

STERESELECTIVE INTRAMOLECULAR ADDITION OF A GRIGNARD REAGENT
 TO THE TERMINAL TRIMETHYLSILYLETHENE MOIETY

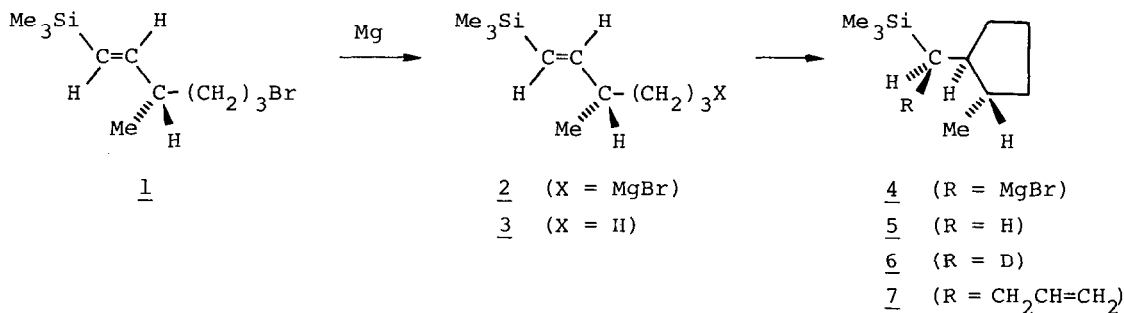
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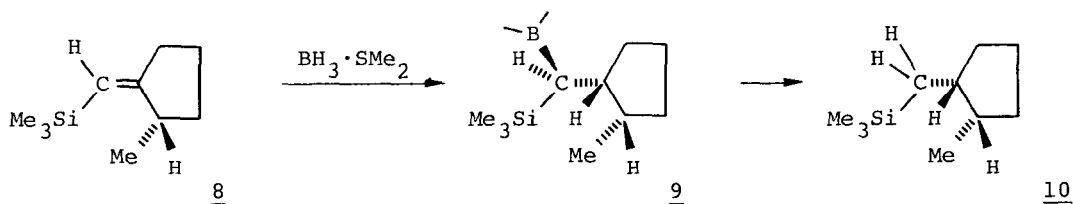
Abstract - Reaction of (E)-6-bromo-3-methyl-1-trimethylsilyl-1-hexene with magnesium produces corresponding Grignard reagent which intramolecularly adds to the silylethene moiety from the less hindered side affording a single stereoisomer.

Intramolecular carbometallation with magnesium, aluminium, or other key metals is an important synthetic tool.¹⁻³ Cyclization of a Grignard reagent reacting with the terminal trimethylsilylethyne moiety has been shown to be a promising means of stereoselective construction of alkylidenecyclopentanes.³ Further extension of the reaction to a silylethene substrate should provide access a cycloalkane having diastereocontrolled substituents, an example of which is described in this paper.

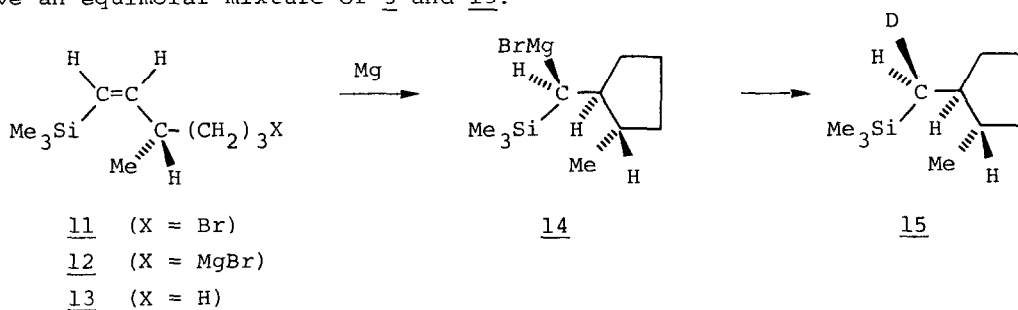
To a mixture of magnesium (0.15 g, 6.2 mmol) and 5 mL of THF (E)-6-bromo-3-methyl-1-trimethylsilyl-1-hexene (1, 1.00 g, 4.02 mmol)⁴ was added and resulting mixture was stirred at 67°C for 6 h. The initially produced Grignard reagent 2 is cyclized to 4 by intramolecular carbometallation in suprafacial and 5-Exo-Trig manner upon heating. Treatment of the reaction mixture containing 4 with water gave trans-1-methyl-2-trimethylsilylmethylcyclopentane (5)^{5,6} in 81% yield, with D₂O monodeuterated product 6, and with allyl bromide stereospecifically allylated product 7 in 93% yield.^{7,8}



Stereochemistry of 5 was determined by the comparison of proton nmr and gas chromatogram with those of the authentic sample 10 obtained from alkylidene-cyclopentane 8 by hydroboration followed by protonolysis.⁹



Similar reaction of (Z)-6-bromo-3-methyl-1-trimethylsilyl-1-hexene (11)¹⁰ gave a mixture of 6 and the diastereomer 15 in about 1:1 ratio. This result is explained by the partial isomerization of 12 to 2 before cyclization. In fact treatment of 11 with magnesium for 30 min at 67°C followed by hydrolysis gave an equimolar mixture of 3 and 13.



The highly diastereoselective intramolecular carbometallation as exemplified by the transformation of 1 into 4 will find synthetic applications to constructing a single diastereomer having three adjacent asymmetric centers.¹¹

REFERENCES AND NOTES

- (1) J. F. Normant and A. Alexakis, *Synthesis*, 841 (1981).
- (2) J. A. Miller and E. Negishi, *Israel J. Chem.*, **24**, 76 (1984).
- (3) S. Fujikura, M. Inoue, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, **25**, 1999 (1984) and references cited therein.
- (4) Prepared from the corresponding acetylenic bromide by hydrosilation.
- (5) NMR in this paper: proton, 200 MHz, CDCl₃, δ ppm from internal TMS, J in Hz.
- (6) 5: NMR 0.00 (s, 9H), 0.26 (dd, J=10.2, 14.4, 1H), 0.84 (dd, J=2.6, 14.4, 1H), 0.92 (d, J=6.2, 3H), 1.02-1.28 (m, 4H), 1.46-1.61 (m, 2H), 1.73-1.89 (m, 2H).
- (7) 6: NMR 0.84 (d, J=2.5 Hz, 1H) and no signal at 0.26.
- (8) 7 containing ca 20% isomer. NMR 0.04 (s, 9H), 0.93 (d, J=6.2, 3H), 1.04-1.25 (m, 1H), 1.27-1.88 (m, 6H), 1.96-2.37 (m, 2H), 3.88-5.10 (m, 2H), 5.70-5.90 (m, 1H).
- (9) 9 was obtained in 27% overall yield. NMR 0.05 (s, 9H), 0.39 (dd, J=9.4, 14.4, 1H), 0.58 (dd, J=4.8, 14.4, 1H), 0.75 (d, J=6.8, 3H), 1.16-1.32 (m, 3H), 1.46-1.94 (m, 5H).
- (10) Prepared from the corresponding silylacetylene by hydroboration-protonolysis.
- (11) The authors thank the Ministry of Education, Science, and Culture for Grant-in-Aid for Special Project Research (59104002).

(Received in Japan 7 February 1985)