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A Novel Route to *N*-Substituted Allylamines by the Reaction of Allylsilanes with (Ethoxycarbonyl)nitrene[1]

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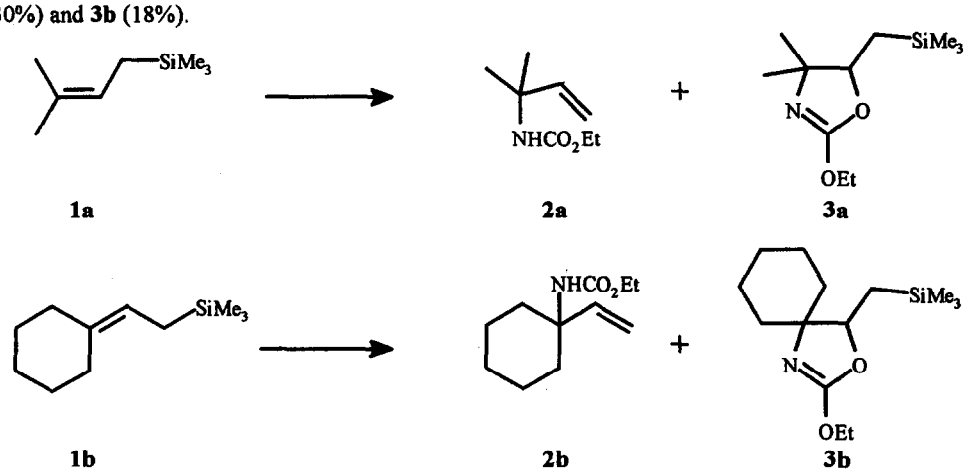
Abstract: The reaction of mono- and disubstituted allylsilanes with (ethoxycarbonyl)nitrene allowed the preparation of the *N*-substituted allylamines **2a**, **2b**, **2c** and **2d** in yields up to 60%. The 2-ethoxyoxazolines **3a**, **3b** and **3c** were isolated as minor products.

The presence of a nucleophilic double bond makes allylsilanes important intermediates in synthetic organic chemistry. They were reported to react with several electrophiles such as epoxides, acetals and carbonyl compounds.[2] However only the reactions with few nitrogen electrophiles such as azodicarboxylate,[3] nitronium[4] and diazonium salts[5] were described. The nucleophilicity of allyltrimethylsilanes was compared to that of enol ethers and silyl enol ethers.[6]

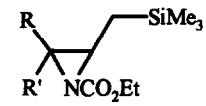
We described the reaction of (ethoxycarbonyl)nitrene (NCO_2Et) with enol ethers[7] and silyl ketene acetals[8] to give *N*-substituted α-amino ketones and α-amino esters. In the past we showed also the formation of *N*-substituted α-chloro allylamines by the reaction of NCO_2Et with vinyl chlorides.[9]

Here we report the first results obtained by Et_3N induced α-elimination of ethyl *N*-{[(4-nitrophenyl)sulphonyl]oxy}carbamate ($NsONHCO_2Et$)[10] with allylsilanes to produce derivatives of allylamines, compounds of synthetic and biological interest,[11] but not easily available by preparative methods.

Starting from the γ,γ-disubstituted allylsilanes **1a**[12] and **1b**[13] the main products isolated after flash-chromatography were the *N*-(ethoxycarbonyl) allylamines **2a** (40%) and **2b** (40%) and the 2-ethoxyoxazolines **3a** (30%) and **3b** (18%).

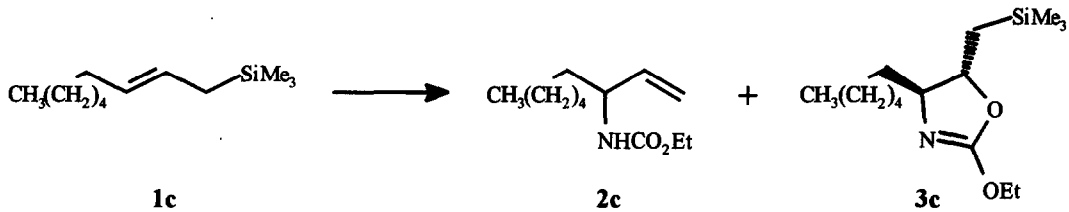


Probably a first addition product, the aziridine **4**, is formed and GC-MS analysis showed its presence in the crude reaction mixture from **1a** and **1b**. In one case, namely in the reaction of **1b**, it was also isolated in 2% yield.[14]



4

Under the same reaction conditions the γ-monosubstituted allylsilane **1c**[13] gave the *N*-(ethoxycarbonyl) allylamine **2c** (46%) and the 2-ethoxyoxazoline **3c** (7%), while the dienic substrate **1d**[12] gave **2d** (20%) and polymeric materials.



1c **2c** **3c**

1d **2d**

Oxazolines were rarely involved in reactions with NCO_2Et, namely in the case of allenes,[15] alkynes[16] and 1-cyclopentenyl trimethylsilyl ether.[17] They were reported to derive from a rearrangement of *N*-acyl aziridines in strong acid media.[18]

We found that a treatment of the crude reaction mixture at reflux in the presence of two equivalent of acetic acid for 3 h allowed the isolation of *N*-(ethoxycarbonyl) allylamines **2a**, **2b** and **2c** in better yields (60%, 57% and 50% respectively) as the only products for all substrates. Non silylated *N*-(ethoxycarbonyl) aziridines can be isomerized into the corresponding allylamines by pyrolysis at 200-255 °C (in neutral or acid media).[19]

General Procedure

To a mixture of 3 mmol of allylsilane in 76 ml of anhydrous CH_2Cl_2 and 9 mmoles of $NsONHCO_2Et$ a solution of 9 mmol of anhydrous Et_3N in 14 ml of anhydrous CH_2Cl_2 was added during 45 min under stirring, under argon, at room temperature. After further 3 h most of the solvent was removed, by distillation, and petroleum ether (bp 30-50 °C) was added. After filtration the solvent was removed and the crude reaction mixture chromatographed on silica gel (flash-chromatography; petroleum ether (bp 30-50 °C) / ethyl ether = 8:2) giving the allylamines.**2**[20] and the oxazolines **3**[21] in the reported yield. A 10% of **1b** and **1c** was recovered.

Repeating the reaction at reflux and treating the reaction mixture without removing solvent with glacial acetic acid (18 mmol, 3 h), after workup only the allylamines **1** without traces of starting material were obtained.

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20. **2a**: IR (CCl_4) 3450, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (t, 3H, OCH_2CH_3), 1.33 (s, 6H, 2 CH_3C), 4.00 (q, 2H, OCH_2CH_3), 4.72 (br s, 1H, NH), 4.95-5.09 (2d, 2H, $CH=CH_2$), 5.92 (dd, 1H, $CH=CH_2$); ^{13}CNMR ($CDCl_3$) δ 14.31 (CH_3CH_2), 27.04 (2 CH_3C), 53.34 (CNH), 60.06 (OCH_2), 111.68 ($CH=CH_2$), 144.25 ($CH=CH_2$), 156.05 (CO); GC-MS *m/z (%)* 157 (M^+, 4), 142 (87), 70 (100), 69 (49), 58 (38).

    2b: IR (CCl_4) 3445, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (t, 3H, OCH_2CH_3), 1.24-2.10 [m,10H, $(CH_2)_5$], 4.06 (q, 2H, OCH_2CH_3), 4.58 (br s, 1H, NH), 5.05-5.14 (2d, 2H, $CH=CH_2$), 5.92 (dd, 1H, $CH=CH_2$); ^{13}C NMR ($CDCl_3$) δ 14.77 (CH_3), 21.82 (2 CH_2), 25.68 (2 CH_2), 35.37 (CH_2), 55.89 (CNH), 60.51 (OCH_2), 112.64 ($CH=CH_2$), 144.29 ($CH=CH_2$), 156.10 (CO); GC-MS *m/z (%)* 197 (M^+,

23), 169 (27), 168 (55), 142 (24), 124 (90), 110 (21), 109 (30), 108 (32), 96 (24), 93 (25), 82 (100), 81 (28), 79 (43), 67 (55), 62 (25), 55 (47), 54 (73), 53 (24).

2c: IR (CCl_4) 3445, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, 3H, CH_3CH_2), 1.20 (t, 3H, OCH_2CH_3), 1.22-1.60 [m, 10H, $CH_3(CH_2)_5$)], 4.07 (q + m, 3H, OCH_2CH_3, and CHN), 4.58 (br s, 1H, NH), 5.02-5.14 (2d, 2H, $CH=CH_2$), 5.65-5.76 (m, 1H, $CH=CH_2$); ^{13}C NMR ($CDCl_3$) δ 13.99 (CH_3), 14.56 (OCH_2CH_3), 22.52 (CH_2), 25.54 (CH_2), 29.00 (CH_2), 31.66 (CH_2), 35.11 (CH_2), 53.12 (CHNH), 60.65 (OCH_2), 114.33 ($CH=CH_2$), 138.92 ($CH=CH_2$), 156.05 (CO); GC-MS *m/z (%)* 213 (M^+, 1), 128 (100), 56 (57).

2d: IR (CCl_4) 3450, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (t, 3H, OCH_2CH_3), 4.12 (q, , 2H, OCH_2CH_3), 4.76 (m, 2H, CHNH), 5.16-5.25 (2d, 4H, 2 $CH=CH_2$), 5.78-5.90 (m, 2H, 2 $CH=CH_2$); ^{13}C NMR ($CDCl_3$) δ 14.40 (CH_3), 54.81 (CHNH), 60.92 (OCH_2CH_3), 115.81 (2 $CH=CH_2$), 137.06 (2 $CH=CH_2$); GC-MS *m/z (%)* 155 (M^+, 2), 126 (55), 90 (27), 82 (87), 67 (74), 66 (27), 65 (22), 62 (27), 56 (100), 55 (35), 54 (46).

21. **3a**: IR (CCl_4) 1657 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H, $SiMe_3$), 0.64 (dd, 1H, CH_2SiMe_3), 0.98 (dd, 1H, CH_2SiMe_3), 1.06 (s, 3H, CH_3C), 1.21 (s, 3H, CH_3C), 1.29 (t, 3H, OCH_2CH_3), 4.16 (q, 2H, OCH_2CH_3), 4.21 (dd, 1H, CH-O); ^{13}C NMR ($CDCl_3$) δ 1.34 ($SiMe_3$), 14.06 (OCH_2CH_3), 17.05 (CH_2SiMe_3), 23.37 (CH_3C), 28.57 (CH_3C), 65.79 (OCH_2CH_3), 66.52 (C-N), 88.26 (CH-O), 161.06 (N=C-O); GC-MS *m/z (%)* 229 (M^+, 1), 84 (100), 73 (22).

3b: IR (CCl_4) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H, $SiMe_3$), 0.64 (dd, 1H, CH_2SiMe_3), 0.96 (dd, 1H, CH_2SiMe_3), 1.25 (t, 3H, OCH_2CH_3), 1.30-2.10 [m, 10H, $(CH_2)_5$], 4.16 (q, 2H, OCH_2CH_3), 4.25 (dd, 1H, CH-O); ^{13}C NMR ($CDCl_3$) δ 1.34 ($SiMe_3$), 14.06 (OCH_2CH_3), 17.05 (CH_2SiMe_3), 21.82 (2 CH_2), 25.68 (2 CH_2), 35.37 (CH_2), 65.79 (OCH_2CH_3), 66.52 (C-N), 88.26 (CH-O), 161.06 (N=C-O); GC-MS *m/z (%)* 269 (M^+, 15), 124 (100), 108 (31), 81 (67), 73 (56).

3c: IR (CCl_4) 1661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H, $SiMe_3$), 0.85 (t, 3H, CH_3CH_2), 0.86-1.11 (m, 2H, CH_2SiMe_3), 1.31 (t, 3H, OCH_2CH_3), 1.20-1.60 [m, 10H, $CH_3(CH_2)_5$], 3.49-3.53 (m, 1H, CH-N), 4.20 (q, 2H, OCH_2CH_3), 4.27-4.34 (m, 1H, CH-O); ^{13}C NMR ($CDCl_3$) δ 0.86 ($SiMe_3$), 14.07 (OCH_2CH_3), 14.37 (CH_3), 22.60 (CH_2), 24.54 (CH_2), 25.48 (CH_2), 29.40 (CH_2), 31.74 (CH_2), 36.26 (CH_2), 66.09 (OCH_2CH_3), 71.64 (CH-N), 84.77 (CH-O), 161.21 (N=C-O); GC-MS *m/z* (%) 270 (M^+-15, 3), 82 (100), 73 (91), 55 (44).

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