



Pergamon

Tetrahedron Letters 41 (2000) 3911–3914

TETRAHEDRON
LETTERS

α -Sulfenylation of acylsilanes and aldehydes with *N*-(phenylthio)succinimide

Chih-Hao Huang, Kang-Shyang Liao, Surya Kanta De and Yeun-Min Tsai*

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, Republic of China

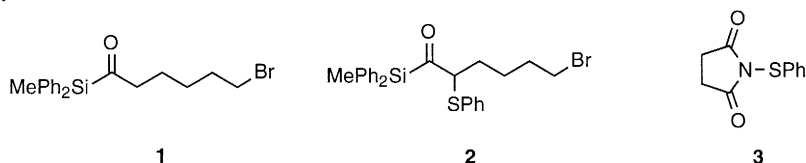
Received 14 February 2000; revised 22 March 2000; accepted 24 March 2000

Abstract

The reactions of acylsilanes with *N*-(phenylthio)succinimide in the presence of *p*-toluenesulfonic acid in acetonitrile give α -sulfenylated acylsilanes in good yields. Aldehydes with α -alkyl substituent afford moderate yields of α -sulfenylated products under the same conditions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: imides; silicon and compounds; sulfides.

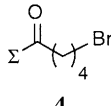
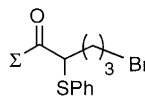
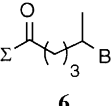
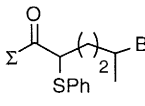
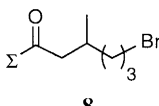
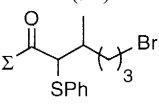
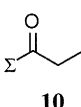
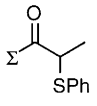
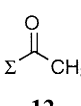
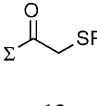
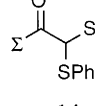
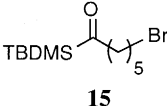
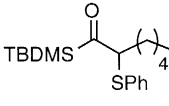
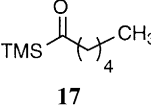
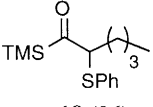
α -Sulfenylated carbonyl compounds are useful intermediates in organic synthesis.¹ Preparation of these compounds often involves S_N2 displacement of α -halogenated carbonyl compounds.^{1a} Direct sulfenylation methods are also available;^{1a,c} however, these methods usually require basic conditions. Recently, we needed to prepare α -sulfenylated acylsilane **2** from bromoacylsilane **1**.^{2,3} Due to the presence of a bromo functional group, we tried to avoid using basic conditions.⁴ We found that *N*-(phenylthio)succinimide **3**⁵ could be used to convert acylsilanes to α -sulfenylated acylsilanes under acidic conditions.^{6,7}



Our results are shown in Table 1. The reaction of acylsilane **1** (entry 1) with 1 equivalent of imide **3** and 0.1 equivalent of *p*-toluenesulfonic acid in dichloromethane at room temperature overnight gave sulfide **2** in excellent yield (92%). Surprisingly, under the same reaction conditions (entry 2), acylsilane **4**² afforded 10% of sulfide **5**. The difference between acylsilanes **4** and **1** is a single methylene unit. We found that this type of reaction is faster in a more polar solvent such as acetonitrile. When acylsilane **4** was treated with imide **3** (1 equiv.) in the presence of a catalytic amount of *p*-toluenesulfonic acid (0.1 equiv.) in acetonitrile for 8 h (entry 3), we obtained an 80% yield of sulfide **5**. The reaction conditions used in entry

* Corresponding author. E-mail: ymtsai@mail.ch.ntu.edu.tw (Y.-M. Tsai)

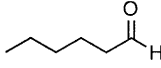
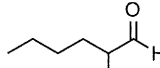
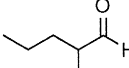
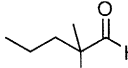
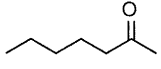
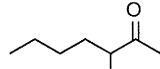
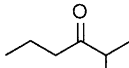
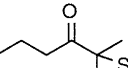
Table 1
 α -Sulfonylation of acylsilanes with *N*-phenylthiosuccinimide **3**^a

entry	substrate $\Sigma = \text{SiPh}_2\text{Me}$	imide 3 (equiv)	acid (equiv)	solvent	time (h)	product (% yield) $\Sigma = \text{SiPh}_2\text{Me}$
1	1	1	TsOH (0.1)	CH ₂ Cl ₂	15	2 (92)
2	 4	1	TsOH (0.1)	CH ₂ Cl ₂	15	 5 (10)
3	4	1	TsOH (0.1)	CH ₃ CN	8	5 (80)
4	 6	1	TsOH (0.1)	CH ₃ CN	6	 7 (92)
5	 8	1	TsOH (0.1)	CH ₃ CN	6	 9 (88)
6	 10	2.2	TsOH (0.1)	CH ₃ CN	6	no reaction
7	10	1	TsOH (1)	CH ₃ CN	5	 11 (90)
8	 12	1	BF ₃ •OEt ₂ (0.5)	CH ₃ CN	6	 13  14 13 : 14 : 12 = 1 : 0.6 : 1 ^b
9	 15	2.2	TsOH (0.1)	CH ₃ CN	6	 16 (83)
10	 17	1.2	TsOH (0.1)	CH ₃ CN	6	 18 (86)

^aAll reactions were performed at room temperature.

^bProducts were not isolated, and the ratio was determined by ¹H NMR analysis.

Table 2
 α -Sulfenylation of aldehydes and ketones with *N*-phenylthiosuccinimide **3**^a

entry	substrate	imide 3 (equiv)	acid (equiv)	time (h)	product (%yield)
1	 19	1.0	BF ₃ •OEt ₂ (1.0)	21	 20 (19)
2	 21	1.0	BF ₃ •OEt ₂ (1.0)	3	 22 (68)
3	 23	2.0	TsOH (1.0)	7	 24 (24)
4	 25	1.0	BF ₃ •OEt ₂ (1.0)	14	 26 (22)

^aThese reactions were performed in acetonitrile at room temperature.

3 turned out to be quite useful for analogous acylsilanes **6** and **8** (entries 4 and 5). However, for shorter acylsilanes such as **10** (entry 6), no reaction occurred when using 0.1 equivalent of *p*-toluenesulfonic acid. In the presence of 1 equivalent of *p*-toluenesulfonic acid, propanoysilane **10** reacted with imide **3** in acetonitrile for 5 h to afford a 90% yield of sulfide **11**.

Ethanoysilane **12** (entry 8) was the least reactive one that we have studied. Under the conditions described above for the preparation of sulfide **11** (entry 7), we observed no reaction for ethanoysilane **12**. Reaction occurred when we used borontrifluoride etherate; however, bis-sulfenylation became competitive. As shown in entry 8, the reaction of ethanoysilane **12** with imide **3** in the presence of borontrifluoride etherate (0.5 equiv.) in acetonitrile for 6 h proceeded in about a 60% conversion. The monosulfide **13** and bis-sulfide **14** were present in a 3:2 ratio, respectively.

The α -sulfenylation reactions are not limited to acylmethyldiphenylsilanes. As shown in entry 9 (Table 1), bromoacylsilane **15**² with a bulky *t*-butyldimethylsilyl group (TBDMS) underwent α -sulfenylation with imide **3** (2.2 equiv.) in the presence of *p*-toluenesulfonic acid (0.1 equiv.) in acetonitrile (6 h) to give sulfide **16** in an 83% yield. Under similar reaction conditions, acyltrimethylsilane **17**⁸ (entry 10) afforded sulfide **18**^{4a} in good yield (86%).

When we applied this method to aldehydes and ketones, only α -substituted aldehydes were sulfenylated in mild yields. As shown in Table 2, a dismal 19% yield of sulfide **20**⁹ (entry 1) was obtained by the reaction of straight chain hexanal **19** with imide **3** in the presence of borontrifluoride etherate (1 equiv.)

at room temperature in acetonitrile for 21 h. With the presence of an α -methyl substituent, aldehyde **21** (entry 2) led to 68% of sulfide **22** in 3 h under similar conditions. All the ketones that we have studied reacted poorly as shown in entries 3 and 4. Sulfenylation occurred preferentially at the more substituted side of the unsymmetric ketones with low yields.

The reactivity pattern observed in these sulfenylation reactions correlates well with the enol content of the carbonyl compounds.¹⁰ It was reported recently that the enol content of acylsilanes is higher than aldehydes and ketones.¹¹ In this study, the acylsilanes show the highest reactivity towards imide **3** under acidic conditions. Among the acylsilanes, ethanoylsilane **12** is the least reactive. Presumably, acylsilane **12** is the least enolizable acylsilane that we have studied. Ketones are known to have lower enol content than aldehyde.¹⁰ Here, we found that the ketones are poor substrates in this reaction.

Acknowledgements

Financial support by the National Science Council of the Republic of China is gratefully acknowledged.

References

1. (a) Trost, B. M. *Chem. Rev.* **1978**, *78*, 363–382. (b) Trost, B. M. *Acc. Chem. Res.* **1978**, *11*, 453–461. (c) Foray, G.; Peñeñory, A. B.; Rossi, R. A. *Tetrahedron Lett.* **1997**, *38*, 2035–2038.
2. Chang, S.-Y.; Jiaang, W.-T.; Cherng, C.-D.; Tang, K.-H.; Huang, C.-H.; Tsai, Y.-M. *J. Org. Chem.* **1997**, *62*, 9089–9098.
3. For recent reviews about acylsilanes, see: (a) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647–660. (b) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147–195. (c) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proc. Int.* **1992**, *24*, 553–582. (d) Page, P. C. B.; McKenzie, M. J.; Klair, S. S.; Rosenthal, S. In *Acyl Silanes*; Rappoport, Z.; Apeloig, Y., Eds. The chemistry of organic silicon compounds. John Wiley & Sons: New York, 1998; Vol. 2, Chap. 27, pp. 1599–1665.
4. For the preparation of α -sulfenylated acylsilanes through enol silyl ethers, see: (a) Minami, N.; Abe, T.; Kuwajima, I. *J. Organometal. Chem.* **1978**, *145*, C1–C3. (b) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609–5617. (c) Thomas, S. E.; Tustin, G. J. *Tetrahedron* **1992**, *48*, 7629–7640.
5. Groebel, W. *Chem. Ber.* **1960**, *93*, 284–285.
6. For α -selenylation of ketones and aldehydes with *N*-(phenylseleno)phthalimide under acidic conditions, see: Cossy, J.; Furet, N. *Tetrahedron Lett.* **1993**, *34*, 7755–7756.
7. For the use of sulfenamide derivatives to convert ketones to their β -ketosulfides, see: (a) Mukaiyama, T.; Kobayashi, S.; Kumamoto, T. *Tetrahedron Lett.* **1970**, 5115–5118. (b) Kumamoto, T.; Kobayashi, S.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 866–870.
8. Miller, J. A.; Zweifel, G. *Synthesis* **1981**, 288–289.
9. Seebach, D.; Teschner, M. *Chem. Ber.* **1976**, *109*, 1601–1616.
10. Guthrie, J. P.; Cullimore, P. A. *Can. J. Chem.* **1979**, *57*, 240–248.
11. Kresge, A. J.; Tobin, J. B. *J. Org. Chem.* **1993**, *58*, 2652–2657.