Pergamon

Tetrahedron Letters, Vol. 35, No. 13, pp. 2081-2082, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0225-M

3-Iodopropenoylsilane: a Further Step in the Chemistry of Unsaturated Acylsilanes

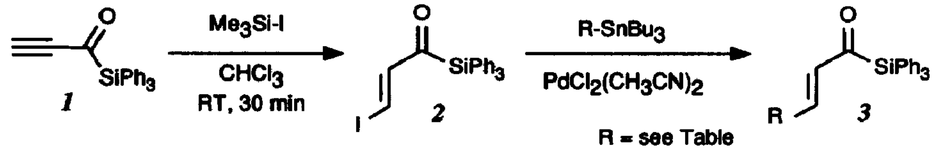
Alessandro Degl'Innocenti[*a], **Antonella Capperucci**[b], **Laura Bartoletti**[b], **Alessandro Mordini**[c], **Gianna Reginato**[c].

[a]*Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, I-85100 Potenza, Italy*
[b]*Dipartimento di Chimica Organica and* [c]*Centro CNR Composti Eterociclici, Via G. Capponi 9, I-50121 Firenze, Italy*

***Abstract**: (E)-3-iodo propenoyltriphenylsilane 2 undergoes smooth coupling reactions with a variety of unsaturated organostannanes to afford polyunsaturated acylsilanes.*

Acylsilanes are versatile reagents, whose popularity has been growing during last years, due to their ability to act as effective *building blocks* in organic synthesis[1]. Our interest in the chemistry of such compounds has recently focused on unsaturated acylsilanes, like ethylenic and acetylenic derivatives[2], a class of compounds that, beside undergoing smooth uncatalysed Michael type additions with several silylated nucleophiles[2], proved more recently very efficient tools in the stereopredetermined synthesis of polyenals and polyenes through carbocupration[3] and stannylcupration[4] reactions. In particular, under stannylcupration conditions, (E)-3-tributylstannyl propenoylsilane could be obtained, a molecule provided with a further functionalization site, nucleophilic in character, thus envisaging the possibility of a fine tuning of the reactional polarity of position 3 of such molecule.

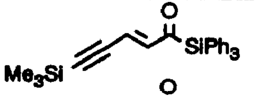
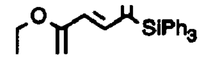
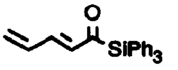
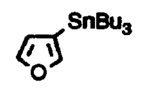
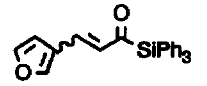
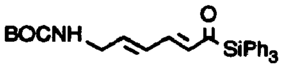
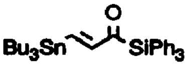
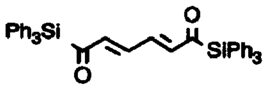
We now report in this communication on the development of such synthetic strategy, through the study of the chemical behaviour of 3-iodo propenoylsilane 2[2], which can be easily obtained by treatment of *1*[5] with an equimolar amount of trimethylsilyl iodide[6] (Scheme).



Compound *2* proved an extremely useful intermediate, undergoing clean palladium catalysed couplings[7] with functionalized tin compounds, to afford a variety of novel 3-functionalized ethylenic silyl ketones *3*[8], thus opening a different methodology for the construction of polyunsaturated acylsilanes[3,4] (Scheme). Results are summarized in the Table.

Outstanding feature of this reactivity are the very mild reaction conditions, which allow the synthesis of a wide range of derivatives, including nitrogen and oxygen functionalized dienoylsilanes, in good yields. These coupling reactions proved to be rather general, leading with different unsaturated stannyl derivatives to a clean functionalization of the C-3 carbon. Reactions are generally stereospecific, only the corresponding *E* isomers being detected in the reaction mixtures. Moreover, when the case, the introduced novel functionalities may be further reacted, as shown by compound *3b*, which, by acidic treatment, affords the corresponding 1-trimethylsilyl-1,4-dioxo-2-pentene. Of particular interest are compounds *3a* and *3f*, in that *3a* allows the synthesis of an enyne framework, while *3f* discloses a route to a novel polyunsaturated bis acylsilane, whose chemical behaviour could prove very interesting. Finally, this reactivity outlines an

Table. Synthesis of polyunsaturated acylsilanes.

Nucleophile	Product [a]		Time	Yield (%) [b]
$Me_3Si{\equiv}SnMe_3$		*3a*	9 h	64
		*3b*	1 h	75
		*3c*	1 h	70
		*3d*	1 h	73 [c]
		*3e*	12 h	86
		*3f*	8 h	84

[a] All compounds showed spectroscopical and analytical data consistent with the assigned structure. [b] Yields refer to chromatographically pure materials. [c] As 1 : 1 mixture of E : Z isomers.

inversion of the reactional polarity of the position 3 of the enonic framework, with respect to the 3-tributylstannyl derivative, this time reacting in an electrophilic fashion.

In conclusion, we may say that the reactional behaviour of 3-iodo-propenoylsilane well complements the one of the 3-stannyl derivative, introducing the possibility of a selective functionalization of the C-3 carbon of the enonic framework and leading to a fine tuning of the reactional polarity of such position.

REFERENCES AND NOTES

1. Panek, J.S.; Cirillo, P.F. *Org. Prep. Proc. Int.* **1992**, *24*, 553. Bulman-Page, P.C.; Klair, S.S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647.
2. Ricci, A.; Degl'Innocenti, A.; Borselli, G.; Reginato, G. *Tetrahedron Lett.* **1987**, *28*, 4093. Degl'Innocenti, A.; Capperucci, A.; Mordini, A.; Reginato, G.; Ricci, A. *Tetrahedron Lett.* **1992**, *33*, 1507. Novick, J.S.; Danheiser, R.L. *J. Org. Chem.* **1989**, *54*, 2798. Reich, H.J.; Holtan, R.C.; Borkowsky, S.L. *J. Org. Chem.* **1987**, *52*, 312. Reich, H.J.; Holtan, R.C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609 and ref. cited therein. Danheiser, R.L.; Fink, D.M. *Tetrahedron Lett.* **1985**, *26*, 2509.
3. Degl'Innocenti, A.; Stucchi, E.; Capperucci, A.; Mordini, A.; Reginato, G.; Ricci, A. *Synlett* **1992**, 332.
4. Degl'Innocenti, A.; Stucchi, E.; Capperucci, A.; Mordini, A.; Reginato, G.; Ricci, A. *Synlett* **1992**, 329.
5. Reich, H.J.; Kelly, M.J.; Olson, R.E.; Holtan, R.C. *Tetrahedron* **1983**, *39*, 949.
6. IR (CCl_4): 3079, 3031, 1599, 1475, 1254, 968, 751 cm^{-1}. ^1H NMR (200 MHz; $CDCl_3$) δ (ppm) : 7.21 (d, 1 H, J=18 Hz), 7.20-7.70 (m, 16 H). ^{13}C NMR ($CDCl_3$) δ (ppm) : 100.9, 128.3, 130.5, 130.7, 136.2, 149.0, 228.0. MS m/z (%): 440 (M^+, 0.2), 439 (2), 313 (60), 259 (100), 180 (28), 105 (27), 77 (7).
7. Lipshutz, B.H.; Alami, M.; Susfalk, R.B. *Synlett* **1993**, 693. Kende, A.S.; De Vita, R.J. *Tetrahedron Lett.* **1990**, *31*, 307 and references cited therein. Pereyre, M.; Quintard, J.P.; Rahm, A. *Tin in Organic Synthesis*, **1987**, Butterworths & Co. Ltd., London.
8. **Typical procedure:** A solution of 30 mg (0.07 mmol) of (E)-3-iodo propenoyltriphenylsilane and 22 mg (0.07 mmol) of vinyltributylstannane in 1 mL of dry DMF was treated, under N_2, with 2 mg (0.007 mmol) of $PdCl_2(CH_3CN)_2$. The reaction was stirred at room temperature in the dark for 1 h and monitored by TLC. Work-up and purification by TLC afforded 17 mg of *3c* (70%). ^1H NMR (300 MHz; $CDCl_3$) δ (ppm): 5.42 (dd, 1H, J=16.8, 0.7 Hz), 5.47 (dd, 1H, J=9.9, 0.7 Hz), 6.35 (dt, 1H, J=16.8, 10.8, 9.9 Hz), 6.52 (bd, 1H, J=15.6 Hz), 6.89 (dd, 1H, J=15.6, 10.8 Hz), 7.20-7.70 (m, 15H). ^{13}C NMR (75 MHz; $CDCl_3$) δ (ppm): 127.4, 128.1, 130.2, 131.8, 135.2, 135.6, 136.2, 142.9, 231.2 . MS (70 eV) m/z (%): 340 (M^+, 26), 313 (3), 259 (100), 236 (11), 199 181 (95), 105 (80), 53 (8).

(*Received in UK* 13 *October* 1993; *revised* 20 *December* 1993; *accepted* 28 *January* 1994)