

Preliminary Communication

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Alkynethiol Derivatives of Group IVB Elements

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Summary

Lithium alkynethiolates,  $RC\equiv CSLi$ , react rapidly with trialkylmetal (IVB) halides,  $R'_3MX$ , to give the novel metal-substituted alkynethiols,  $RC\equiv CSMR'_3$ .

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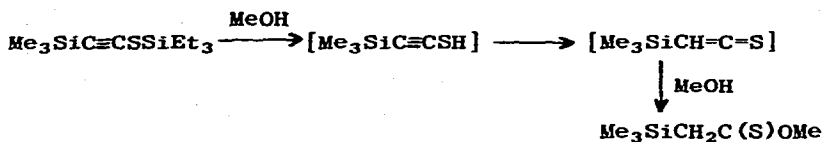
During the course of a research programme aimed at developing the chemistry of the hitherto unknown group IVB metal substituted thioketens [1], reagents of synthetic potential [2], we find that lithium alkynethiolates,  $RC\equiv CSLi$ , react readily with trialkylmetal halides,  $R'_3MX$ , at low temperatures to give a new class of group IVB metal alkynethiol derivatives,  $RC\equiv CSMR'_3$ . Examples of these compounds are given in the Table.

The products, obtained as distillable liquids, may convert slowly upon storage into either the corresponding thioketens,  $R(R'_3M)C=C=S$  (from 1 - 4), or crystalline 1,3-dithioles (from 5, 8 - 10). Bulky  $R'$  groups retard the conversion rates in all cases. Compound 6 tends to polymerise upon distillation and/or storage whereas the *t*-butyl compound, 7, remains unchanged when heated for long periods. In the light of previously recorded examples [3,4], thioketens, although not isolated, may be intermediates in the formation of dithioles.

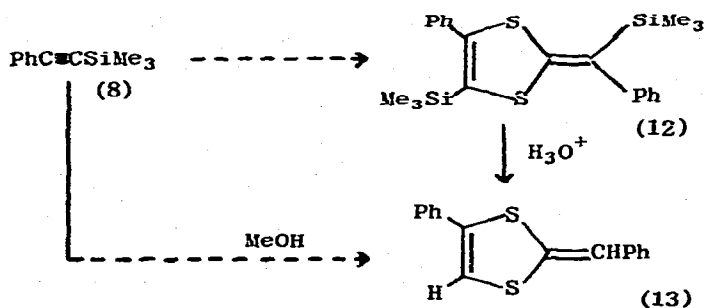
The S-Metal bonds in compounds 1 - 11 are particularly

C2

sensitive to protic reagents, for example treatment of 2 with methanol yields  $\text{Me}_3\text{SiCH}_2\text{C(S)OMe}$ ; presumably, initially formed  $\text{Me}_3\text{SiC}\equiv\text{CSH}$  tautomerises rapidly to  $\text{Me}_3\text{SiCH}=\text{C}=\text{S}$  which adds a further mole of methanol to give the thioester, viz.:



Treatment of 8 on the other hand with methanol yields a crystalline product, 13[4], identical with that obtained from the appropriate dithiole, 12[5], and acid.



The S-Si bonds in compounds 1 - 9 react cleanly with acyl halides, (Lewis acid catalysis is unnecessary) to give the corresponding  $\text{RC}\equiv\text{CSCOR}$  derivatives, e.g.:



Transmetalations occur with germanium, tin and lead halides, these reactions being the method of choice for preparing alkynethiol derivatives of the heavier IVB elements; e.g.:

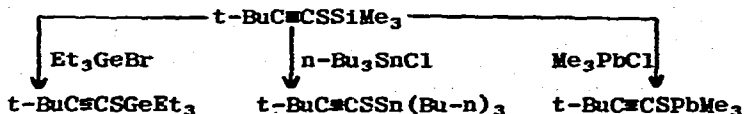


Table.  $RC\equiv CSMR_3$  Derivatives prepared from  $RC\equiv CSLi$  and  $R_3MX$  Compounds.

R	$R_3MX$		Products <sup>a</sup>
$Me_3Si$	$Me_3SiBr$	1	$Me_3SiC\equiv CSSiMe_3$ (ref. 2)
$Me_3Si$	$Et_3SiBr$	2	$Me_3SiC\equiv CSSiEt_3$
$Et_3Si$	$Et_3SiBr$	3	$Et_3SiC\equiv CSSiEt_3$
$Et_3Ge$	$Et_3SiBr$	4	$Et_3GeC\equiv CSSiEt_3$ <sup>b</sup>
Ph	$Et_3SiBr$	5	$PhC\equiv CSSiEt_3$
$n-C_6H_{11}$	$Me_3SiCl$	6	$n-C_6H_{11}C\equiv CSSiMe_3$
t-Bu	$Me_3SiCl$	7	$t-BuC\equiv CSSiMe_3$
Ph	$Me_3SiCl$	8	$PhC\equiv CSSiMe_3$
p-Tolyl	$Me_3SiCl$	9	$p-TolylC\equiv CSSiMe_3$
Ph	$Me_3SnCl$	10	$PhC\equiv CSSnMe_3$ <sup>c</sup>
$Me_3Si$	$Me_3SnCl$	11	$Me_3SiC\equiv CSSnMe_3$ <sup>d</sup>

<sup>a</sup> Reaction conditions:  $-40$  to  $-70^\circ$  in ether. Yield, ca. 80% except where noted otherwise. All products were characterized by elemental analyses and exhibited  $\nu(C\equiv C)$  at  $2081\text{ cm}^{-1}$  (compounds 1 - 4, 11) or  $2173\pm 18\text{ cm}^{-1}$  (compounds 5 - 10).

<sup>b</sup> Yield 60%;  $Et_3Ge(Et_3Si)C=C=S$  (20%) present in the distillate exhibited  $\nu(C=C=S)$  at  $1750\text{ cm}^{-1}$ .

<sup>c</sup> Dithiole formation lowers the yield (25%).

<sup>d</sup> Yield 40%;  $Me_3Sn(Me_3Si)C=C=S$  (40%), present in the distillate, exhibited  $\nu(C=C=S)$  at  $1764\text{ cm}^{-1}$ .

#### Acknowledgements

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#### References

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C4

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