

STEREOSELECTIVE SYNTHESIS OF VINYLSILANES FROM ALKYNYSILANES VIA  
HYDROMAGNESIATION. APPLICATION TO A SYNTHESIS OF 7(E)-DODECENYL  
ACETATE AND DIHYDROJASMONE

Fumie Sato,\* Hiroshi Watanabe, Youichi Tanaka, Takafumi Yamaji,  
and Masao Sato

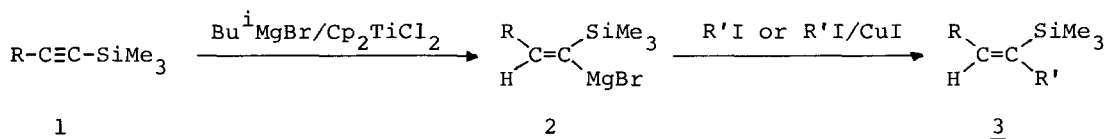
Department of Chemical Engineering, Tokyo Institute of Technology,  
Meguro, Tokyo 152, Japan

Summary: Hydromagnesiation of 1-trimethylsilyl-1-alkynes with isobutylmagnesium bromide in the presence of a catalytic amount of  $\text{Cp}_2\text{TiCl}_2$  followed by treatment of the resulting vinyl Grignard reagents with alkyl iodides and copper iodide affords (Z)-1,2-dialkyl-vinylsilanes in excellent yields. The utility of the reaction sequence is illustrated by a simple synthesis of 7(E)-dodecenyl acetate and dihydrojasmone.

Vinylsilanes have been shown to be useful precursors for carbonyl compounds, vinyl halides, and olefins of predictable stereochemistry.<sup>1</sup> Prompted by the reports on preparation of 1,2-disubstituted vinylsilanes from alkynylsilanes via hydroalumination<sup>2</sup> or hydroboration<sup>3</sup>, we would like to report a novel and generally applicable procedure for the stereoselective synthesis of 1,2-dialkyl-vinylsilanes, which is based on hydromagnesiation of alkynylsilanes to vinyl Grignard reagents and the following coupling with alkyl halides.

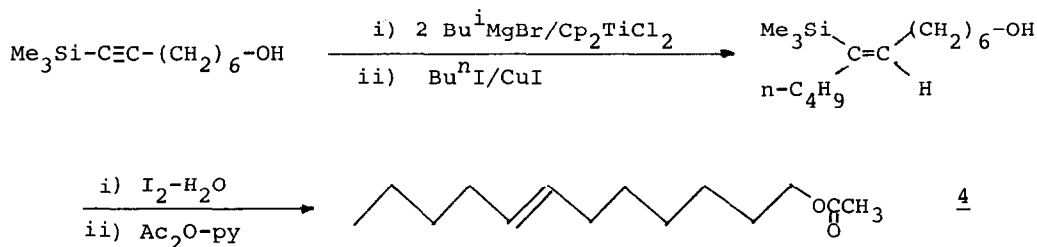
The  $\text{Cp}_2\text{TiCl}_2$  catalyzed hydromagnesiation of 1-trimethylsilyl-1-hexyne (1,  $\text{R} = \text{n-C}_4\text{H}_9$ ) with isobutylmagnesium bromide in ether (25°C, 6 h) proceeded in a

stereo and regioselective manner affording vinyl Grignard reagent 2 ( $R = n\text{-C}_4\text{H}_9$ ).<sup>4</sup> After removal of the ether under reduced pressure (r.t., 2h/1 Torr), the residue was dissolved in THF and treated with methyl iodide at 0°C for 10 min and then at room temperature for 2h. The usual work-up and distillation afforded the coupling product 3 ( $R = n\text{-C}_4\text{H}_9$ ,  $R' = \text{CH}_3$ ) in 91% yield (Z/E = 97/3).<sup>5</sup> Similarly, reaction of 2 ( $R = n\text{-C}_4\text{H}_9$ ) with allyl iodide in THF (r.t., 5h) gave the coupling product 3 ( $R = n\text{-C}_4\text{H}_9$ ,  $R' = \text{CH}_2=\text{CHCH}_2$ ) in 89% yield.<sup>6</sup> The reagent 2 was found to present low reactivity with alkyl halides other than methyl iodide and allyl halides, however, it was readily alkylated by alkyl iodides in THF in the presence of CuI.<sup>7</sup> Thus, with butyl iodide and 10% CuI, 2 ( $R = n\text{-C}_4\text{H}_9$ ) gave 3 ( $R = R' = n\text{-C}_4\text{H}_9$ ) [Z/E = 98/2]<sup>5</sup> in 87% yield.<sup>8</sup>

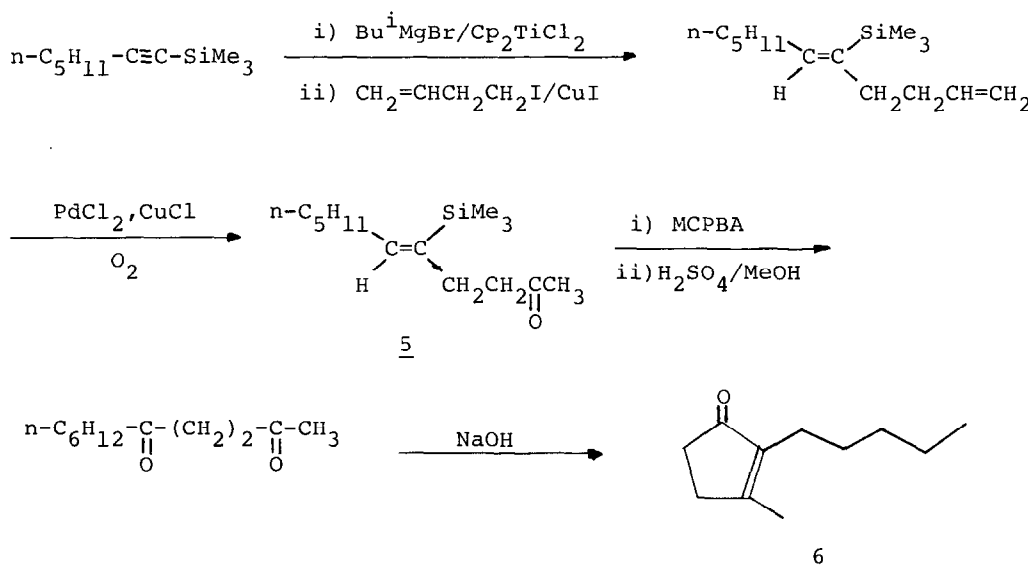


This synthetic method of 1,2-dialkylvinylsilanes was adapted to the synthesis of sex pheromone of the false coddling moth (*Argyroprocta leucotreta*), 7(E)-dodecenyl acetate 4, and dihydrojasmonone 6.

Hydromagnesiation of 8-trimethylsilyl-7-octyn-1-ol with two equivalents of isobutylmagnesium bromide in the presence of  $\text{Cp}_2\text{TiCl}_2$  followed by treatment with butyl iodide and CuI in THF afforded vinylsilane 3 [ $R = -(\text{CH}_2)_6\text{-OH}$ ,  $R' = n\text{-C}_4\text{H}_9$ ] in 84% yield. Desilylation with iodine<sup>9</sup> followed by acetylation gave the pheromone 4 (E/Z = 96/4)<sup>10</sup> in 84% yield.<sup>11</sup>



Dihydrojasmonone 6 was prepared in the following way. Treatment of alkenyl Grignard reagent 2 ( $R = n\text{-C}_5\text{H}_{11}$ ), prepared from 1-trimethylsilyl-1-heptyne (1,  $R = n\text{-C}_5\text{H}_{11}$ ), with 3-butenyl iodide and CuI afforded vinylsilane 3 ( $R = n\text{-C}_5\text{H}_{11}$ ,  $R' = \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ) in 86% yield. Palladium catalyzed oxidation of 3 gave the methyl ketone 5 in 74% yield.<sup>12,13</sup> Epoxidation of 5 with m-chloroperbenzoic acid in methylene chloride followed by refluxing with 20% methanolic-sulfuric acid for 13 h afforded 2,5-undecadione in near quantitative yield<sup>14</sup> which was cyclized in base to dihydrojasmonone 6.<sup>15</sup>



## References

1. E. Colvin, "Silicon in Organic Synthesis", Butterworths, London, Chap. 7, 1981
2. J.J. Eisch, G.A. Damasevitz, J. Org. Chem., 41, 2214 (1976). K. Uchida, K. Utimoto, H. Nozaki, *ibid.*, 41, 2215 (1976). G. Stork, M.E. Jung, E. Colvin, Y. Noel, J. Am. Chem. Soc., 96, 3684 (1978). G. Zweifel, W. Lewis, J. Org. Chem., 43, 2739 (1978).
3. K. Uchida, K. Utimoto, H. Nozaki, J. Org. Chem., 41, 2941 (1976); Tetrahedron, 33, 2987 (1977).
4. F. Sato, H. Ishikawa, M. Sato, Tetrahedron Lett., 22, 85 (1981).
5. The stereochemistry was determined by g.l.c. after desilylation with iodine<sup>9</sup>

6. Allyl chloride and allyl bromide also afforded the coupling product.
7. C. Huynh, G. Linstrumelle, *Tetrahedron Lett.*, 1073 (1979).
8. The following procedure is representative. To a solution of isobutylmagnesium bromide in ether (13 ml of a 0.84 M solution; 10.9 mmol) was added  $\text{Cp}_2\text{TiCl}_2$  (0.12 g, 0.5 mmol) at 0°C under argon, and the mixture was stirred for 30 min at that temperature. To this solution was added 1-trimethylsilyl-1-hexyne (1.5 g, 9.7 mmol), and the mixture was stirred for 6h at 25°C. After removal of the ether under reduced pressure (2h, r.t./2 Torr), the residue was dissolved in THF (15 ml), cooled to -30°C, and treated with butyl iodide (2.1 g, 11 mmol) and CuI (0.18 g, 1.0 mmol). The reaction mixture was brought to room temperature gradually and stirred for 2 h. The usual work-up and distillation gave 5-trimethylsilyl-5(Z)-decene (1.8 g, 87% yield) [b.p. 80-81°C/5 Torr].
9. K. Utimoto, M. Kitai, H. Nozaki, *Tetrahedron Lett.*, 2825 (1975).
10. The stereochemistry was established by preparing epoxide from 4 (m-chloro-perbenzoic acid in  $\text{CH}_2\text{Cl}_2$ ) and by g.l.c. comparison with authentic samples.
11. R.S. Berger, T.D. Canerday, *J. Econ. Entomol.*, 61, 452 (1968). H.E. Henderson, F.L. Warren, *J. South African Chem. Inst.*, 23, 9 (1970). See also ref. 3.
12. J. Tsuji, I. Shimizu, K. Yamamoto, *Tetrahedron Lett.*, 2975 (1976).
13. Recently, T. Nakai, et al. have synthesized 5 via an entirely different route: K. Mikami, N. Kishi, T. Nakai, *Chem. Lett.*, 1643 (1982).
14. G. Stork, E. Colvin, *J. Am. Chem. Soc.*, 93, 2080 (1971). G. Stork, M.E. Jung, *ibid.*, 96, 3682 (1974).
15. R.A. Ellison, *Synthesis*, 397 (1973).

(Received in Japan 24 November 1982)