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REACTION OF α,α'- BIS(TRIMETHYLSILOXY)SULFIDES WITH LOW VALENT TITANIUM REAGENTS

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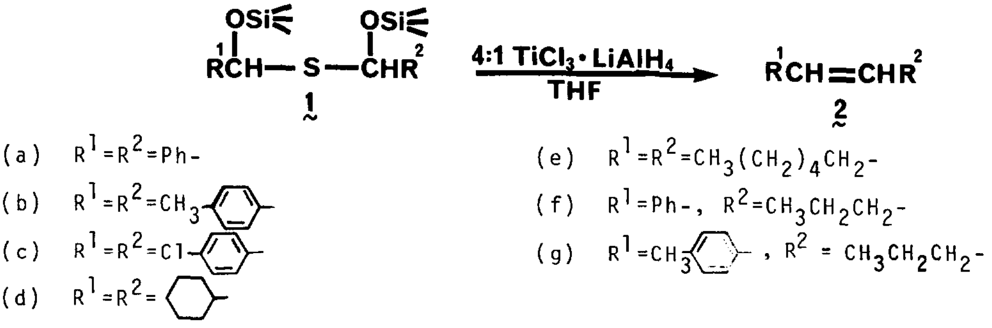
Summary: We have shown that low valent titanium reagents reductively couple α,α'-bis-(trimethylsiloxy) sulfides giving olefins in good yield. With unsymmetrical 1, mixed olefins are obtained suggesting an intermolecular pathway. Finally, we have demonstrated that trans-episulfide 3 is quantitatively converted to trans-stilbene.

Ever since their discovery by McMurry[1] in 1974, low valent titanium compounds have been found to be effective deoxygenation reagents because of the high affinity of titanium for oxygen. Such reagents have been used for the reductive coupling of carbonyl compounds to olefins[1], deoxygenation of epoxides[2] and 1,2-glycols, and the intramolecular cyclization of certain 1,3-glycols to cyclopropanes[3]. However, little work has been done on the reaction of such reagents with organosulfur compounds; we wish to report on some of our results in this area.

Recently, we initiated a program to examine the chemistry of α-functionalized sulfides[4]. In the course of the study, a series of α,α'-bis-(trimethylsiloxy)-sulfides (1) have been prepared[5,6]. We became interested in the possibility of the reductive deoxygenation of 1. We found that 1 reacts with the titanium (II) reagent derived from a 4:1 mixture of $TiCl_3$ and $LiAlH_4$[1] to give the corresponding olefin (2) in good yield (Table).



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A general procedure is as follows: to 30 ml of dry THF was added 10 mmol of a 4:1 premix $TiCl_3$-$LiAlH_4$ reagent in small portions at room temperature under N_2 atmosphere. After the mixture was stirred for 3/4 hour, a solution of 1 mmol of α,α'- bis(trimethylsiloxy)sulfide (1) in 2 ml THF was added and the reaction mixture was refluxed for 12-48 hrs. The cooled reaction mixture was poured into 40 ml of water and extracted with ether. The organic solution was washed, dried ($MgSO_4$) and evaporated *in vacuo* to yield the product olefin 2. They were identified by GC/MS and purified by preparative GC or TLC; structures were confirmed by ^1H nmr.

The following observations are relevant.

(1) Most of the reactions were carried out using commercially available titanium reagent (4:1 $TiCl_3$-$LiAlH_4$)[7]. Reagent prepared by ourselves was equally effective.

(2) Under identical conditions, benzaldehyde gave a much poorer yield of stilbene than the conversion of 1a to stilbene. This suggests that the reaction of α,α'- bis(trimethylsiloxy)sulfides (1) with low valent titanium reagent does not proceed by the reversion of 1 to aldehyde first.

(3) Aliphatic olefins (Table, entries 10 and 11) were formed in good yield as well. In our hands, the conventional McMurry coupling of simple aliphatic aldehydes gives olefins in poor yield.

(4) When *trans*-1,2-diphenylepisulfide (3) was reacted under identical conditions with the titanium reagent, *trans*-stilbene was formed quantitatively[8]. Thus, an episulfide is a plausible intermediate in the transformation of 1 to 2.

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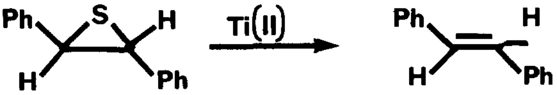

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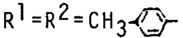
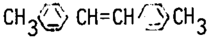
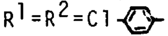
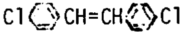
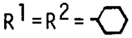
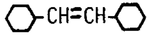
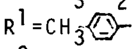
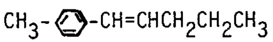
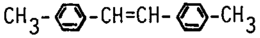
(5) Using either a cross-over experiment or unsymmetrical 1 (1f or 1g), it is clear that the product olefin is a mixture of symmetrical and unsymmetrical 2 (Table, entries 12 and 13). We have further established by a control experiment that the unsymmetrical olefin 2f (R^1=Ph-, R^2=$CH_3CH_2CH_2$-) could not have undergone metathesis under the reaction conditions by the titanium reagent. This suggests that in the transformation of 1 to 2, an intermolecular pathway predominates over any intramolecular pathway.

It is clear from our results that low valent titanium reagents can be effective as desulfurization agents as well. We intend to examine the reaction of other organosulfur compounds so that a general pattern may emerge in the future.

TABLE. Conversion of α,α'- bis(Trimethylsiloxy)sulfides (1) to Olefins (2).

Entry	Sulfide or aldehyde	Reagnet[a] $TiCl_3/LiAlH_4$	Ratio of Ti/starting material	Reaction Time (h)	Olefin (% yield)[b,c]	Reference
1	1a $R^1=R^2=Ph$	4:1	10:1	12	Ph-CH=CHPh (87)[d]	f
2	1a "	4:1*	10:1	12	" (85)	
3	1a "	4:1	4:1	12	" (33)	
4	1a "	2:1*	2:1	12	" (33)	
5	PhCH=O	4:1	10:1	12	(18)	
6	PhCH=O	2:1*	2:1	12	_e	(1)
7	PhCH=O	2:1*	10:1	21	(24)	
8	1b 	4:1	10:1	12	 (98)	(9)
9	1c 	4:1	10:1	12	 (84)	(10)
10	1d 	4:1	10:1	36	 (82)	(11)
11	1e $R^1=R^2=CH_3(CH_2)_5$-	4:1	10:1	48	$CH_3(CH_2)_5CH=CH(CH_2)_5CH_3$ (70)	f
12	1f $R^1=Ph$ $R^2=CH_3CH_2CH_2$-	4:1	10:1	48	$PhCH=CHCH_2CH_2CH_3$ (45) PhCH=CHPh (20)[g]	(12)
13	1g  $R^2=CH_3CH_2CH_2$-	4:1	10:1	48	 (35)[h]  (30)[g]	

(a) Commercial reagent[7] except those with * which were prepared by ourselves.

(b) The yields were determined by GC using internal standard.

(c) The olefin is mainly the E isomer (> 80%) by ^1H nmr.

(d) Isolated Yield 84%.

(e) Pinacol was formed.

(f) Structure confirmed by comparison with authentic samples.

(g) 4-Octene was found by GC but its amount was not quantitatively determined because its b.p. is close to that of solvent THF.

(h) ^1H nmr of 2g (δ, $CDCl_3$): 7.14 (q, 4H), 6.33 (d, 1H, J=16 Hz), 6.13 (dt, 1H, J=16 Hz, 7 Hz), 2.29 (s, 3H), 2.08-2.20 (m, 2H), 1.38-1.54 (m, 2H), 0.90 (t, 3H).

References and Notes

(1) a) J.E. McMurry and M.P. Fleming, *J. Amer. Chem. Soc.*, **96**, 4708 (1974) and *J. Org. Chem.*, **41**, 896 (1976); b) J.E. McMurry and L.R. Krepski, *J. Org. Chem.*, **41**, 3929 (1976); c) J.E. McMurry, *Acc. Chem. Res.*, **7**, 281 (1974); d) A.L. Baumstark, E.J.H. Bechara and M.J. Semigran, *Tetrahedron Lett.*, 3265 (1976).

(2) J.E. McMurry and M.P. Fleming, *J. Org. Chem.*, **40**, 2355 (1975).

(3) a) A.L. Baumstark, C.J. McCloskey, T.J. Tolson, G.T. Syriopoulos, *Tetrahedron Lett.*, 3003 (1977); b) H.M. Walborsky, M.P. Murari, *J. Amer. Chem. Soc.*, **102**, 426 (1980).

(4) T. Aida, D.N. Harpp and T.H. Chan, *Tetrahedron Lett.*, 3247 (1980).

(5) T. Aida, T.H. Chan and D.N. Harpp, *Tetrahedron Lett.*, 1089 (1981).

(6) NMR data (δ, in CCl_4) of **1** are as follows. **1a** 7.43-7.10 (m, 10H), 5.97 (s, 2H), 0.06 (s, 18H); **1b** 7.13 (q, 8H), 5.93 (s, 2H), 2.27 (s, 6H), 0.04 (s, 18H); **1c** 7.28 (s, 8H), 6.02 (s, 2H), 0.10 (s, 18H); **1d** 4.84 and 4.76 (each d, J = 4 Hz, 2H), 2.14-0.97 (broad, 22H), 0.19 (s, 18H); **1e** 4.90-5.26 (m, 2H), 2.10-0.84 (broad, 26H), 0.22 (s, 18H); **1f** 7.47-7.04 (m, 5H), 5.96 (s, 1H), 4.97 and 4.62 (each t, J = 6 Hz, 1H), 2.05-1.14 (broad, 4H), 0.94 (t, 3H), 0.12 (s, 9H), 0.04 (s, 9H); **1g** 7.04 (q, 4H), 5.97 (s, 1H), 4.93 and 4.67 (each t, J = 6 Hz, 1H), 2.33 (s, 3H), 2.00-1.17 (broad, 4H), 0.90 (t, 3H), 0.13 (s, 9H), 0.04 (s, 9H).

(7) Available from Ventron (Alfa) Corporation.

(8) *Trans*-1,2-diphenylepisulfide remained unchanged in refluxing THF overnight in the absence of the titanium reagent.

(9) T. Tanabe and T. Nagai, *Bull. Chem. Soc. Japan*, **51**, 1459 (1978).

(10) R.S. Tewari, N. Kumari and P.S. Kenddurkar, *J. Chem. Eng. Data*, **21**, 125 (1976).

(11) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato and M. Kumada. *Bull. Chem. Soc. Japan*, **49**, 1958 (1976).

(12) H. Umezaki, Y. Fujiwara, K. Sawara and S. Teranishi, *Bull. Chem. Soc. Japan*, **46**, 2230 (1973).

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