Tetrahedron Letters,Vol.24,No.10,pp 1041-1044,1983
Printed in Great Britain
0040-4039/83/101041-04$03.00/0

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

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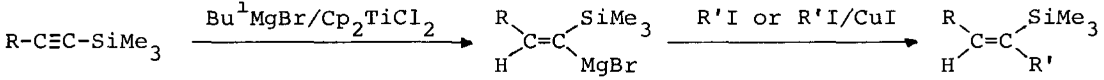
Summary: Hydromagnesiation of 1-trimethylsilyl-1-alkynes with isobutylmagnesium bromide in the presence of a catalytic amount of Cp_2TiCl_2 followed by treatment of the resulting vinyl Grignard reagents with alkyl iodides and copper iodide affords (Z)-1,2-dialkylvinylsilanes in excellent yields. The 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.[1] Prompted by the reports on preparation of 1,2-disubstituted vinylsilanes from alkynylsilanes via hydroalumination[2] or hydroboration[3], we would like to report a novel and generally applicable procedure for the stereoselective synthesis of 1,2-dialkylvinylsilanes, which is based on hydromagnesiation of alkynylsilanes to vinyl Grignard reagents and the following coupling with alkyl halides.

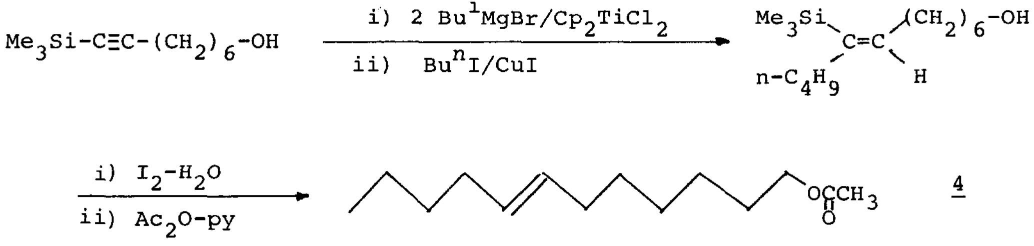
The Cp_2TiCl_2 catalyzed hydromagnesiation of 1-trimethylsilyl-1-hexyne (1, $R = n\text{-}C_4H_9$) with isobutylmagnesium bromide in ether (25°C, 6 h) proceeded in a stereo and regioselective manner affording vinyl Grignard reagent 2 (R = n-C_4H_9).[4] After removal of the ether under reduced pressure (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-C_4H_9, R' = CH_3) in 91% yield (Z/E = 97/3).[5] Similarly, reaction of 2 (R = n-C_4H_9) with allyl iodide in THF (r.t., 5h) gave the coupling product 3 (R = n-C_4H_9, R' = CH_2=$CHCH_2$) in 89% yield.[6] 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.[7] Thus, with butyl iodide and 10% CuI, 2 (R = n-C_4H_9) gave 3 (R = R' = n-C_4H_9) [Z/E = 98/2][5] in 87% yield.[8]



1 2 3

This synthetic method of 1,2-dialkylvinylsilanes was adapted to the synthesis of sex pheromone of the false colding moth (Argyroploce leucotrete), 7(E)-dodecenyl acetate 4, and dihydrojasmone 6.

Hydromagnesiation of 8-trimethylsilyl-7-octyn-1-ol with two equivalents of isobutylmagnesium bromide in the presence of Cp_2TiCl_2 followed by treatment with butyl iodide and CuI in THF afforded vinylsilane 3 [R = $-(CH_2)_6-OH$, R' = n-C_4H_9] in 84% yield. Desilylation with iodine[9] followed by acetylation gave the pheromone 4 (E/Z = 96/4)[10] in 84% yield.[11]



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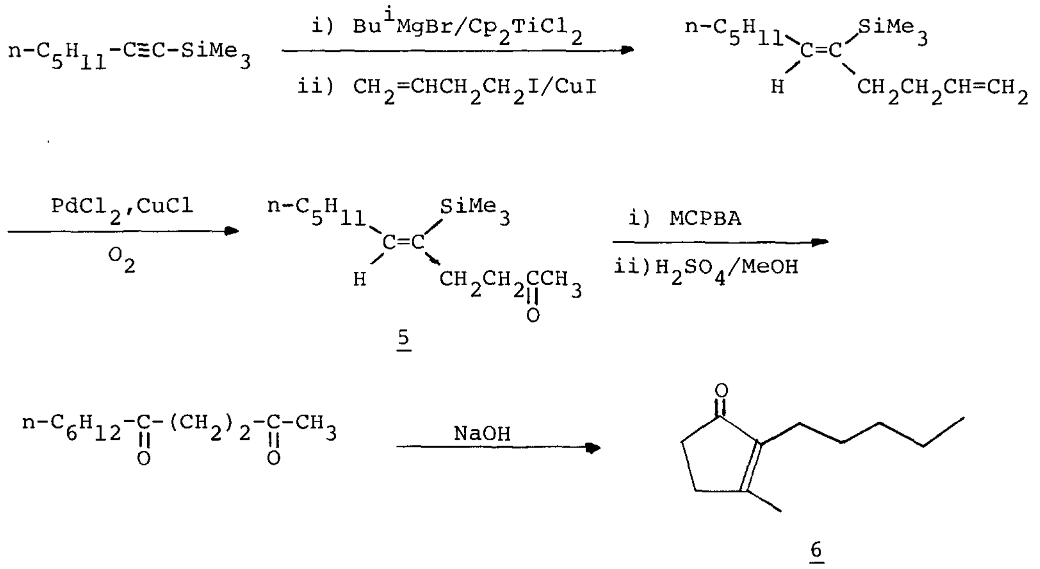
Dihydrojasmone 6 was prepared in the following way. Treatment of alkenyl Grignard reagent 2 (R = n-C_5H_{11}), prepared from 1-trimethylsilyl-1-heptyne (1, R = n-C_5H_{11}), with 3-butenyl iodide and CuI afforded vinylsilane 3 (R = n-C_5H_{11}, R' = $CH_2CH_2CH{=}CH_2$) in 86% yield. Palladium catalyzed oxidation of 3 gave the methyl ketone 5 in 74% yield.[12,13] 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[14] which was cyclized in base to dihydrojasmone 6.[15]



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5. The stereochemistry was determined by g.l.c. after desilylation with iodine[9]

6. Allyl chloride and allyl bromide also afforded the coupling product.
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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 Cp_2TiCl_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].
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10. The stereochemistry was established by preparing epoxide from 4 (m-chloroperbenzoic acid in CH_2Cl_2) and by g.l.c. comparison with authentic samples.
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(Received in Japan 24 November 1982)