Tetrahedron Letters, Vol. 34, No. 3, pp. 411-414, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

2-(*N,N*-DIETHYLCARBAMOYLOXY)ALLYLSILANE. DUAL REACTIVITY WITH α,α'-ACETONE DIANION AND ALLENE 1,2-DIPOLE EQUIVALENCY

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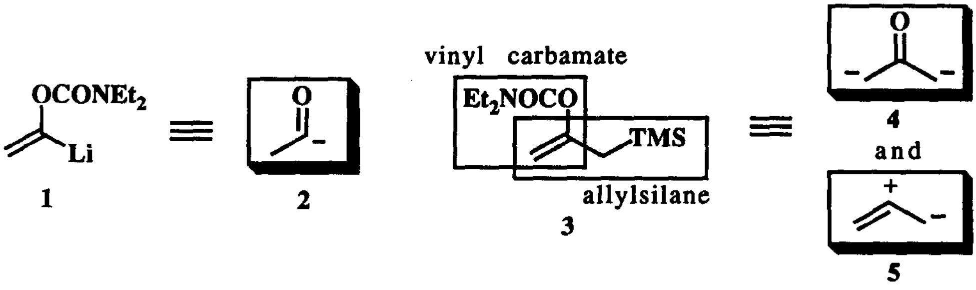
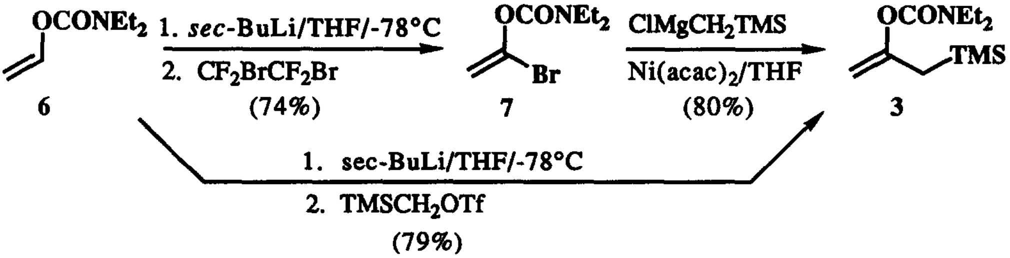
Abstract: The title compound displays the dual role of an α,α'-acetone dianion **4** and an allene 1,2-dipole **5** equivalent allowing the preparation of versatile synthetic intermediates **10a-c** and **11a-d** (**Tables** 1 and 2).

In the course of developmental work on α-lithio *O*-vinyl carbamates **1** as new acyl anion equivalents,[1,2] we prepared 2-(*N,N*-diethylcarbamoyloxy)allylsilane **3** and recognized its potential dual reactivity as an α,α'-acetone dianion **4**[3] and an allene 1,2-dipole **5**[4] equivalent. The former is manifested in both of these reactivity patterns while the latter is based on the concurrent finding[1,5] that vinyl carbamates undergo transition metal catalyzed cross coupling reactions. Herein we report results which verify these concepts and thereby provide new methods for construction of functional acyclic building blocks. In the accompanying Letter,[6] we report preliminary observations concerned with the preparation and reactions of the 2,2-difluoro analogue of **1**.



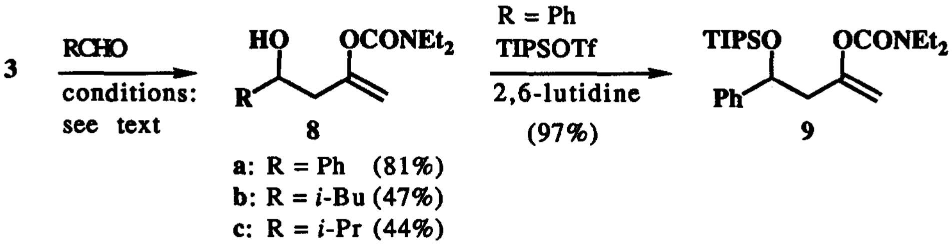
Two routes were developed for gram-scale synthesis of **3** (**Scheme 1**): metalation (*s*-BuLi/THF/-78°C) of **6** followed by quench with CF_2BrCF_2Br, an efficient Br^+ source,[7] afforded **7**, which, upon Ni(0)-catalyzed cross coupling[5] with the commercial Grignard reagent, $TMSCH_2MgCl$, furnished **3** in 59% overall yield. Alternatively, identical metalation followed by treatment with $TMSCH_2OTf$ led to **3** in higher overall yield (79%).

Scheme 1



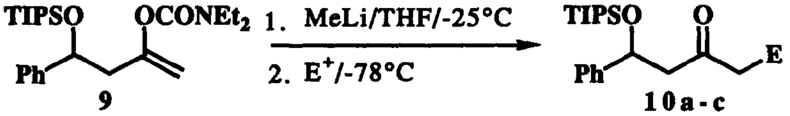
Although the allylsilane reactivity of **3** with benzaldehyde was not observed under the standard Lewis acid catalyzed conditions,[8] use of TMSI[9] afforded the condensation product **8a** (Scheme 2) in good yield. In contrast, enolizable aliphatic aldehydes failed to react or led to desilylation under these conditions. However, treatment of **3** with *i*-BuCHO using the exceptional Lewis acid $TMSB(OTf)_4$[10] afforded the expected product **8b** in modest yield. Condensation of **3** with *i*-PrCHO was also achieved under TBAF catalysis to give **8c**, thus demonstrating the viability of **3** to the well developed electrophilic reactivity mode of allylsilanes.[8]

Scheme 2



TIPS protection of the secondary alcohol of **8a** to give **9** set the stage for evaluation of the acetone dianion equivalency (**4**). In order to develop conditions for decarbamoylation, compound **9** was treated with MeLi followed by aqueous workup to afford **10a** (**Table 1**). Methylation (MeI) and carbomethoxylation ($NCCO_2Me$)[11] was also achieved to yield products **10b** and **10c** respectively.

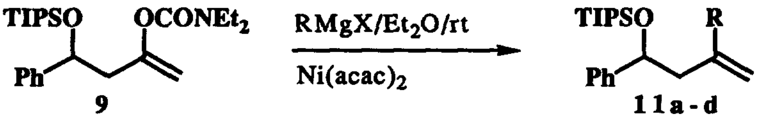
Table 1



E^+	Product	E	Yield, %
H_2O	**10a**	H	59
MeI	**10b**	Me	47
$NCCO_2Me$	**10c**	CO_2Me	67

Compound **9a** also served as a test substrate for evaluation of **3** as an allene 1,2-dipole equivalent **5**. **Table 2** shows results of selected Ni(0)-catalyzed cross coupling reactions of **9** with Grignard reagents under previously defined[5] conditions to provide protected homoallylic alcohols **11a-d** with alkyl, aryl, vinyl and TMS-methyl functionality.

Table 2



RMgX	Product	Yield, %
MeMgBr	**11a**	72
CH_2=CHMgBr	**11b**	61
PhMgCl	**11c**	43
$TMSCH_2MgCl$	**11d**	53

The above preliminary results demonstrate the utility of 2-(*N,N*-diethylcarbamoyloxy)allylsilane **3** as a dual α,α'-acetone dianion **4** and allene 1,2-dipole **5** equivalent. Thus the useful enolate and allylsilane reactivities are enhanced by the recently discovered cross coupling component,[5] making **3** a versatile synthetic unit for diverse alicyclic manipulations.[12,13,14]

References and Footnotes

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12. The following procedures are illustrative: Preparation of **10b**: To a solution of **9** (265 mg, 0.63 mmol) in THF (5 mL) at -25 °C was added a solution of MeLi (1.25 mL of a 1.5 M Et_2O solution, 1.88 mmol) and the mixture was stirred for 1 h. The yellow solution was cooled to -78 °C, treated with MeI (0.16 mL, 2.50 mmol) and the mixture was warmed to rt over 3 h. Standard NH_4Cl quench followed by column chromatography (Et_2O-hex 1:20) gave pure 97 mg (47% yield) of **10b**, oil: IR υ(max) 1717 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.84-1.05 (m, 24H), 2.24 (dq, 1H, *J* = 7.3, 18.1 Hz), 2.37 (dq, 1H, *J* = 7.3, 18.1 Hz), 2.67 (dd, 1H, *J* = 6.4, 15.0 Hz), 2.94 (dd, 1H, *J* = 6.4, 15.0 Hz), 5.28 (t , 1H, *J* = 6.4 Hz), 7.19-7.37 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 7.3, 12.3 17.8, 17.9, 37.7, 53.8, 71.8, 125.9, 127.3, 128.1, 144.8, 209.2; MS (CI, CH_4) 335 (MH^+).

    Preparation of **11a**: A suspension of **9** (419 mg, 1.00 mmol) and $Ni(acac)_2$ (13 mg, 0.05 mmol) in Et_2O (10 mL) cooled to 0 °C was treated with a solution of MeMgBr (0.67 mL of a 3.0 M solution in Et_2O, 2.00 mmol) and the mixture was warmed to rt over 2 h. Standard workup and column chromatography (hex) gave 228 mg (72% yield) of **11a**, oil: ^1H NMR (250 MHz, $CDCl_3$) δ 0.95-1.07 (m, 21H), 1.61 (s, 3H), 2.35 (dd, 1H, *J* = 7.5, 13.1 Hz), 2.58 (dd, 1H, *J* = 5.8, 13.1 Hz), 4.51 (s, 1H), 4.67 (s, 1H), 4.85 (dd, 1H, *J* = 5.8, 7.5 Hz), 7.18-7.30 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 12.4, 18.0, 18.1, 23.3, 49.7, 74.7, 113.7, 126.3, 127.0, 127.8, 141.8, 145.2; MS (CI, CH_4) 319 (MH^+).
13. All yields correspond to isolated chromatographically purified materials. All compounds show analytical and spectroscopic (IR, ^1H and ^{13}C NMR, HRMS) data fully consistent with the assigned structures.

14 We are grateful to Professor S. Sengupta (Jadavpur University) for insightful discussion and NSERC Canada for sustaining support of our synthetic work under Operating (Research) and Industrial Research Chair programs.

(Received in USA 9 October 1992)