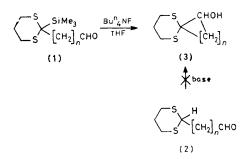
Carbocyclizations employing 2-Silyl-1,3-dithians

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Summary Dithianyl anions capable of carbocyclization via either direct or Michael addition to a carbonyl unit can be generated from 2-trimethylsilyl-1,3-dithians.

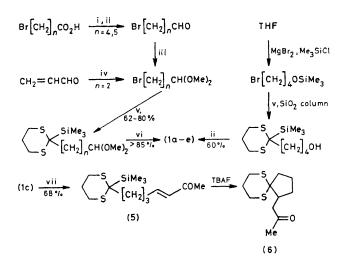
To date the carbonyl anion equivalence of the 1,3-dithian function¹ has not been realized in intramolecular additions to carbonyl compounds.[†] Any base strong enough to deprotonate a dithian, *e.g.* (2) (Scheme 1), can also react with the carbonyl group either as a base or as a nucleophile. The proposed intermediacy of carbanions in the fluoride ion-induced reactions of alkynyl-,³ oxiranyl-,⁴ and allyl-silanes⁵ supports the notion that a C-SiR₃ moiety is a protected carbanion, which may be unmasked under relatively mild conditions. We report the clean cyclizations of ω -(2-trimethylsilyl-1,3-dithian-2-yl)alkanals (1) (Scheme 1), and of the related enone (5) (Scheme 2), by tetrabutyl-ammonium fluoride (TBAF), as synthetically valuable additions to the aforementioned reactions.



SCHEME 1. THF = Tetrahydrofuran.

The syntheses of the aldehydes (1) are summarized in Scheme 2. Of the homologous series (1a-e), the aldehyde (1d) alone was prone to trimerization (trimer m.p. 65-70 °C). The others were stable oils or solids, *e.g.* (1a), m.p. *ca.* 15-20 °C.

[†] Cycloalkylations based on 1,3-dithian-2-yl anions generated directly or via the 2-stannyl derivatives are, however, known.²



SCHEME 2. Reagents: i, $1\cdot 1-1\cdot 5$ equiv. BH₃·THF, 2-4 h, 25 °C; ii, pyridinium chlorochromate, CH₂Cl₂, 2-3 h, 25 °C; iii, (MeO)₃CH, MeOH, Amberlyst-15, 3-12 h, 25 °C; iv, HBr, m, $(HeO)_3CH, MeOH, Amberlyst-10, 3-12 h, 25 C, b, HG, min, MeOH, CH_2Cl_2; v, 2-trimethylsilyl-1,3-dithian-2-yl-lithium in THF, -78 to 0 °C during 1 day; vi, 1·1 equiv. of SnCl_0 or TiCl_4, -78 °C, 1 h, then aqueous NH₄Cl; vii, <math>[(MeO)_2P(:O)CHCOMe]$ -Na in 1,2-dimethoxyethane, 0 °C.

To solutions of the aldehydes (1b-e) in THF were added 1·1-5 equiv. of TBAF in THF. After 10-30 min, aqueous work-up and column chromatography afforded the spiro-alcohols (3b-e) as shown. Presumably, the acidic methylene protons α to the carbonyl group were responsible for the competing protonation in the case of (1e).

TABLE. Isolated yields of spiro-alcohols (3)^a from trimethylsilylalkanals (1)^a.

	Yield of (3) ^b
a, n = 1	<5 %°
b , $n = 2$	56%
c , $n = 3$	60-76%
d, n = 4	57-61%
e , $n = 5$	1020 % ^a

^a The structures of all starting materials and products were supported by their ¹H n.m.r., i.r., and g.l.c.-mass spectral data. ^b The yields of individual reactions have not been optimized. ° The products of the reaction of (1a) were not identified, but the data are inconsistent with the presence of significant quantities of the spiro-alcohol (3a). ^d The spiro-alcohol (3e) is accompanied by ca. 10% of (2e) and uncharacterized material (oligomers?).

Exposure of (1d) and (1e) to the Lewis acids $SnCl_4$ and BF_3 ·Et₂O at -78 °C left these aldehydes unchanged; at higher temperatures, complex product mixtures which did not contain (3d or e) or their silvl ethers were obtained. Moreover, exposure of the precursor acetals (4c--e) to SnCl₄, TiCl₄, BBr₃, BF₃.Et₂O, or MgBr₂ under a wide variety of conditions failed to promote cyclization. ‡ Thus, the behaviour of the 2-trimethylsilyl-1,3-dithian system is quite unlike that of allylsilane systems, which react easily with Lewis acid-activated carbonyl compounds⁶ or, still better, activated acetals.7

Finally, TBAF treatment (1.5 equiv., 30 min, 25 °C) of the enone (5) afforded the intramolecular Michael adduct (6), a masked 1,4-dicarbonyl compound, in 64% yield.

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 $1 \text{ In fact, Lewis acid treatment followed by quenching with aqueous NH₄Cl proved to be the best means for acetal hydrolysis (>85%) without competing reaction at the silyldithian unit.$

¹ For earlier studies see N. H. Andersen, P. F. Duffy, A. D. Denniston, and D. B. Grotjahn, Tetrahedron Lett., 1978, 3415.

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