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STEREOSELECTIVE SYNTHESIS OF (E)-ALKENYLSILANES FROM ALDEHYDES WITH A REAGENT PREPARED BY CHROMIUM(II) REDUCTION OF $Me_3SiCHBr_2$

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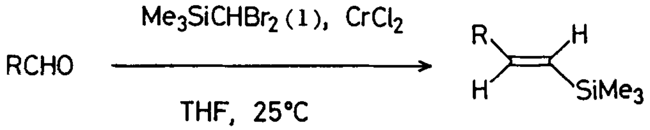
Abstract: Aldehydes are converted to the corresponding (E)-alkenylsilanes with one carbon homologation by means of a gem-dichromium reagent prepared by $CrCl_2$ reduction of $Me_3SiCHBr_2$ in THF. Transformation of aldehydes into alkenyl sulfides is also achieved with a combination of $PhSCHCl_2$ and $CrCl_2$.

Although there are many interesting reactions using alkenylsilanes,[1] most of their precursors are limited to the corresponding acetylenes because of availability of the starting materials and stereoselectivity of the transformations.[2] Attempts to obtain alkenylsilanes from a reaction between aldehydes and a trimethylsilyl-substituted phosphorus ylide, $Me_3SiCH{=}PPh_3$, are not successful.[3] Transformation with $(Me_3Si)_2CHMtl$ via Peterson-type elimination does not give good yields and selectivity.[4] Here we introduce a simple access to an (E)-alkenylsilane from an aldehyde with one carbon homologation by means of a gem-dichromium reagent[5] prepared by $CrCl_2$ reduction of $Me_3SiCHBr_2$ (1).



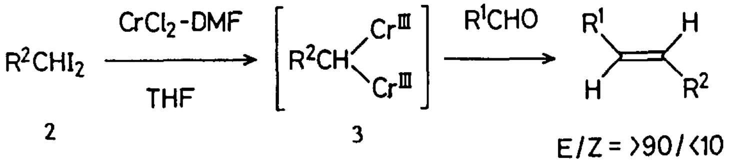
(1)

A solution of benzaldehyde (0.11 g, 1.0 mmol) and 1 (0.49 g, 2.0 mmol)[6] in THF (4 mL) under an argon atmosphere is added at 25°C to a stirring suspension of $CrCl_2$ (purchased from Aldrich Co., 0.98 g, 8.0 mmol) in THF (20 mL). The resulting mixture is stirred at 25°C for 24 h. The color of the mixture changes gradually from gray to brownish purple. The mixture is poured into water (20 mL) and extracted with hexane (2x15 mL). The combined extracts are dried (Na_2SO_4) and concentrated. Purification of the crude product by short column chromatography on silica gel (hexane) affords (E)-β-trimethylsilylstyrene in 82% yield (0.15 g).

The results of the preparation of (E)-alkenylsilanes from aldehydes are shown in Table 1.

Cyclododecanone was recovered after exposure to the reagent at 25°C for 60 h (run 11). Selective transformation of an aldehyde to an (E)-alkenylsilane group in the presence of a ketone or a cyano group was performed (runs 9 and 10).[7]

Two alternative preparations of low valent chromium are examined. A combination of $CrCl_3$ and $LiAlH_4$ can be employed without significant decrease of the yields of alkenylsilanes (run 4). Reaction with a $CrCl_3$-Zn system also produced (E)-1-trimethylsilyl-1-decene in 40% yield along with unchanged nonanal (27% recovery, run 5). Treatment of benzaldehyde with **1** and other low valent metals, such as Zn,[8] Zn-$TiCl_4$,[9] Mg,[8] Sn,[10a] SnF_2,[10b] gave little or none of the desired alkenylsilane.

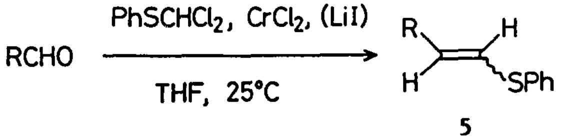


(2)

Recently we reported[5b] that reduction of 1,1-diiodoalkanes **2** proceeds smoothly with $CrCl_2$-DMF (1:1 molar ratio) in THF to give gem-dichromium reagent 3, which react with aldehydes to yield olefins (Eq. 2). Two salient features are worth noting concerning the olefination reaction. i) (E)-Olefins are produced selectively (E/Z=>90/<10) but not exclusively and the E/Z ratio depends on the bulkiness of R^1 and R^2. ii) gem-Diiodo compounds are essential to obtain good yield. For example, reaction of 1,1-diiodoethane with benzaldehyde affords β-methylstyrene (4) in 88% yield, while only 14% of 4 was produced when using 1,1-dibromoethane.

The trimethylsilyl group of **1** plays important roles in the reaction shown in Eq. 1 and overcomes these two drawbacks. Alkenylsilanes having the E-configuration are produced exclusively in all cases, because of the bulkiness of the Me_3Si group. The presence of the Me_3Si group facilitates the reduction of gem-dihalogen compounds with $CrCl_2$. Thus, gem-dibromo compound **1** can be used instead of a diiodo compound.[11]

Transformation of aldehydes into phenyl 1-alkenyl sulfides 5 (E/Z mixture) is also achieved with a combination of $PhSCHCl_2$[12] and $CrCl_2$ in THF (Eq. 3).[13,14]

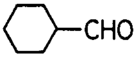
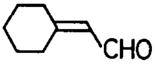
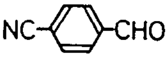


(3)

5

R=Ph, 6 h, 83% (E/Z=82/18)
Oct, 4 h, 68% (E/Z=71/29)

Table 1. Preparation of (E)-alkenylsilanes from aldehydes[a]

Run	Aldehyde	Time/h	Yield/%[b]
1	PhCHO	24	82
2	$Ph(CH_2)_2CHO$	24	86
3	$CH_3(CH_2)_7CHO$	24	82
4		24	80[c]
5		48	40[d]
6		18	81
7	PhCH=CHCHO	18	79
8		18	77
9		16	76[e]
10		24	72
11	(cyclododecanone)	60	recov. 99[f]

a) A mixture of an aldehyde (1.0 mmol) and $Me_3SiCHBr_2$ (2.0 mmol) in THF was treated with $CrCl_2$ (8.0 mmol) at 25°C. b) Yields represent isolated, purified products. c) A combination of $CrCl_3$ (8.0 mmol) and $LiAlH_4$ (4.0 mmol) was used instead of $CrCl_2$. d) As a low-valent chromium, $CrCl_3$ (4.0 mmol)-Zn (6.0 mmol) system was employed. Unchanged nonanal was recovered in 27%. e) See ref. 15. f) See text.

References and Notes

(1) For reviews, see: (a) E. Colvin, "Silicon in Organic Synthesis," Butterworths and Co., London, 1981, Chap. 7, pp. 44-82. (b) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin, 1983, Chap. 7, pp. 79-113.

(2) For preparation of 1-alkenylsilanes from terminal acetylenes or 1-trimethylsilylacetylenes, see: (a) Hydrosilylation: R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961); R. A. Benkeser, R. F. Cunico, S. Dunny, P. R. Jones, and P. G. Nerlekar, *J. Org. Chem*, **32**, 2634 (1967). (b) Hydrogenation: W. P. Weber, A. K. Willard, and H. G. Boettger, *ibid.*, **36**, 1620 (1971). (c) Hydroboration: R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, **1974**, 543. (d) Hydroalumination: K. Uchida, K. Utimoto, and H. Nozaki, *J. Org. Chem.*, **41**, 2215 (1976); J. J. Eisch and G. A. Damasevitz, *ibid.*, **41**, 2214 (1976); R. B. Miller and G. McGarvey,