Pergamon

Tetrahedron Letters, Vol. 37, No. 43, pp. 7767-7770, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01773-X

Group Transfer from Silicon to Carbon via Tandem Radical Cyclizations of Acylsilanes

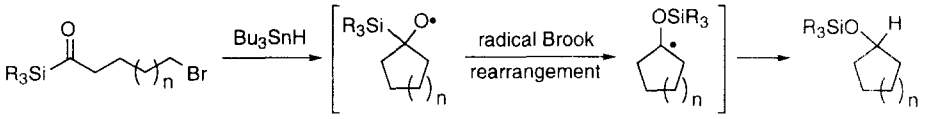
Yeun-Min Tsai,* Kuo-Hsiang Tang and Weir-Torn Jiaang

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

Abstract: Tandem radical cyclizations of acylsilanes with alkene or alkyne functionalities attached to silicon afforded cyclic silyl ethers which were oxidatively hydrolyzed to give diols or ketone alcohols.

Acylsilane is an useful functional group which has gained more and more attentions.[1] Recently, we reported radical cyclizations of acylsilanes **1** (scheme I).[2a] The key step of this process involves a radical Brook rearrangement[2,3] of the initially formed β-silyl alkoxy radicals **2** to give silyloxy substituted radicals **3**. Hydrogen atom abstraction of **3** then affords cycloalkyl silyl ethers **4**. However, with suitable design, radicals of the type **3** can be employed to construct carbon-carbon bond through intermolecular processes[2b] or intramolecular tandem cyclizations.[2c] In this communication, we report the intramolecular transfer of substituent from silicon to carbon through tandem radical cyclizations.

Scheme I

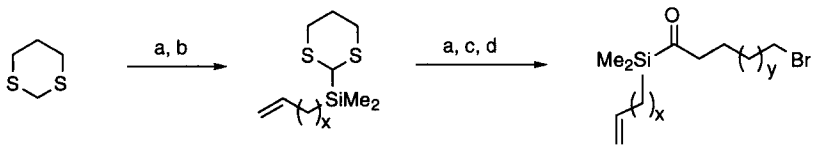


1 n = 1,2 **2** **3** **4**

As shown in scheme II, silylation of 1,3-dithiane with allylchlorodimethylsilane or (3-butenyl)chlorodimethylsilane gave the corresponding 2-silyl-1,3-dithianes **5a** (83%) and **5b** (64%). Alkylation of **5a** or **5b** with 1,4-dibromobutane or 1,5-dibromopentane followed by hydrolysis of the dithiane moiety with ceric ammonium nitrate (CAN)[4] or iodobenzene bis(trifluoroacetate)[5] gave bromo acylsilanes **6a-6d** in mild yields.

When **6a** was treated with tributyltin hydride in refluxing benzene (scheme III), a mixture of **7a-9a** was obtained. Since these silyl ethers were volatile and difficult to isolate, we directly treated the crude product mixture under Tamao oxidation condition[6] to afford diols **10a** (21%) and **11a**[7] (40%). The isolation of **10a** indicated the formation of **8a** in the radical cyclization step. The origin of **11a** should be the spiral silyl ether **9a**. Analysis of the crude cyclization mixture by GC[8] showed three peaks with a ratio of 1:3:9. Coinjection of authentic **7a** indicated that this monocyclic product was the minor component. Since silyl ether **7a** was only present in small quantity, we were not able to isolate the corresponding cyclopentanol after the oxidative hydrolysis step. From the relative amounts of the diols isolated, we believed that silyl ether **9a** should correspond to the major component observed in our GC analysis.

Scheme II



5a x = 1 (83%)
5b x = 2 (64%)

6a x = 1, y = 1 (43%)
6b x = 1, y = 2 (52%)
6c x = 2, y = 1 (36%)
6d x = 2, y = 2 (43%)

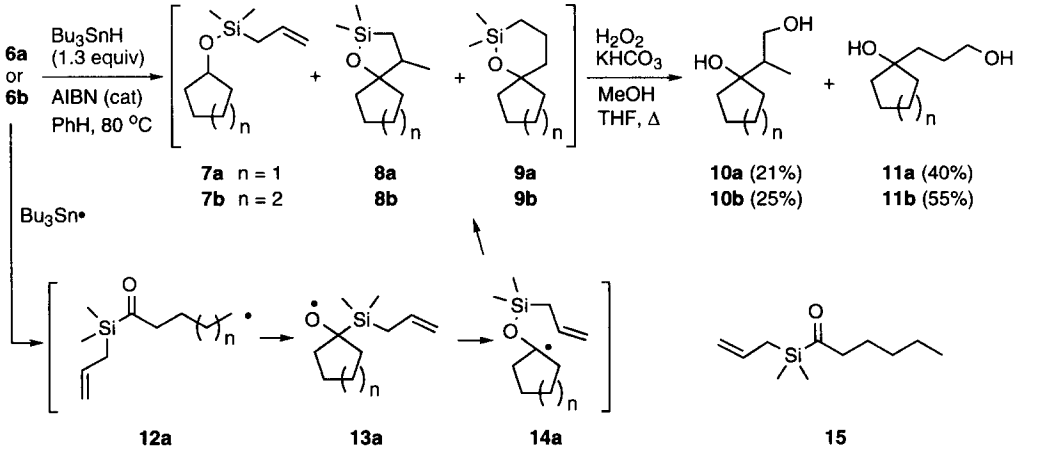
Reagents and conditions: (a) BuLi, THF, −78 °C; (b) CH_2=$CHCH_2SiMe_2Cl$ or CH_2=$CH(CH_2)_2SiMe_2Cl$; (c) $Br(CH_2)_4Br$ (2 equiv) or $Br(CH_2)_5Br$ (2 equiv), −20 °C; (d) CAN (4.1 equiv), MeOH, CH_2Cl_2 for **6a**; $(CF_3COO)_2IPh$ (1.7 equiv), $NaHCO_3$ (7 equiv), CH_3CN, H_2O, −20 °C for **6b-6d**.

Mechanistically, the cyclization involved the generation of radical **12a** which cyclized to give alkoxy radical **13a**. Radical Brook rearrangement[2,3] of **13a** afforded **14a**. Direct hydrogen atom abstraction of **14a** from tributyltin hydride gave **7a**. 5-*Exo*-trig and 6-*endo*-trig cyclization of **14a** led to **8a** and **9a**, respectively. It is well-known that γ-silicon substituted radical undergoes 6-*endo*-trig cyclization preferentially.[9a-9c] Our results are in coherence with this trend.

Radical cyclization of **6b** followed by oxidative hydrolysis gave 25% of **10b** and 55% of **11b**. Again, the *endo*-cyclization product prevailed. Analysis by GC[8] showed the presence of four peaks with ratio of 1:5:13:1 corresponding to **7b**, **8b**, **9b**, and **15**, respectively. The presence of the uncyclized product **15** was confirmed by coinjection of an authentic sample.[10] Homoallyl substituted silanes **6c** and **6d** cyclized in much better regioselectivity in favor of 7-*endo*-trig over 6-*exo*-trig.[9d] From **6c**, we isolated diol **16a** (67%) and **17a** (3%) after oxidative hydrolysis. Analysis of the crude cyclization mixture by GC[8] showed **18a**:**19a**:**20a** = 4:24:1. Similarly, Diol **16b** was obtained from **6d** in 79% yield. We did not observe the presence of **20b** by GC. However, monocyclic **18b** and uncyclized **21** were present in 10% and 9% , respectively, by GC analysis.[8]

This methodology also worked nicely in a triple cyclization cascade. Dithiane **23** prepared from alkyne **22** (47%) was converted to acylsilane **24** (65%) as shown in scheme IV. Radical cyclization of **24** with tributyltin hydride in refluxing benzene gave two isomeric tricyclic products **25a** (24%) and **25b** (8%). Treatment of **25a** and **25b** independently under oxidative hydrolysis condition afforded the same ketone diol **27** in 60% and 56%

Scheme III



7a n = 1
7b n = 2

8a
8b

9a
9b

10a (21%)
10b (25%)

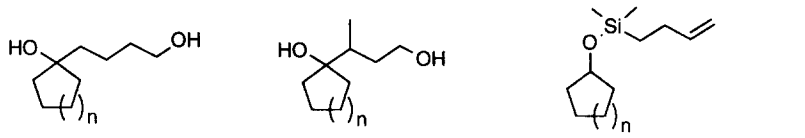
11a (40%)
11b (55%)

12a

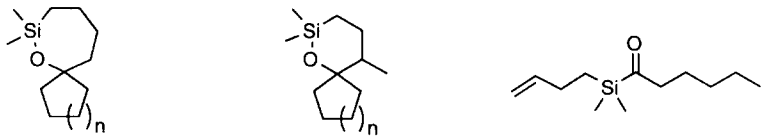
13a

14a

15



16a n = 1 **16b** n = 2 **17a** **17b** **18a** **18b**



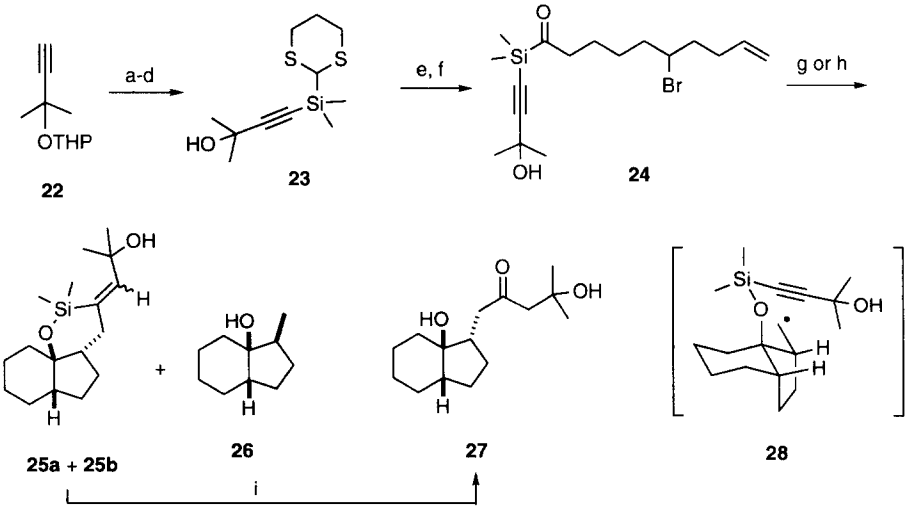
19a **19b** **20a** **20b** **21**

yield, respectively. These experiments confirmed that **25a** and **25b** were *Z*, *E* isomers in respect to the carbon-carbon double bond.[11] In addition to the tricyclic products, we have also isolated 5% of a desilylated bicyclic alcohol **26**[12] and 23% of uncyclized straight reduction product. The relative stereochemistry of the indane nucleus in **25** was assigned based on our previous results[3d] and other similar systems[12,14] that the first two cyclizations preferred to give radical **28**. Furthermore,[13]C NMR of **26**[13] showed that C_{3a} appeared at δ 81.0. While in the *endo*-methyl isomer of **26**,[12b] C_{3a} appeared at δ 78.2. Compared with these values, C_{3a} of **27** appeared at δ 77.2. This number correlates well with the *endo*-isomer of **26**.

When the cyclization reaction of **24** with tributyltin hydride was performed at room temperature using triethylborane-air for initiation,[15] much better yields of **25a** (42%) and **25b** (9%) were obtained. It was noted that the cyclization of **28** provided a rare example of ε-silicon substituted radical cyclized in a 6-*exo*-dig fashion.

In summary, radical cyclizations of acylsilanes with alkene or alkyne functionalities attached on silicon

Scheme IV



22 **23** **24** **25a + 25b** **26** **27** **28**

Reagents and conditions: (a) BuLi, THF, 0 °C; (b) Me_2SiCl_2 (4 equiv), 0 °C; (c) 1,3-dithiane, BuLi, 0 °C; (d) MeOH, TsOH (cat); (e) 5,9-dibromononene (1.2 equiv), LDA (2.4 equiv), THF, –78 °C; (f) CAN (2.5 equiv), $NaHCO_3$ (6 equiv), CH_3CN, CH_2Cl_2, H_2O, –50 °C; (g) Bu_3SnH (1.2 equiv), AIBN (cat), PhH, 80 °C; (h) Bu_3SnH (1.2 equiv), Et_3B/hexane (1.0 M, 2 equiv), dry air, PhH, rt; (i) H_2O_2 (10 equiv), $KHCO_3$ (3 equiv), KF (3 equiv), MeOH, THF.

underwent tandem cyclizations to generate cyclic silyl ethers. Oxidative hydrolysis of these silyl ethers resulted in a net transfer of the substituent from silicon of the acylsilanes to carbon.

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

REFERENCES AND NOTES

1. (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.
2. (a) Tsai, Y.-M.; Cherng, C.-D. *Tetrahedron Lett.* **1991**, *32*, 3515-3518. (b) Curran, D. P.; Jiaang, W.-T.; Palovich, M.; Tsai, Y.-M. *Synlett* **1993**, 403-404. (c) Tsai, Y.-M.; Tang, K.-H.; Jiaang, W.-T. *Tetrahedron Lett.* **1993**, *34*, 1303-1306. (d) Tsai, Y.-M.; Chang, S.-Y. *J. Chem. Soc., Chem. Commun.* **1995**, 981-982.
3. (a) Dalton, J. C.; Borque, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 699-700. (b) Harris, J. M.; MacInnes, I.; Walton, J. C.; Maillard, B. *J. Organomet. Chem.* **1991**, *403*, C25-C28. (c) Tsai, Y.-M.; Ke, B.-W. *J. Chin. Chem. Soc.* **1993**, *40*, 641-642. (d) Robertson, J.; Burrows, J. N. *Tetrahedron Lett.* **1994**, *35*, 3777-3780.
4. (a) Ho, T.-L.; Ho, H. C.; Wong, C. M. *J. Chem. Soc., Chem. Commun.* **1972**, 791-791. (b) Cristau, H.-J.; Chabaud, B.; Labaudinière, R.; Christol, H. *Synth. Commun.* **1981**, *11*, 423-428.
5. Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 287-290.
6. (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694-1696. (b) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.*, **1986**, *108*, 6090-6093.
7. Canonne, P.; Foscolos, G. B.; Bélanger, D. *J. Org. Chem.* **1980**, *45*, 1828-1835.
8. Analyzed using a 3.3 mm x 2 m column packed with 10% SE-30 on Chromosorb W under a flow rate of 30 mL/min. Retention time (min) at column temperature = 130 °C: **7a** = 6.3, **8a** = 7.1, **9a** = 7.9. Retention time (min) at column temperature = 140 °C: **7b** = 8.5, **8b** = 9.4, **9b** = 10.5, **15** = 11.6, **18a** = 7.8, **19a** = 10.5, **20a** = 9.4, **18b** = 13.2, **19b** = 16.0, **21** = 16.9.
9. (a) Wilt, J. W. *J. Am. Chem. Soc.*, **1981**, *103*, 5251-5253. (b) Wilt, J. W. *Tetrahedron* **1985**, *41*, 3979-4000. (c) Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.*, **1988**, *110*, 281-287. (d) Myers, A. G.; Gin, D. Y.; Rogers, D. H. *J. Am. Chem. Soc.*, **1994**, *116*, 4697-4718.
10. Acylsilane **15** was synthesized using methods similar to the synthesis of **6b** as shown in scheme II. Instead of 1,5-dibromopentane, 1-bromopentane was used.
11. We did not determine the exact olefin geometry of **25a** and **25b**.
12. (a) Shono, T.; Nishiguchi, I.; Ohmizu, H.; Mitani, M. *J. Am. Chem. Soc.*, **1978**, *100*, 545-550. (b) Belotti, D.; Cossy, J.; Pete, J. P.; Portella, C. *J. Org. Chem.* **1986**, *51*, 4196-4200.
13. **26**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (d, J = 6.7 Hz, 3 H, methyl), 0.98-2.20 (m, 15 H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.7, 23.2, 25.0, 27.8, 29.6, 31.1, 33.7, 36.2, 47.1, 81.0 ppm.
14. See also: (a) RajanBabu, T. V.; Fukunaga, T. *J. Am. Chem. Soc.*, **1989**, *111*, 296-300. (b) RajanBabu, T. V. *Acc. Chem. Res.* **1991**, *24*, 139-145.
15. (a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.*, **1987**, *109*, 2547-2549. (b) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 143-147. (c) Clive, D. L. J.; Postema, M. H. D. *J. Chem. Soc., Chem. Commun.* **1993**, 429-430.

(*Received in Japan* 23 *July* 1996; *revised* 2 *September* 1996; *accepted* 10 *September* 1996)