

Nickel-catalysed Coupling of Dithioacetals with Silylmethylmagnesium Chloride. A Simple Synthesis of Allylsilanes

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Allylsilanes are conveniently synthesized from the reaction of dithioacetals of ketones with trimethylsilylmethylmagnesium chloride.

Allylsilanes are increasingly useful in organic synthesis.¹ Direct reaction of silylmethylmagnesium halide reagent with carbonyl compounds, known as Peterson olefination, affords exclusively the corresponding desilylated alkenes.² Since the affinity between silicon and sulphur would be much less than that between silicon and oxygen, the sulphur analogue of a carbonyl equivalent may behave differently towards silylmethyl Grignard reagents. Recently we reported that dithioacetals can couple with Grignard reagents in the presence of a nickel catalyst to give the alkylated alkene.³ The organonickel intermediate (1) may undergo β -elimination in either direction leading to a mixture of alkenes. We felt that the regioselectivity of this elimination step may depend on the steric environment of (1). Hence, the introduction of a sterically bulky trimethylsilyl group in the starting Grignard

reagent would lead to the intermediate (2) which may yield allylsilanes selectively.

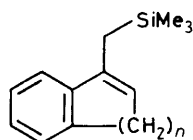
In a typical procedure, a mixture of dithioacetal, $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (3 equiv.), and $\text{NiCl}_2(\text{PPh}_3)_2$ (5 mol%) in ether-benzene was heated under reflux overnight. After work-up and chromatographic separation, the corresponding allylsilane was obtained.[†] The results are summarised in Table 1.

As can be seen from Table 1, dithioacetals afforded the corresponding allylsilanes in satisfactory yields. Thus, indanone dithioacetal (3) afforded (5) in 71% yield. Tetralone derivative (4) gave similar results. In the acyclic substrates (7–10), the reactions yielded predominantly allylsilanes. Vinylsilanes[‡] were obtained as side products. The regioselectivity of the reaction can be understood within the framework of the steric requirement in the elimination step of the intermediate (2). It is noteworthy that no desilylated products were obtained at all from these reactions.⁴

Steric environment on the aryl group may also affect the regiochemistry of the reaction. Thus, more sterically crowded substrate (10) gave less selectively a mixture of (14) and (18). Preliminary examination showed that the regioselectivity was



(1) R, R' = H, Alkyl, Aryl

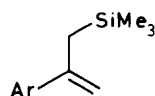
(2) R = H, R' = Me_3Si (3) $n = 1$ (4) $n = 2$ (5) $n = 1$ (6) $n = 2$ 

(7) Ar = Ph

(8) Ar = 2-Fluorenyl

(9) Ar = 4-Ph-C₆H₄

(10) Ar = 1-Naphthyl

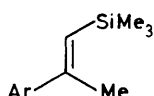


(11) Ar = Ph

(12) Ar = 2-Fluorenyl

(13) Ar = 4-Ph-C₆H₄

(14) Ar = 1-Naphthyl

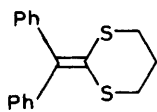


(15) Ar = Ph

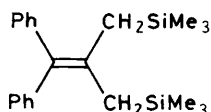
(16) Ar = 2-Fluorenyl

(17) Ar = 4-Ph-C₆H₄

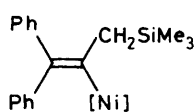
(18) Ar = 1-Naphthyl



(19)



(20)



(21)

Table 1. Coupling of dithioacetals with $\text{Me}_3\text{SiCH}_2\text{MgCl}$.

Dithioacetal	Product	% Yield
(3)	(5)	70
(4)	(6)	71
(7)	(11) and (15) (85:15)	82
(8)	(12) and (16) (90:10)	72
(9)	(13) and (17) (89:11)	81
(9) ^a	(13) and (17) (80:20)	69
(10)	(14) and (18) (62:38)	60
(10) ^a	(14) and (18) (27:73)	89
(19)	(20)	48

^a The reaction was carried out in ether-tetrahydrofuran (THF).

[†] Selected spectroscopic data. ¹H n.m.r. (δ , CDCl_3 , Me_4Si as external standard): (5): -0.15 (s, 9H), 1.75 – 1.88 (m, 2H), 3.05 – 3.18 (m, 2H), 5.82 (br s, 1H), 6.85 – 7.33 (m, 4H). (6): -0.22 (s, 9H), 1.72 (s, 2H), 2.68 – 1.82 (m, 4H), 5.43 (t, J 4 Hz, 1H), 6.78 – 7.0 (m, 4H). (11): -0.02 (s, 9H), 3.75 (br s, 2H), 4.92 (br s, 1H), 5.15 (br s, 1H), 7.17 – 7.42 (m, 5H). (12): -0.07 (s, 9H), 2.07 (br s, 2H), 3.86 (s, 2H), 4.86 (br s, 1H), 5.17 (br s, 1H), 7.16 – 7.82 (m, 7H). (13): -0.02 (s, 9H), 2.08 (br s, 2H), 4.95 (br s, 1H), 5.25 (br s, 1H), 7.12 – 7.78 (m, 9H). (14): -0.15 (s, 9H), 2.08 (br s, 2H), 4.93 (br s, 1H), 5.13 (br s, 1H), 7.03 – 8.16 (m, 7H).

[‡] With the exception of (18) only one stereoisomer was detected. The stereochemical assignments are based on nuclear Overhauser effect experiments. In the n.m.r. spectra, vinylsilanes (15)–(17) showed three singlets at δ 0.23–0.25 (9H), 2.20–2.28 (3H), and 5.95–6.03 (1H). The *E/Z* ratio in (18) was found to be 2.6:1. The *E* isomer exhibited absorptions at 0.23 (s, 9H) and 5.55 (s, 1H) and the *Z* isomer at -0.40 (s, 9H) and 5.83 (s, 1H) in addition to other signals due to methyl groups (both at 2.20) and aromatic protons. The poor regio- and stereoselectivity in the reaction of (10) is understandable because the intermediate (2, Ar = 1-naphthyl) is too crowded.

very much solvent dependent. In general, the yield of allylsilane increased when a non-polar solvent such as benzene was employed as the solvent. It is noted that the selectivity was reversed when the reaction of (10) was carried out in ether-tetrahydrofuran (THF) solvent.

The reaction with ketene dithioacetal (19), gave in 48% yield bis-allylsilane (20). Presumably the intermediate (21) cannot undergo β -elimination but rather proceed *via* a coupling reaction to give (20).⁵

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