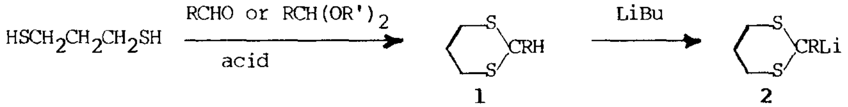
Tetrahedron Letters,Vol.27,No.52,pp 6305-6306,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A RAPID, EFFICIENT AND SELECTIVE CONVERSION OF ALDEHYDES AND ACETALS TO THEIR 1,3-DITHIANE DERIVATIVES WITH 2,2-DIMETHYL-2-SILA-1,3-DITHIANE[1]

John A. Soderquist* and Edgar I. Miranda[2]
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Abstract: Aldehydes and acetals are cleanly and rapidly converted to the corresponding dithianes with 2,2-dimethyl-2-sila-1,3-dithiane and stoichiometric amounts of boron trifluoride etherate even in the presence of ketones, which do not react competitively with the reagent.

The pioneering studies of Corey and Seebach[3] on the chemistry of 2-lithiated-1,3-dithianes as acyl anion equivalents rapidly established these compounds as important reagents for organic synthesis.[4] The prerequisite dithianes are prepared from the aldehydes and 1,3-propanedithiol employing an acid catalyst such as HCl, BF_3-OEt_2 or $ZnCl_2$. The lithiated derivatives are obtained from the corresponding dithiane by deprotonation with butyllithium.[5]



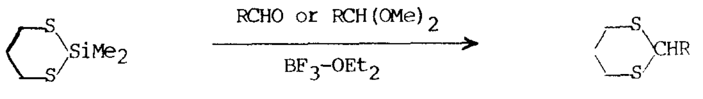
1 2

Our interest in the chemistry of **1** and **2** stems from their importance in the preparation of acylsilanes.[6] Invariably, as has been pointed out by Seebach and Corey,[5] the preparation of **1** results in the formation of a yellowish contaminant in minor amounts. It must be removed from **1** either by recrystallization or fractional distillation prior to carrying out the lithation. Moreover, the reaction times employed in preparation of **1** from aldehydes and propanedithiol are quite variable (1-15 h).

Often, silyl-modified reagents offer synthetic advantages to their protic counterparts and, thiosilane/zinc iodide systems are selective in the case of dithiane formation.[7] Seeking a silyl-modified reagent that could be obtained in high yield and chemical purity from commercial (97%) 1,3-propanedithiol, 2,2-dimethyl-2-sila-1,3-dithiane (**3**)[8] was particularly attractive in that we find that its isolation removes the yellow impurities to result in colorless dithianes.

In contrast to the Corey-Seebach acid-catalyzed procedure, the reaction of **3** proceeds to completion only with a stoichiometric amount of BF_3-OEt_2 (ie. **1**:BF_3 = 3:1 for RCHO and ca. 2:1 for $RCH(OMe)_2$). However, this is certainly not a drawback to the use of **1** because the reaction can be precisely controlled by the amount of BF_3 added and occurs instantaneously and essentially quantitatively by GC analysis (cf. Table 1).

As a representative procedure, the synthesis of **1f** was carried out as follows: To a stirred mixture of **3** (4.56g; 27.8 mmol) and pivaldehyde (2.35g; 27.3 mmol) in CH_2Cl_2 (12.5 mL) at 0°C was added BF_3-OEt_2 (1.2 mL; 9.6 mmol) dropwise. After the addition was completed, NaF solution (10mL, 1.00 M) was added, and, after separation with ether, the organic layer was dried (K_2CO_3), concentrated at reduced pressure, and the colorless residue was recrystallized from 90% aqueous MeOH to give 4.0g (82%) of chromatographically and spectroscopically pure **1f** (mp 33-34.5; [lit][5] 35.5-36).



3 **1**

TABLE 1. 1,3-DITHIANES FROM ALDEHYDES OR ACETALS AND 3/BF$_3$-ETHERATE.

RCHO or RCH(OMe)$_2$	Product Dithiane	% Yield [a]
MeCHO	**1a**	99
n-PrCHO	**1b**	98
n-BuCHO	**1c**	99
i-PrCHO	**1d**	98
PhCHO	**1e**	98
t-BuCHO	**1f**	99 (82)[b]
piperonal	**1g**	94[b]
EtCH(OMe)$_2$	**1h**	95
MeCH(OMe)CH$_2$CH(OMe)$_2$	**1i**	94

[a] Yields were determined by GC analysis of reaction mixtures containing an internal hydrocarbon standard. Complete spectroscopic data, consistent with the assigned structures, were obtained for all products. [b] Isolated yield.

The reaction is completely selective for aldehydes showing no tendency to react with ketones in competitive experiments. Thus, with pentanal vs 2-heptanone and one eq of **3**, only **1c** (98%) was formed. However, with pentanal vs benzaldehyde, **1c** (46%) and **1e** (47%) were formed in essentially equal amounts as was the case with pentanal vs 1,1-dimethoxypropane (**1c** (51%) and **1h** (41%)). The Corey-Seebach procedure exhibits a similar selectivity (ie. 64:24 for **1c** and **1e**; only **1c** (98%) for pentanal vs 2-heptanone).

With acetals, the principal by-products are Me$_2$SiF$_2$ and B(OMe)$_3$ as determined by NMR and GC/MS.[8] With aldehydes, the major by-product by NMR is consistent with the formulation, B(OSiMe$_2$F)$_3$. However, with an excess of BF$_3$, the methylsilane region, in both the ^{1}H and ^{13}C NMR of the reaction mixtures, becomes very complex, indicating that additional products are formed. Moreover, the direct distillation of reaction mixtures gives small amounts of cyclic siloxanes (ie. [Me$_2$SiO]$_n$ n = 5,6 and 7) by GC/MS[10] which might be expected to originate from the decomposition of a fluorosilylborate species. Thus, the formation of fluorosilane products explains the stoichiometric requirement for the BF$_3$ in these reactions.

REFERENCES

1. Dedicated to Professor George Zweifel on the occasion of his 60th birthday.
2. Research student supported by the UPR-FIPI program.
3. Corey, E. J.; Seebach, D. Angew. Chem. Inter. Ed. Engl. **1965**, 4, 1075, 1077.
4. a) Gröbel, B.-T.; Seebach, D. Syn. **1977**, 357. b) Lever Jr., W. O. Tetrahedron **1976**, 32, 1943. c) Hase, T. A.; Koskimies, J. K. Aldrichimica Acta **1982**, 15, 35.
5. Corey, E. J.; Seebach, D. J. Org. Chem. **1975**, 40, 231.
6. a. Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. J. Am. Chem. Soc. **1967**, 89, 431. b. Corey, E. J.; Seebach, D.; Freedman, R. J. Am. Chem. Soc. **1967**, 89, 434.
7. a) Evans, D. A.; Truesdale, L. K.; Grimm, K. G.; Nesbitt, S. L. J. Am. Chem. Soc. **1977**, 99, 5009. b) Sakarai, H. private communication.
8. Weibert, M.; Schmidt, M. J. Organomet. Chem. **1964**, 1, 336. See also: Yamazaki, N.; Nakahama, S.; Yamaguchi, K.; Yamaguchi, T. Chem. Lett. **1980**, 1355.
9. a. For acetals: B(OMe)$_3$ (^{11}B 18.9 ppm; ^{1}H 3.3 ppm; ^{13}C 50.6 ppm); SiMe$_2$F$_2$ (^{1}H 0.1(t) ppm, J = 6.2 Hz; ^{13}C -3.8(t) ppm, J = 17 Hz; MS m/z 96(16%); 81(100%). b. For aldehydes: B(OSiFMe$_2$)$_3$: (^{11}B 15-17(variable) ppm; ^{1}H -0.05(d) ppm, J = 6.4 Hz; ^{13}C -2.1(d) ppm, J = 18 Hz).
10. Vanden Heuvel, W. J. A.; Smith, J. L.; Firestone, R. A.; Beck, J. L. Anal. Letters **1972**, 5, 285.

(Received in USA 29 September 1986)