Tetrahedron Letters No. 12, pp 1073 - 1076.
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0040-4039/79/0315-1073$02.00/0

A new synthesis of substituted vinylsilanes and vinyl iodides

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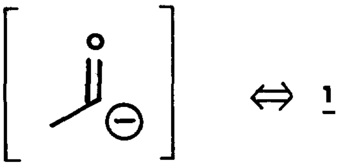
Vinylsilanes have been shown to be useful precursors for carbonyl compounds, vinylhalide and olefins of predictable stereochemistry [1].

We would like to report the efficient preparation of substituted vinylsilanes

1) via the copper-catalysed reaction of the easily obtainable silylvinyl Grignard reagents 1 and 4.

2) via the palladium-catalysed reaction of Grignard reagents with haloalkenylsilanes 3 and 6.

The reagents 1 and 4 represent respectively the synthetic equivalents of the acylanion



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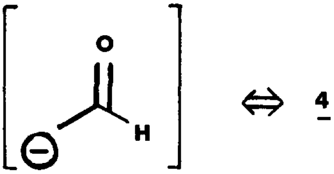

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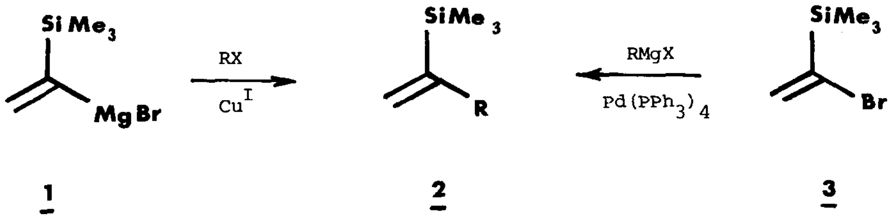
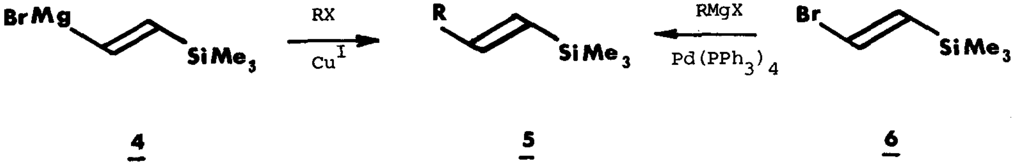
7 and of the aldehyde enolate 8 ; they are synthetically more attractive than the corresponding lithium reagents [2] since they are quantitatively prepared [3,4] on a large scale from the halides 3 [3] and 6 [5].

These Grignard reagents 1 and 4 were found to present low reactivity [6] with alkylhalides. However, when treated with copper iodide [7] (10%), they were alkylated in high yield by alkyl iodides , bromides and tosylates. Thus, when the reagent 1 (1.3 equiv.) in THF was treated with octyl iodide [8] (1 equiv.) and copper iodide (10%) at 0°C for 1 hr, pure 2-trimethylsilyl-decene 2 was obtained in 97% yield [9].

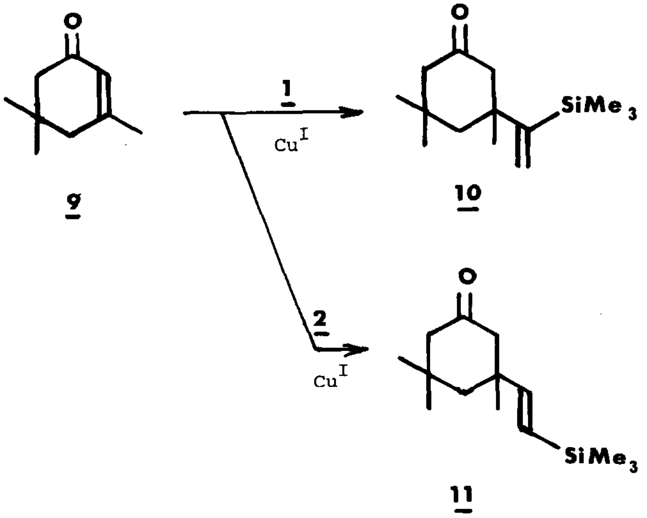


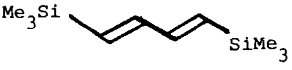


R = n-C_8H_{17}

In the same way, the reagent 4, obtained quantitatively from the (E)-bromosilane 6 when treated with copper iodide and an alkyl iodide [10] gave (77%) [11] the (E)-alkenylsilane 5 in 95% purity [12].

Under the copper catalysed conditions, the Grignard reagents 1 and 4 can add in a 1-4 fashion to conjugated ketones[2a]. Thus, with isophorone 9, they gave ketones 10 (80%) and 11 (62%). With reagent 4, a lower yield was observed due to formation (24%) of a side product 12.





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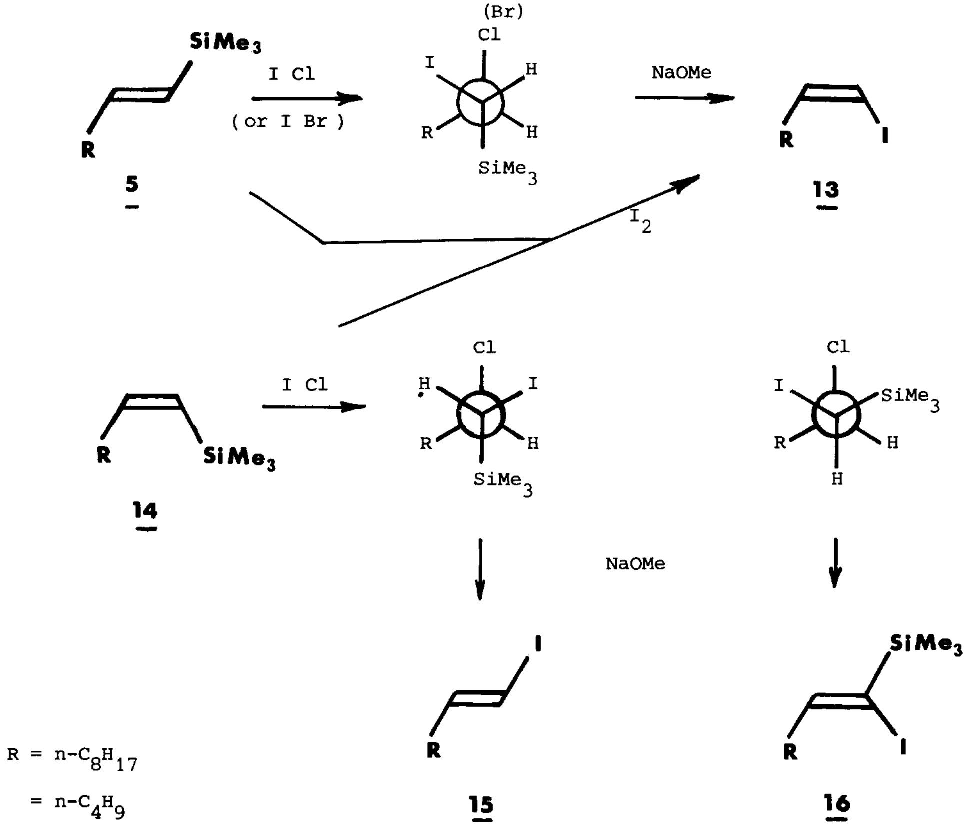
The alkenyl silanes 2 and 5 were also obtained by the palladium catalysed reaction [13] of a Grignard reagent with the halides 3 and 6. Thus, when bromosilane 3 (1 equiv.) was treated sequentially with tetrakis (triphenylphosphine) palladium (0.1 equiv.) and n-octylmagnesium bromide (2 equiv.) in benzene-tetrahydrofuran at 80°C for 4 hr, pure vinylsilane 2 was obtained in 75% yield. The bromosilane 6 was found to be more reactive : under the palladium catalysed conditions, with n-octylmagnesium bromide, it gave, within 1 hr at room temperature, 53% of pure silane 5.

By treatment with halogens [1,14,15], vinylsilanes are useful precursors of vinylhalides. We have found that the pure trans vinylsilane 5 [16], treated with iodine in methylene chloride (2 hr at room temperature) gave [17] (65%) the cis vinyliodide 13 (containing 5% of 1-decene). When treated with iodine monochloride [18], followed by a methanolic solution of sodium methoxide 1.1 N (1 hr, room temperature), the vinylsilane 5 gave [19] (77%) the same iodide 13 in high purity (2% of the trans isomer 15 were detected).



The reaction of the vinylsilane 14 with iodine also gave the cis iodide 13 [14a] (40%) ; however, when treated with iodine monochloride, then with sodium methoxide as above, a mixture (3 : 1) of the trans iodide 15 and iodosilane 16 was obtained. These compounds were separated by distillation. The stereochemistry of iodosilane 16 was assigned by metallation with butyllithium and hydrolysis to give the trans vinylsilane 5.

The stereoselective formation of cis vinyliodide 13 from 5 and 14 contrasts with the retention of configuration observed for some reactions of iododesilylation [20] reported in the literature.

Notes and references

(1) E.W. COLVIN, Chem. Soc. Rev., 7, 15 (1978).

(2) These organometallics cannot be obtained from the corresponding halides 3 and 6 by reaction with lithium, but were prepared with 2 equivalents of t-butyllithium : a) R.K. BOECKMAN, Jr, and K.J. BRUZA, Tetrahedron Letters, 3365 (1974) ; b)B.T. GROBEL and D. SEEBACH, Chem. Ber., 110, 867 (1977).

(3) A. OTTOLENGHI, M. FRIDKIN and A. ZILKHA, Can. J. Chem., 41, 2977 (1963).

(4) a) G. STORK and B. GANEM, J. Amer. Chem. Soc., 95, 6152 (1973) ;
b) A.G. BROOK and J.M. DUFF, Can. J. Chem., 51, 2024 (1973).

(5) O.G. YAROSH, V.K. VORONOF and N.V. KOMAROV, Isv. Akad. Nauk. SSSR Ser. Khim., 875 (1971); English Edition, 795 (1971) .

(6) with n-octyliodide in THF, after 4 hr at room temperature, the reagent 1 gave 12% of alkylated product 2. In the same conditions, 25% of 5 were obtained from 4.

(7) For a review on copper reagents, see G.H. POSNER, Organic Reactions, 22, 253 (1975).

(8) The alkylated product 2 was also obtained with n-octyltosylate (2 hr at 0°C, 83% yield) and with n-octylbromide (16 hr at room temperature, 91% yield).

(9) The yields given are for distilled products. All new compounds exhibited satisfactory spectral and physical properties.

(10) The alkylated product 5 was also obtained with n-octyltosylate (3 hr at 0°C, 40% yield) and with n-octylbromide (4 hr at 0°C then 2 hr at room temperature, 38% yield).

(11) 10% of the dimer 12, easily separated by distillation, were formed.

(12) 5% of the cis isomer 14 (R = nC_8H_{17}) were formed.

(13) For the stereospecific synthesis of olefins by the palladium catalysed reaction of Grignard reagents with iodoalkenes, see : H.P. DANG and G. LINSTRUMELLE, Tetrahedron Letters, 191 (1978), and references therein.

(14) a) R.B. MILLER and T. REICHENBACH, Tetrahedron Letters, 543 (1974) ;
b) R.B. MILLER and G. McGARVEY, Synthetic Communications, 7, 475 (1977).

(15) The addition of iodine monochloride to vinylsilanes and the subsequent transformation of the adduct into vinyliodides, when treated with potassium fluoride, has recently been reported : R.B. MILLER and G. McGARVEY, Synthetic Communications, 8, 291 (1978).

(16) A new preparation of (E) vinylsilanes has been reported : M. OBAYASHI, K. UTIMOTO and H. NOZAKI, Tetrahedron Letters, 1805 (1977).

(17) An unidentified product (3%) was also formed.

(18) In the same conditions, iodine monobromide led to 60% of cis vinyl iodide 13.

(19) 4% of (1 E)-chloro-decene were detected.

(20) T.H. CHAN, P.W.K. LAV and W. MYCHAJLOWSKIJ, Tetrahedron Letters, 3317 (1977) ; K. UTIMOTO, M. KITAI and H. NOZAKI, Tetrahedron Letters, 2825 (1975) ; K. UTIMOTO; M. KITAI, M. NARUSE and H. NOZAKI, ibid., 4233 (1975).

(Received in UK 5 December 1978)