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UNUSUAL RING CLEAVAGE REACTIONS OF 2-SUBSTITUTED 1,3-DITHIANES. ACCESS TO 2-ALKYLTHIOVINYLSILANES.

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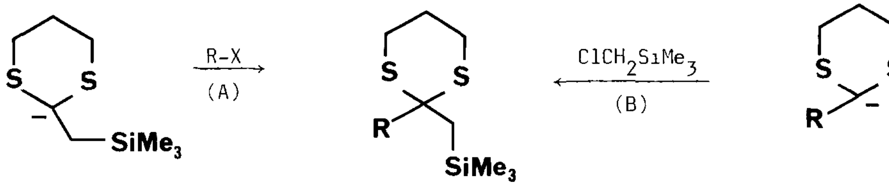
Two new cleavage reactions, under carbanion forming conditions, of the 1,3-dithiane ring system are reported.

In connection with another study, various 2-alkyl-2-trimethylsilylmethyl-1,3-dithianes 1 were required. Applying 2-lithio-1,3-dithiane chemistry, there are two possible routes (A and B) to these compounds:



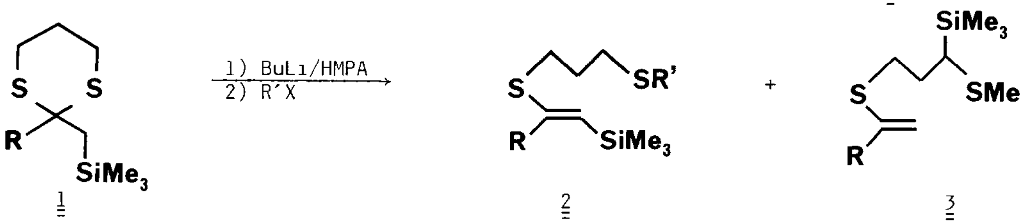
Indeed, route B was found to give ready access to 1, whereas the more general route A, using n-BuLi for lithiodithiane generation, gave but low yields of 1. Seeking to improve the latter the reaction was performed in the presence of 2 eq's of HMPA which is known to give "naked", i.e., more reactive carbanions. This however completely changed the outcome as the isolated product was shown to be 2 (R = H), obviously a result of carbanion formation α to silicon, followed by thiolate elimination and alkylation[1]. The alternative deprotonation at dithiane C-2 is apparently not favoured, possibly because of steric reasons or the destabilising effect of the Si atom towards β-carbanionic sites.

1 (R = H) $\xrightarrow[2)\ \mathrm{MeI}]{1)\ \mathrm{BuLi/HMPA}}$

2

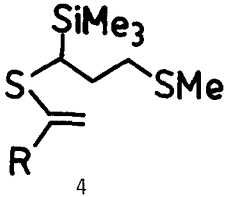
In view of the above result, we were interested in seeing whether analogous 2-alkyl derivatives (2, R = alkyl) would be available from 1 (R = alkyl). This indeed turned out to be the case (see Table) but now a competing ring cleavage reaction also operates, giving the Me$_3$Si-migrated products[2] 3 (R = alkyl; Table). In fact, the formation of 3 is the dominant reaction pathway, to the near or complete absence of vinylsilanes 2, when the R alkyl group is branched. Presumably, in the last-mentioned cases, a bulky 2-alkyl substituent will severely restrict the accessibility towards base of the α-CH$_2$ group. Instead, an unusual[3] proton abstraction from dithiane C-4 takes place. If the 2-silylmethyl side chain is axial in a twist or chair ring conformation[4], the C-4 carbanionic center will be sufficiently close to Si to allow C-4 to Si bond formation. Following Si-CH$_2$(α) bond cleavage, the C-2 to C(α) double bond is formed with suprafacial expulsion of S-3 as the thiolate anion (see 5, route a), as the substituents are then properly aligned at C-2 and C(α) for these to become sp^2 hybridised. Double bond formation via S-1 thiolate expulsion (5, route b) would require rotation about the C(α) - C-2 bond *after* (α)-anion formation, which explains why the isomeric 4 is not formed[5].

TABLE[7] Ring Cleavage Products from 2-Trimethylsilylmethyl-1,3-dithianes (1).

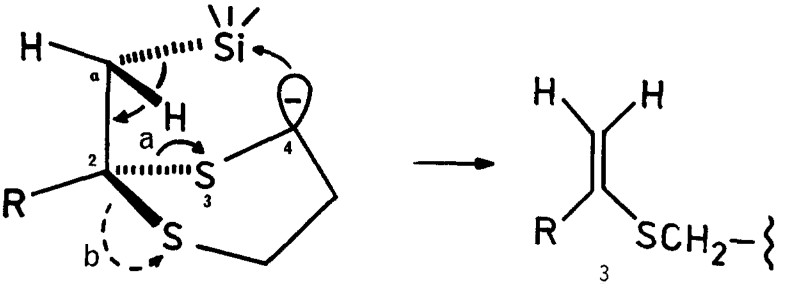


R	R′	yields		other products
		2	3	
H[8]	Me, n-Bu or MeOCH$_2$	(60 %)		6, 10 %
H	D	(36 %)		
Me	Me		17 % (12 %)	6 (53 %); 7, 9 %
Et	Me	27 %	44 % (35 %)	6, 10 % ; 7 (16 %)
n-Pr	Me	26 %	49 % (38 %)	6, 8 % ; 7, 10 %
n-Bu	Me	(30 %)	38 % (33 %)	6, 11 % ; 7, 9 %
i-Pr	Me	6 %	83 % (65 %)	
i-Bu	Me	10 %	66 % (45 %)	7, 7 %
sec-Bu	Me		(65 %)	
cyclohexyl	Me		91 % (73 %)	

The 2-alkylthiovinylsilanes 2 are an interesting class of functionalised silylalkenes[6], and obviously have potential for further chemical elaboration. Thus, for example, 2 (R = H) was Friedel-Crafts acylated to furnish 8 (46 %).



4



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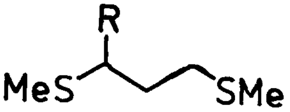
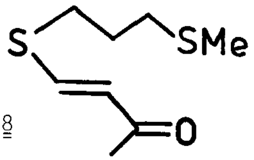
3



6 R = H

7 R = SiMe$_3$



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In view of the widespread use of 1,3-dithiane derivatives as acyl anion equivalents, we find it remarkable how readily this ring system may undergo (premature) cleavage, either via side chain or, more surprisingly, via ring C-4 deprotonation.

A representative experimental procedure follows: n-BuLi in hexane (2.1 M, 4 mmol) was added within 2 min at 0° to a solution of 2-isopropyl-2-trimethylsilylmethyl-1,3-dithiane (0.5 g, 2 mmol) and HMPA (0.7 ml, 4 mmol) in THF (6 ml) under Ar. After 1 min, methyl iodide (0.25 ml, 4 mmol) was added. After 1 h, water was added and the mixture extracted with ether, dried and 3-methyl-2-(3-methylthio-3-trimethylsilylpropylthio)-1-butene isolated by prep. TLC (silica gel, hexane-CH_2Cl_2 10:1) in 65 % yield (0.338 g); ^1H NMR δ (CCl_4) 4.97 and 4.62 (each 1 H, s), 3.0-2.7 (2 H, m), 2.7-1.6 (4 H, m), 2.10 (3 H, s), 1.12 (6 H, d, 7 Hz), 0.10 (9 H, s); ^{13}C NMR δ ($CDCl_3$) -2.1 ($SiMe_3$), 17.3 (SMe), 22.5 (Me_2), 29.4 and 29.6 (CH_2CH_2), 33.6 (CH-S), 35.9 (CH), 102.4 (=CH_2), 152.4 (S-C=); m/z 262 (18 %), 247 (3), 147 (19), 142 (44), 141 (16), 105 (16), 99 (52), 73 (100).

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Footnotes and references

1. Related ring cleavage reactions have been reported to occur with 2-(1,3-dithiane)acetic esters. See C.G. Kruse, A.C.V. Janse, V. Dert and A. van der Gen, J. Org. Chem. **44**, 2916 (1979).
2. These 2-alkylthio-1-alkenes must be isolated and purified under strictly non-acidic conditions. Traces of acid (as in bench $CHCl_3$, for example) suffice to cause isomerisation into the thermodynamically more stable 2-alkylthio-2-alkenes.

3. 2-Cyclohexylidene-1.3-dithiane has been deprotonated at C-4 (BuLi/THF, 0°, 24 h; LDA/HMPA deprotonates allylically): D. Seebach and M. Kolb, *Justus Liebigs Ann. Chem.*, 811 (1977).
4. Results of NMR studies to obtain evidence for this requirement will be reported shortly.
5. Structures **3** were assigned (and **4** excluded) by NMR and mass spectra. The latter characteristically show an intense peak at m/z 147 which is also shown by **7**, and corresponds to $^{+}CH_2CH(SMe)SiMe_3$. Peaks resulting from the attachment of Me_3Si to the alternative site (cf. **4**) were absent from the mass spectra.
6. Analogous 1,2-disubstituted ethenes (**2**, R = H, *E* + *Z* mixtures) have been made by homolytic addition of RSH to $HC{\equiv}CSiMe_3$. See M.G. Voronkov, V.I. Rakhlin, R.G. Mirskov, S.K. Khangazheev, O.G. Yarosh and E.O. Tsetlina, *Zh. Obshch. Khim.* **49**, 119 (1979).
7. GC yields; isolated yields (prep. TLC) in parentheses. New 2-alkyl-2-trimethylsilylmethy 1,3-dithianes, and isolated products, were fully characterised by the usual physical methods. The *E* geometry at the double bond is secure in **2** (R = H) only, as shown by a characteristic trans *J* value (18 Hz). Homologues (**2**, R = alkyl) were obtained in one, presumably *E* form only according to GC and NMR.
8. P.F. Jones, M.F. Lappert and A.C. Szary, *J. Chem. Soc. Perkin I*, 2272 (1973).

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