, Si, Ge, Sn). Since calculated $\Delta\varepsilon_{n\pi^*}$ values increase continuously from $H_2Sn=S$ to $H_2C=S$, a long wavelength absorption for $H_2C=S$ (and hence for **32**) obviously results from a large repulsion integral ($J_{n\pi^*}$) for the carbon-sulfur double bond.

TABLE I Electronic Spectra (n→π*) of Double-bond Compounds between Group 14 Elements and Sulfur

Observed[a]		Calculated[c]		
	λ_{max}/nm		λ_{max}/nm	$\Delta\varepsilon_{\pi^*}$/eV[d]
Tbt(H)C=S(**32**)	587[b]	$H_2C=S$	458	10.81
Tbt(Tip)Si=S(**20**)	396	$H_2Si=S$	345	10.39
Tbt(Tip)Ge=S(**11**)	450	$H_2Ge=S$	363	9.97
Tbt(Tip)Sn=S(**13**)	473	$H_2Sn=S$	380	9.30

[a]In hexane. [b]Ref 15. [c]CIS/DZ+d. [d]$\varepsilon_{LUMO(\pi^*)}-\varepsilon_{HOMO(n)}$.

CONCLUSION

Three synthetic methods have been developed for heavy ketones Tbt(Ar)M=S (M=Si, Ge, Sn Pb). Among these is best the desulfurization of the corresponding tetrathiametallolanes Tbt(Ar)MS_4 with trivalent phosphorus compounds, resulting in the first isolation of stable silanethione **20** and germanethione **11**. Both metallanethiones have been revealed by X-ray crystallography to have a trigonal planar geometry around the central metal and a double bond nature for the M=S bonds.

In spite of the presence of two highly crowded substituents on the group 14 metals, these heavy ketones show extremely high reactivities toward water and an alcohol. They also undergo [2+2], [2+3], and [2+4] cycloadditions with phenyl isothiocyanate, mesitonitrile oxide, and 1,3-dienes, respectively, affording a variety of novel types of heterocycles. Thus, these heavy ketones are interesting not only from theoretical and structural viewpoints but also from a synthetic viewpoint.

The successful synthesis of these heavy ketones suggests that many other congeners $R^1R^2M{=}X$ (M=Si, Ge, Sn, Pb; X=O, S, Se, Te) will be also capable of existence as stable species. A further study on the synthesis of these unknown heavy ketones is currently in progress in our laboratory.

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