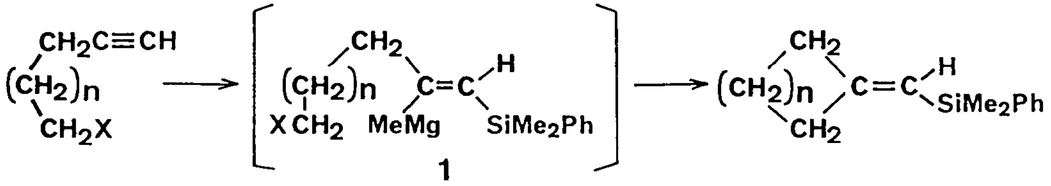
Tetrahedron Letters,Vol.25,No.23,pp 2483-2486,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

INTRAMOLECULAR CYCLIZATION MEDIATED BY SILYLMETALATION OF ACETYLENES WITH $PhMe_2SiMgMe/CuI$ AND RADICAL NATURE OF THE REAGENT

Yasuhiro Okuda, Yoshitomi Morizawa, Koichiro Oshima*, and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606, Japan

Abstract: Whereas CuI catalyzed silylmagnesation of the tosylate of 5-hexyn-1-ol with the title reagent affords dimethylphenylsilylmethylenecyclopentane exclusively, the mesylate of 3-butyn-1-ol gives a mixture of unexpected silylcyclobutene and cyclopropylidene derivative.

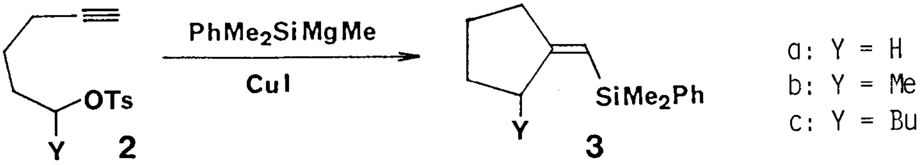
The silylmagnesium compound prepared from $PhMe_2SiLi$ and MeMgI reacts with terminal acetylenes to give vinylsilanes in the presence of various transition metal catalysts.[1] Among them, copper(I) iodide catalyzed reaction affords 1-silyl-1-alkene with high regio- and stereoselectivity. Further application of this reaction to substrates carrying a terminal acetylenic moiety and a leaving group such as OTs, OMs, or Br has provided a novel synthesis of cycloalkanes with a silylmethylene substituent.

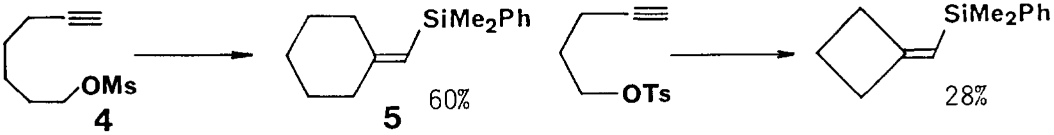


$PhMe_2SiMgMe/CuI$ THF 0°–25°C X = OTs, OMs, Br

A THF solution of $PhMe_2SiLi$ (0.5 M, 12 ml, 6.0 mmol) was treated with MeMgI (1.0 M ether solution, 6.0 ml, 6.0 mmol) in THF (5.0 ml) at 0°C. CuI (19 mg, 0.1 mmol) was added and the resulting mixture was stirred for 5 min. A THF solution of the tosylate of 5-hexyn-1-ol **2a** (0.51 g, 2.0 mmol) was added and the whole was stirred for 30 min at 0°C, then for an additional 1 h at 25°C. Extractive workup (ether, 1N HCl) followed by purification by silica gel column chromatography gave dimethylphenylsilylmethylenecyclopentane **3a**[2] (Y = H) in 91% yield: bp 72-78°C (bath temp, 2 Torr); IR (neat) 1580, 1420, 1250, 1110, 835 cm^{-1}; NMR (CCl_4) δ0.33 (s, 6H), 1.35-1.80 (m, 4H), 1.85-2.50 (m, 4H), 5.40 (bs, 1H), 7.10-7.50 (m, 5H). Found: C, 77.89; H, 9.55%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

Acetylenes **2b** and **2c** gave the corresponding cyclopentane derivatives **3b** and **3c** in 46% and 43% yields. Mesylates of 6-heptyn-1-ol and 4-pentyn-1-ol afforded the corresponding six-membered ring compound **5**[3] and four-membered one, respectively. These reactions proceed as follows. The addition of $PhMe_2SiMgMe$ to terminal acetylene linkage takes place at 0°C to provide alkenyl Grignard compound **1**. In a second step the organomagnesium reagent **1** attacks the carbon bearing the leaving group intramolecularly at 25°C to give the cyclized products. The intermediary alkenyl metal species **1** ($n = 3$, $X = OMs$) could be trapped by quenching the reaction mixture with D_2O at 0°C to give the mesylate of (E)-6-deuterio-7-dimethylphenylsilyl-6-hepten-1-ol[4] quantitatively.

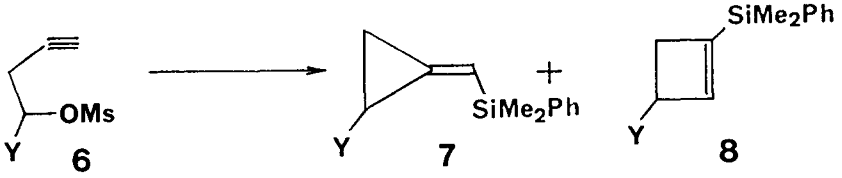




Bromides such as 7-bromo-1-heptyne or 6-bromo-1-hexyne also gave the cyclized products but the yields were rather low as compared with the corresponding mesylate or tosylate. For instance, treatment of 7-bromo-1-heptyne with $PhMe_2SiMgMe$ in the presence of CuI gave cyclohexylidene compound **5** in 25% yield along with (E)-1-dimethylphenylsilyl-1-heptene (15%) which is apparently generated by the replacement of Br group by hydrogen followed by silylmagnesation of the resulting 1-heptyne. The latter bromide gave a mixture of 1-dimethylphenylsilylmethyl-1-cyclopentene[5] (40%) and (E)-1-dimethylphenylsilyl-1-hexene (20%).

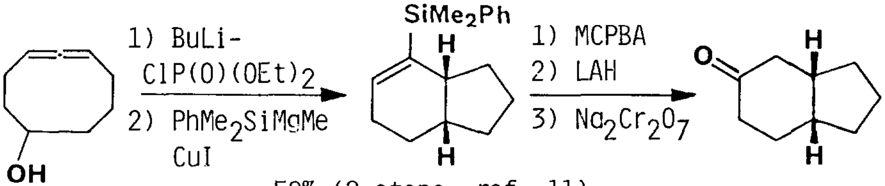
The reaction of prosaic tosylates or alkyl halides provided an evidence for the radical nature of the reagent, $PhMe_2SiMgMe$. The tosylate of dodecyl alcohol gave a mixture of 1-dodecyldimethylphenylsilane (20%), tridecane (3%), and dodecane (36%) on treatment with $PhMe_2SiMgMe$ in the presence of CuI catalyst. 1-Bromododecane also provided a mixture of these three compounds in 22%, 10%, and 24% yields, respectively. The silane and tridecane are ordinary coupling reaction products between the magnesium reagent and dodecyl group. On the other hand, the formation of dodecane could be ascribed to the intermediary dodecyl radical generated by a single electron transfer from the reagent.

Extension of this new method to mesylates (**6a**, **6b**) derived from homopropargyl alcohols provided 1-dimethylphenylsilyl-1-cyclobutenes **8a**[6] and **8b** in addition to the expected three membered ring products **7a** and **7b**. The structure of **8a** was confirmed by the comparison with a sample prepared from 4-bromo-1-dimethylphenylsilyl-1-butyne and ${}^{i}Bu_2AlH$ according to the reported procedure.[7,8]



a: Y = H 45% 41%
b: Y = Me 30% 10%

The new cyclization technique could be applied to the allenic compound[9] bearing leaving group and provided us with a simple route to bicyclic compounds which has been exemplified by the synthesis of cis-bicyclo[4.3.0]nonan-3-one.[10]



50% (2 steps, ref. 11)

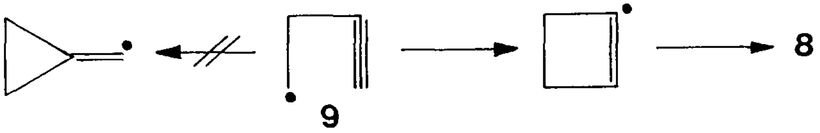
Acknowledgement: We thank Prof. Ei-ichi Negishi at Purdue University for helpful discussion and the Japan Science Promotion Society for support as Japan (Prof. H. Nozaki)-U.S. (Prof. E. Negishi) Cooperative Science Program.

REFERENCES AND NOTES

1. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, and H. Nozaki, J. Am. Chem. Soc., **105**, 4491 (1983). For the reaction of allenes, see Y. Morizawa, H. Oda, K. Oshima, and H. Nozaki, Tetrahedron Lett., in press.
2. Most recently intramolecular carbometalation of Grignard reagents having terminal trimethylsilylacetylene group has been reported to give cycloalkane having alkylidene substituents. S. Fujikura, M. Inoue, K. Utimoto, and H. Nozaki, Tetrahedron Lett., in press. The compound **3a** was identical with a sample prepared from $PhMe_2SiC{\equiv}C(CH_2)_4Br$ and Mg in THF. We are grateful to Dr. Kiitiro Utimoto for helpful discussion.
3. Bp 78-82°C (bath temp, 2 Torr); IR (neat) 1610, 1440, 1420, 1250, 1110, 830 cm^{-1}; NMR (CCl_4) δ0.30 (s, 6H), 1.10-1.80 (m, 6H), 1.90-2.40 (m,

4H), 5.15 (s, 1H), 7.10-7.50 (m, 5H). Found: C, 78.23; H, 9.63%. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62%.

4. IR (neat) 1590, 1420, 1350, 1250, 1170, 1115 cm^{-1}; NMR (CCl_4) δ0.33 (s, 6H), 1.3-2.3 (m, 8H), 2.83 (s, 3H), 4.10 (t, J = 6 Hz, 2H), 5.66 (bs, 1H), 7.15-7.65 (m, 5H).
5. NMR ($CDCl_3$) δ0.29 (s, 6H), 1.7-1.9 (m, 4H), 2.0-2.4 (m, 6H), 5.22 (bs, 1H), 7.3-7.6 (m, 5H). The compound was identified by the comparison with a sample prepared from diethyl phosphate of 1-hydroxymethyl-1-cyclopentene and $PhMe_2SiAlEt_2$ according to our previous work. Y. Okuda, M. Sato, K. Oshima, and H. Nozaki, Tetrahedron Lett., **24**, 2015 (1983).
6. IR (neat) 1635, 1420, 1245, 1115, 815, 690 cm^{-1}; NMR (CCl_4) δ0.30 (s, 6H), 1.4-1.8 (m, 2H), 1.9-2.4 (m, 2H), 5.40 (bs, 1H), 7.1-7.5 (m, 5H).
7. E. Negishi, L. D. Boardman, J. M. Tour, H. Sawada, and C. L. Rand, J. Am. Chem. Soc., **105**, 6344 (1983).
8. The reaction of **6** (Y = H) proceeded fast at 0°C and intermediacy of alkenyl metal compound could not be detected by TLC. Cyclopropylidene compounds could be formed by the same addition-substitution sequence as the formation of 4 to 6 membered ring products. We are tempted to assume that the cyclobutene **8** arises from a radical intermediate **9** cyclizing to give the four membered ring. The Baldwin's rule prefers 4-Endo-Dig mode rather than 3-Exo-Dig (J. E. Baldwin, J. Chem. Soc., Chem. Commun., **1976**, 734; A. L. J. Beckwith, Tetrahedron, **37**, 3073 (1981)).



9. The starting material was prepared according to the following sequence: (1) addition of dibromocarbene to 1,5-cyclooctadiene to give mono-dibromocyclopropane, (2) hydroboration of olefin linkage followed by oxidative workup to alcohol, (3) treatment with ^nBuLi at -78°C to allenic alcohol.
10. ^{13}C-NMR ($CDCl_3$) δ 24.0, 27.2, 31.5, 32.6, 37.1, 38.3, 38.4, 43.3, 213.6. The compound was identical with a sample prepared from hydrogenation of 5,6,7,8-tetrahydroindanone-5. R. L. Augustine and A. D. Broom, J. Org. Chem., **25**, 802 (1960); T. L. Macdonald and S. Mahalingam, J. Am. Chem. Soc., **102**, 2113 (1980).
11. As allenic phosphate was not stable, the crude product was used without further purification. IR (neat) 1590, 1420, 1245, 1105, 760, 725, 690 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.35 (s, 6H), 1.0-2.5 (m, 12H), 6.05 (t, J = 7.8 Hz, 1H), 7.2-7.6 (m, 5H); MS m/z (%) 256 (M^+, 2), 241 (3), 135 (100), 90 (62).

(Received in Japan 3 March 1984)