This article was downloaded by: [University of Arizona] On: 04 February 2015, At: 08:05 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

Preparation of Allenoyltrmethylsilanes

Robert F. Cunico^a & Cui-ping Zhang^a ^a Department of Chemistry Northern, Illinois University DeKalb, IL, 60115, USA Published online: 23 Sep 2006.

To cite this article: Robert F. Cunico & Cui-ping Zhang (1995) Preparation of Allenoyltrmethylsilanes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:4, 503-506, DOI: 10.1080/00397919508011383

To link to this article: http://dx.doi.org/10.1080/00397919508011383

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

PREPARATION OF ALLENOYLTRIMETHYLSILANES

Robert F. Cunico* and Cui-ping Zhang

Department of Chemistry Northern Illinois University DeKalb, IL 60115 USA

ABSTRACT: Dehydrochlorination of 3-chloro-2- or -3-alkenoyltrimethylsilanes with DBU affords the parent 2,3-butadienoyltrimethylsilane, as well as 4-monoalkyl- and 4,4-dialkyl homologues.

Both saturated and unsaturated acylsilanes have become useful components in numerous synthetic applications.¹ However, only one general protocol² (Scheme 1) exists for the preparation of allenoylsilanes, and subsequent chemistry of these species lies largely unexplored.³ We now report an alternative entry to allenoylsilanes (4) based on the availability of chloroketones 2, 3 obtained from monosubstitution of template molecule 1⁴ (Scheme 2, yields of 4a-d indicated). Thus, brief (0.1 h - 1.0 h)

Scheme 1

$$R \xrightarrow{R} OTMS \xrightarrow{1.2 \text{ (BuLi}} R \xrightarrow{R} OTMS \xrightarrow{H_3O^+} R \xrightarrow{R} TMS$$

^{*}To whom correspondence should be addressed.

exposure of 2/3 mixtures (composition immaterial) to DBU under ambient conditions effected smooth dehydrochlorination into the corresponding allenoyltrimethylsilanes 4. Triethylamine was found to be an effective, albeit slower, alternative to DBU for the formation of 4c and 4d, but did not lead to complete conversions for 4a,b, even when employed in large excess.

Scheme 2



During an attempt to isolate a sample of **4a** by preparative gas chromatography, it was found that complete isomerization to 2-trimethylsilylfuran had occurred (Scheme 3). This parallels behavior previously reported for 4-trimethylsilyl-2,3-butadienoyltrimethyl-silane.³ Thermolysis of **4b** (80 °C, 3 h) completely transformed it into 2-propyl-5-trimethylsilylfuran, but **4c** afforded no furan at this or higher temperatures.

Scheme 3



Experimental Section

General: Diethyl ether and THF were distilled from benzophenone sodium ketyl. NMR data were obtained at 4.6T in CDCl3. IR data were obtained from neat films. Column chromatography utilized 70-230 mesh silica gel 60. 1, 2a, 2b+3b and 2c+3c were prepared as reported.⁴ Cyclohexylmagnesium chloride, 2M in ether, was obtained from Aldrich Chemical Co.

4-Methyl-2,3-hexadienoyltrimethylsilane (4c). Except as noted, this procedure is typical of preparations of all **4.** A mixture of **2c/3c** (0.32 g, 1.4 mmol) and 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU)(0.24 g, 1.6 mmol) in 10 mL of ether was stirred 1h at 25 °C. The mixture was partitioned into pentane-water, the organic phase washed with 0.1N HCl and dried (MgSO4). Column chromatography (10% ether-hexane) gave 0.20 g (80%) of **4c**. IR: 1940, 1595, 1245, 845 cm⁻¹. ¹H NMR: δ 0.16 (s, 9H); 1.06 (t, 3H, J = 7 Hz); 1.84 (m, 3H); 2.12 (m, 2H); 5.81 (m, 1H). ¹³C NMR: δ -2.0, 11.8, 18.9, 27.0, 102.6, 105.9, 213.1, 235.8. Anal. Calcd for C10H18OSi: C, 65.87; H, 9.95. Found: C, 65.82; H, 10.05.

2,3-Butadienoyltrimethylsilane (4a). The starting material (**2a**) was isomerically homogenous and was subjected to DBU treatment for 0.5h. The product was short-path distilled, bp 50-55 °C(1 torr). IR: 1940, 1600, 1250, 840 cm⁻¹. ¹H NMR: δ 0.22 (s, 9H); 5.24 (d, 2H, J = 8 Hz); 5.85 (t, 1H, J = 8 Hz). ¹³C NMR: δ -1.8, 80.1, 101.3, 219.9, 234.8. Anal. Calcd for C7H12OSi: C, 59.94; H, 8.63. Found: C, 59.96; H, 8.72.

Attempted preparative gas chromatography (2 ft x 0.25 in 20% SE-30 column, 110 °C; injector, 230 °C, detector, 250 °C) completely converted **4a** into 2-trimethylsilylfuran.⁵

2,3-Heptadienoyltrimethylsilane (4b). Treatment of **2b/3b** with 50% excess DBU was carried out for 10 min. IR: 1945, 1602, 1250, 840 cm⁻¹. ¹H NMR: δ 0.22 (s, 9H); 0.99 (t, 3H, J = 7 Hz); 1.52 (m, 2H); 2.16 (m, 2H); 5.61 (apparent q, 1H, J = 8 Hz); 5.82 (m, 1H). ¹³C NMR: δ -1.9, 13.7, 22.1, 30.3, 95.4, 102.0, 215.3, 235.0. Anal. Calcd for C10H18OSi: C, 65.87; H, 9.95. Found: C, 65.93; H, 9.95.

Heating a solution of **4b** in benzene at reflux for 3h gave only 2-propyl-5trimethylsilylfuran⁶ upon solvent removal; ¹³C NMR: δ -1.0, 14.0, 21.9, 30.5, 105.0, 120.6, 158.1, 161.8. **4,4-Pentamethylene-2,3-butadienoyltrimethylsilane (4d).** Due to purification difficulties, the **2d/3d** mixture was employed as obtained below. Cyclohexylmagnesium chloride (2.4 mL, 4.8 mmol) was added to a mixture of dry CuCN (0.22 g, 2.4 mmol) in 10 mL of THF at -78 °C. After warming to -10 °C and recooling to -78 °C, 0.39 g (2.0 mmol) of **1** was added and the reaction held at -78 °C for 1h. After hydrolysis with HOAc-HOH at -78 °C, the organic phase was isolated in hexane and filtered through florisil. The crude **2d/3d** mixture (0.26 g, 1.1 mmol) was combined with triethylamine (0.11 g, 1.1 mmol) in 5 mL THF and the mixture stirred 5h at 25 °C. Chromatography gave 0.19 g (86%) of **4d**. IR: 1945, 1600, 1250, 840 cm⁻¹. ¹H NMR: δ 0.19 (s, 9H); 1.64 (m, 6H); 2.26 (m, 4H); 5.72 (m, 1H). ¹³C NMR: δ -2.0, 25.6, 26.3, 30.5, 100.6, 106.1, 210.3, 235.1. Anal. Calcd for C12H20OSi: C, 69.17; H, 9.68. Found: C, 68.90; H, 9.88.

References and Notes

- Reviews: (a) Cirillo, P.F. and Panek, J.S., Org. Prep. and Proced. Int., 1992, <u>24</u>, 553.
 (b) Bulman-Page, P.C., Klair, S.S. and Rosenthal, S., Chem. Soc. Rev., 1990, <u>19</u>, 147.
 (c) Ricci, A. and Degl'Innocenti, A., Synthesis, 1989, 647.
- 2. Visser, R.G., Brandsma, L. and Bos, H.J.T., Tetrahedron Lett., 1981, 22, 2827.
- The photolysis of 2,5-bis(trimethylsilyl)furan affords 4-trimethylsilyl-2,3butadienoyltrimethylsilane which thermolyzes to 2,4-bis(trimethylsilyl)furan, but acylsilane formation is restricted to the 2,5-bis(trimethylsilyl) precursor: Barton, T.J. and Hussman, G.P., J. Am. Chem. Soc., 1983, <u>105</u>, 6316.
- 4. Cunico, R.F. and Zhang, C., Tetrahedron Lett., 1992, 33, 6751.
- 5. Wrackmeyer, B. and Nöth, H., Chem. Ber., 1976, 109, 1075.
- 6. Pappalardo, P., Ehlinger, E. and Magnus, P., Tetrahedron Lett., 1982, 23, 309.

(Received in the USA 16 June 1994)