Pergamon

Tetrahedron Letters 39 (1998) 3533–3536

TETRAHEDRON
LETTERS

Desulfurizative Silation, Germation, and Stannation of Thioacetals and Their Analogues Utilizing Titanocene(II)

Takeshi TAKEDA,* Naoki NOZAKI, and Tooru FUJIWARA

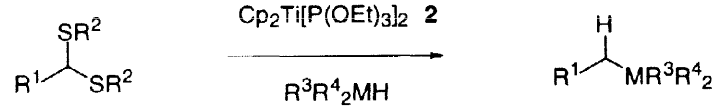
Department of Applied Chemistry, Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184-8588, Japan

Received 4 February 1998; accepted 27 February 1998

Abstract: Desulfurization of thioacetals with the low valent titanium species $Cp_2Ti[P(OEt)_3]_2$ in the presence of trialkylsilanes afforded the corresponding tetraalkylsilanes. Allylsilanes were obtained regioselectively using β,γ-unsaturated thioacetals or 1,3-bis(phenylthio)alk-1-enes as starting materials. The similar titanocene(II)-promoted reactions of these organosulfur compounds with triethylgermane and tributylstannane gave tetraorganogermanes and stannanes, respectively.

Synthesis of group 14 organometallic compounds has been extensively studied because of their characteristic reactivities and easiness of handling as synthetic reagents.[1] In this communication, we wish to describe the reaction of titanium-carbene complexes formed from thioacetals or their analogues with trialkylsilane, germane, and stannane which constitutes a new method for the preparation of group 14 organometallic compounds.

Recently we found that the treatment of thioacetals **1** with the titanocene(II) species $Cp_2Ti[P(OEt)_3]_2$ **2** produced the carbene complexes of titanium **3**. These react with various organic molecules having a multiple bond such as carbonyl compounds,[2] alkenes,[3] allylsilanes,[4] and alkynes[5] to afford Wittig-type olefination products, vinylcyclopropanes, γ-substituted allylsilanes, and conjugated dienes, respectively. All these results indicate that the organotitanium species **3** is a valuable and versatile intermediate in organic synthesis. The formation of group 14 organometallic compounds by the transition metal-catalyzed reactions of diazo compounds with triorganosilanes, germanes, and stannanes have been extensively investigated.[6] These reactions were employed for the preparation of certain allylsilanes.[7] Synthesis of organosilicon and tin compounds including those having an allylic substituent by the treatments of various Fischer carbene complexes with silanes and stannanes were also reported.[8] On the basis of these observations, we assumed that the reaction of carbene complexes formed from thioacetals with trialkylsilane would proceed to produce the corresponding tetraorganosilane **4** (Eq. 1).



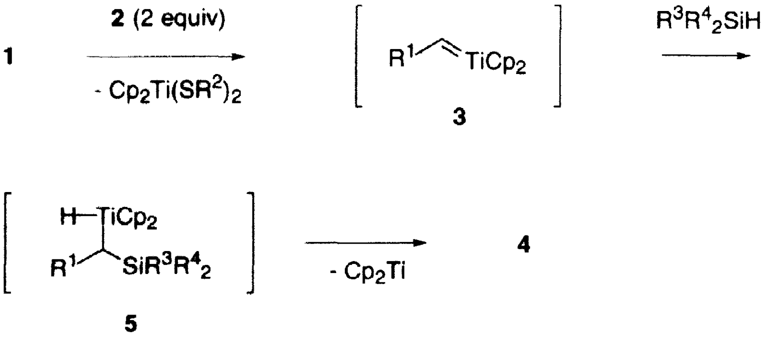
(1)

1

4: M = Si
6: M = Ge
7: M = Sn

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)00524-3

As would be expected, when 3-phenylpropionaldehyde diphenylthioacetal (**1a**) was treated with the low valent titanium **2** (2.2 equiv) for 10 min and then with dimethylphenylsilane (1.1 equiv) for 1.5 h at room temperature, dimethylphenyl(3-phenylpropyl)silane (**4a**) was produced in 73% yield. The silane **4a** was obtained in better yield when the desulfurization of **1a** with **2** was carried out in the presence of dimethylphenylsilane (Table 1, Entry 1). It was confirmed that the reaction using 1.1 equiv of **2** afforded **4a** only in 11% yield. The tetraorganosilanes **4b** and **4d** were also obtained using triethylsilane (Entries 2 and 6). The probable course of this reaction is outlined below. Alkylidenetitanocene **3** formed by the desulfurization of thioacetal **1** reacts with trialkylsilane to form the α-silylalkyltitanium species **5**. The following elimination of the titanocene(II) species affords tetraorganosilane **4** (Eq. 2).



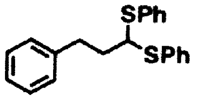
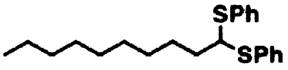
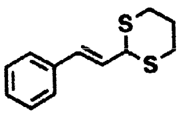
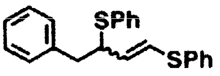
(2)

It is easy to imagine that the reactions of titanium-carbene complexes with trialkylgermane or stannane would proceed through a similar reaction pathway to give the corresponding organogermanium or tin compounds. This idea was substantiated when thioacetals **1** were treated in the presence of triethylgermane; the tetraalkylgermanes **6a** and **6b** were obtained in good yields (Entries 3 and 7). On the other hand, it was found that the reaction using tributylstannane was complicated, and only a small amount of the tetraalkylstannane **7a** was obtained (Entry 4).

We next examined the application of this new method to the preparation of allylsilanes. The treatment of thioacetals of α,β-unsaturated aldehydes **1** with **2** and trialkylsilanes afforded the corresponding primary allylsilanes **4** exclusively with *E* stereosectivity (see Entries 8, 9, and 12). By using 1,3-bis(phenylthio)alk-1-enes **8** as starting materials, allylsilanes **4** were obtained in high yields (Entries 14, 15, 18, and 19). The reactions of unsaturated thioacetals **1** and their analogues **8** with triethylgermane afforded allylgermanes **6** in good yields. Similarly to the saturated counterpart, however, the unsaturated compounds **1c** and **8a** gave allylstannanes **7b** and **7c** in moderate yields when being treated with the titanocene(II) species **2** and tributylstannane (Entries 11 and 17).

The typical experimental procedure is as follows; to a flask charged with finely powdered molecular sieves 4A (110 mg), magnesium turnings (32 mg, 1.3 mmol), and Cp_2TiCl_2 (274 mg, 1.1 mmol) was added THF (2 ml) and $P(OEt)_3$ (0.38 ml, 2.2 mmol) with stirring at room temperature under argon. After 3 h, dimethylphenylsilane (75 mg, 0.55 mmol) in THF (1.5 ml) was added to the mixture, and stirring was continued for 10 min. Then **1a** (168 mg, 0.5 mmol) in THF (1.5 ml) was added, and the mixture was further stirred for 1.5 h at room temperature. Then the mixture was diluted with hexane (20 ml). The resulting insoluble materi-

Table 1. Preparation of Tetraorganosilanes, Germanes, and Stannanes[a]

Entry	Thioacetal **1** or 1,3-bis-(phenylthio)alk-1-ene **8**	$R^3R^4{}_2MH$	Product		$E : Z$[b]	Yield (%)
1		$PhMe_2SiH$		**4a**	-	89
2		Et_3SiH		**4b**	-	84
3		Et_3GeH		**6a**	-	62
4	**1a**	Bu_3SnH		**7a**	-	20
5		$PhMe_2SiH$		**4c**	-	85
6		Et_3SiH		**4d**	-	87
7	**1b**	Et_3GeH		**6b**	-	61
8[c,d]		$PhMe_2SiH$		**4e**	100 : 0	73
9[c,d]		Et_3SiH		**4f**	100 : 0	58
10[c,d]		Et_3GeH		**6c**	e	70
11[c]	**1c**	Bu_3SnH		**7b**	e	30
12[c,d]		$PhMe_2SiH$		**4g**	79 : 21	74
13[c,d]	(E : Z = 87 : 13) **1d**	Et_3GeH		**6d**	86 : 14	64
14		$PhMe_2SiH$		**4h**	91 : 9	88
15		Et_3SiH		**4i**	92 : 8	83
16	(E : Z = 98 : 2)	Et_3GeH		**6e**	95 : 5	86
17	**8a**	Bu_3SnH		**7c**	92 : 8	60
18		$PhMe_2SiH$		**4j**	95 : 5	90
19	(E : Z = 75 : 25)	Et_3SiH		**4k**	95 : 5	89
20	**8b**	Et_3GeH		**6f**	96 : 4	90

---

a) All reactions were performed following the procedure described in the text, unless otherwise noted. b) Determined by NMR spectroscopy. c) Cp_2TiCl_2 (3 equiv), magnesium (3.6 equiv), and triethyl phosphite (6 equiv) were used. d) The reaction was quenched with 1N NaOH, and the organic materials were extracted with ether. e) Only the one stereoisomer was obtained. Its stereochemistry was assumed to be E on the basis of coupling constant of vinyl proton.

als were filtered off through Celite and the filtrate was concentrated. The residue was purified by PTLC (hexane) to yield 113 mg (89%) of **4a**.

It should be noted that the present reaction is the first [2+1] carbenoid insertion reaction of titanium-carbene complexes with silanes and related group 14 organometallics. Since the starting materials, thioacetals **1** and 1,3-bis(phenylthio)alk-1-enes **8**, are accessible by various methods, this reaction provides a convenient tool for the preparation of group 14 organometallic compounds.

This work was supported by the Grant-in-aid for Scientific Research on Priority Area No. 09231213 from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. Takeda, T. In *Synthesis of Organometallic Compounds - A Practical Guide*; Komiya, S., Ed.; John Wiley & Sons: Chichester, 1997; p. 391. Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. Larson, G. L. In *The Chemistry of Organic Silicon Compounds*, Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1989; Vol. 1, p. 763. Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel E. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, p. 515. Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Nozaki, H. In *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley & Sons: Chichester, 1994; p. 535. Wardel, J. L. In *Chemistry of Tin*, Harrison, P. G., Ed.; Blackies & Son: Glasgow, 1989; p. 315. Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: Guildford, 1987.
2. Horikawa, Y.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Am. Chem. Soc.*, **1997**, *119*, 1127. Takeda, T.; Watanabe, M.; Nozaki, N.; Fujiwara, T. *Chem. Lett.* **1998**, 115. Rahim, Md. A.; Taguchi, H.; Watanabe, M.; Fujiwara, T.; Takeda, T. *Tetrahedron Lett.* in press.
3. Horikawa, Y.; Nomura, T.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Org. Chem.*, **1997**, *62*, 3678.
4. Fujiwara, T.; Takamori, M.; Takeda, T. *Chem. Commun.* **1998**, 51.
5. Takeda, T.; Shimokawa, H.; Miyachi, Y.; Fujiwara, T. *Chem. Commun.* **1997**, 1055.
6. Rijkens, F.; Janssen, M. J.; Drenth, W.; Van Der Kerk, G. J. M. *J. Organomet. Chem.*, **1964**, *2*, 347. Seyferth, D.; Damrauer, R.; Mui, J. Y.-P.; Jula, T. F. *J. Am. Chem. Soc.* **1968**, *90*, 2944. Watanabe, H.; Nakano, T.; Araki, Y.; Matsumoto, H.; Nagai, Y. *J. Organomet. Chem.* **1974**, *69*, 389. Bagheri, V.; Doyle, M. P.; Taunton, J.; Claxton, E. E. *J. Org. Chem.* **1988**, *53*, 6158. Andrey, O.; Landais, Y.; Planchenault, D. *Tetrahedron Lett.* **1993**, *34*, 2927. Landais, Y.; Planchenault, D. *Tetrahedron Lett.* **1994**, *35*, 4565. Andrey, O.; Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron* **1995**, *51*, 12083. Barnier, J.-P.; Blanco, L. *J. Organomet. Chem.* **1996**, *514*, 67. Buck, R. T.; Doyle, M. P.; Drysdale, M. J.; Ferris, L., Forbes, D. C.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Zhou, Q.-L. *Tetrahedron Lett.* **1996**, *37*, 7631. Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *Tetrahedron Lett.* **1997**, *38*, 229. Landais, Y.; Planchenault, D. *Tetrahedron* **1997**, *53*, 2855.
7. Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron Lett.*, **1994**, *35*, 9549. Davies, H. M. L.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. *Tetrahedron Lett.*, **1997**, *38*, 1741.
8. Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Organomet. Chem.* **1973**, *55*, 111. Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 108. Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 283. Nakamura, E.; Tanaka, K.; Aoki, S. *J. Am. Chem. Soc.* **1992**, *114*, 9715. Mak, C. C.; Chan, K. S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2143. Mak, C. C.; Tse, M. K.; Chan, K. S. *J. Org. Chem.* **1994**, *59*, 3585. Merlic, C. A.; Albaneze, J. *Tetrahedron Lett.* **1995**, *36*, 1007. Merlic, C. A.; Albaneze, J. *Tetrahedron Lett.* **1995**, *36*, 1011.