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New Transformations from a 3-Silyloxy 2-Aza-1,3-diene: Consecutive Zr-Mediated Retro-Brook Rearrangement and Reactions with Electrophiles

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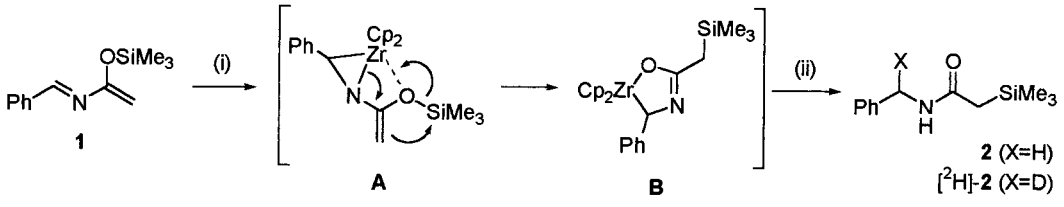
Abstract—A one-pot procedure for the transformation of the title compound to α-functionalized (silylated) and α,β-unsaturated *secondary* amides was described. The following steps were involved: a Zr-mediated retro-Brook rearrangement, selective deprotonation with *n*-BuLi on the organometallic intermediate, and trapping with electrophiles including alkyl and acyl halides and aldehydes. The electrophilic addition step occurred at a stabilized α-silyl carbanion center without affecting the near transition metal residue. In the case of aldehydes, the Peterson alkenation reaction took place on the transition metal complex in a highly stereoselective way. © 2000 Elsevier Science Ltd. All rights reserved.

2-Aza-1,3-dienes have attracted much attention due to their particular reactivity pattern and synthetic interest.[1] Both electron-rich and neutral azadienes have found a synthetic use as 4π components in hetero Diels–Alder reactions,[2] and participated in some heterocyclization and nucleophilic addition reactions.[3] The recent development of new practical methods for the preparation of differently functionalized 2-azadienes could facilitate further investigations.[1b,4] In this respect, the imine and enamine reactivities of these compounds are almost unknown. The organometallic reactions involving the 2-azadiene system are restricted to the regiospecific generation of lithioenamines.[5] It appears of current interest to explore the early transition-metal chemistry of 2-azadienes, in order to activate them towards a selective attack of suitable electrophiles and to induce insertion reactions through organometallic intermediates. In this matter, group IV metallocenes should be taken into account. In fact, simpler titanocene- and zirconocene–imine complexes have been demonstrated to undergo coupling reactions with various polar and non-polar unsaturated molecules.[6]

Results and Discussion

We recently reported the complexation of electron-rich 2-azadienes having trimethylsilyloxy group at C3 to zirconocene ('Cp_2Zr').[7,8] As we have noticed, these reactions involved an unprecedented transition metal mediated retro-Brook rearrangement. For example, by using 1-phenyl-3-trimethylsilyloxy-2-aza-1,3-butadiene (**1**), the reaction with a zirconocene equivalent (Cp_2Zr(butene) or Cp_2ZrCl_2 and Mg) in THF afforded the α-silylated amide **2** after hydrolysis (Scheme 1).

To gain some information on this surprising reaction, we have performed deuterolysis and NMR monitoring experiments. Thus, quenching of the reaction with D_2O afforded



Scheme 1. (i) Cp_2ZrCl_2, 2 equiv. *n*-BuLi, THF, −78°C to rt or Cp_2ZrCl_2, Mg, THF, rt; (ii) $NaHCO_3$ aq or D_2O then $NaHCO_3$ aq.

Keywords: zirconium; retro-Brook; azadiene; electrophilic addition.

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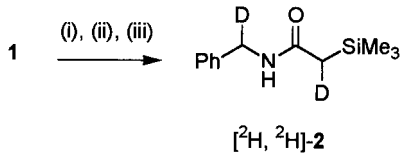


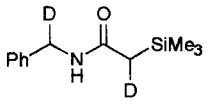
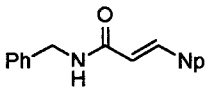
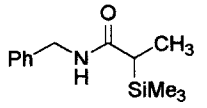
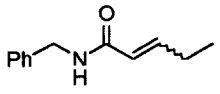
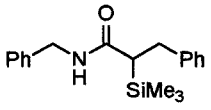
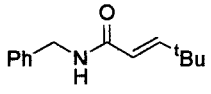
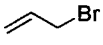
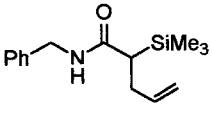
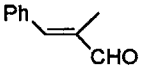
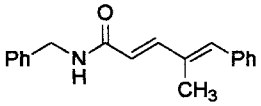
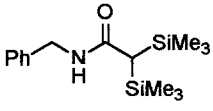
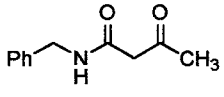
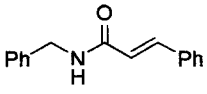
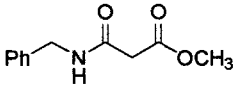
Scheme 2. (i) Cp_2ZrCl_2, 2 equiv. *n*-BuLi, THF, −78°C to rt; (ii) *n*-BuLi, −78°C, (iii) D_2O, rt.

the monodeuterated α-silylated amide [^{2}H]-**2**. Monitoring the reaction by ^{1}H NMR spectroscopy in THF-d_8 indicated a progressive formation of the rearranged organometallic complex. On the other hand, no oxygen to carbon migration took place using the nitrogen-free analog of azadiene **1**, i.e. 1-phenyl-3-trimethylsilyloxy-1,3-butadiene as a substrate. Based on these results, the rearrangement process as shown in Scheme 1 has been proposed. In the initial stage of the reaction, the zirconaaziridine complex **A** is formed, similarly to the reaction involving simpler imines or 1-azadienes.[6,9] Thereafter, the retro-[1,3]-Brook rearrangement is indirectly induced by the strongly oxophilic zirconium to afford the zirconaoxazoline complex **B**. In this reaction, the cleavage of the Zr–N bond rather than the Zr–C bond occurred, because of the concomitant easy formation of the C1–Si bond.[10]

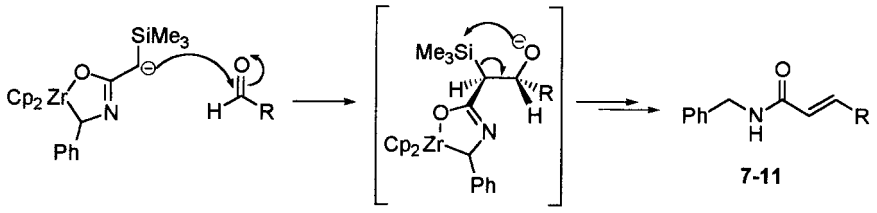
The above reactivity pattern of the azadiene **1** prompted us to envisage further synthetic developments. In keeping with this aim, we considered the presumed organozirconium structure **B**. We reasoned that it might be readily deprotonated at C4, i.e. in the α position towards both silicon and zirconaoxazoline moiety. In fact, the ability of silicon to stabilize adjacent carbanions is well known.[11] On the other hand, 2-substituted 2-oxazolines can be metallated and alkylated to afford synthons for carboxylic acids.[12] By assuming the structure **B**, a generation of an efficiently stabilized α-carbanion should be anticipated. Trapping of the carbanion by several electrophiles would provide α-functionalized (silylated) *secondary* amides after hydrolysis.

In order to test the viability of this hypothesis, the azadiene **1** was reacted with Cp_2ZrBu_2, as previously described.[7] The reaction mixture was then cooled to −78°C and treated with 1 equiv. of *n*-BuLi. After stirring for 1 h the electrophile was added and the reaction carried out at room temperature.

Table 1. Tandem reactions of azadiene **1**

Entry	Electrophile	Product	Yield [%][a]	Entry	Electrophile	Product	Yield [%][a]
1	D_2O	 **[^{2}H, ^{2}H]-2**	66	7	NpCHO	 **8**	58
2	MeI	 **3**	61	8	EtCHO	 **9** (*E*/*Z* = 85:15)	52
3	BnBr	 **4**	60	9	^{t}BuCHO	 **10**	47
4		 **5**	59	10		 **11**	38
5	Me_3SiCl	 **6**	30	11	MeCOCl	 **12**	39
6	PhCHO	 **7**	50	12	MeOCOCl	 **13**	61

[a] Yields of isolated products after column chromatography; Np: 2-naphthyl.



Scheme 3.

Initially, a deuterolysis was performed to examine the metallation step. Quenching of the reaction with D_2O gave the bis(deuterated) α-silylated amide [^{2}H,^{2}H]-**2** (≥95% D) (Scheme 2). In comparison with the monodeuteration observed in the absence of *n*-BuLi (Scheme 1), this result proved the complex **B** to be lithiated at C4 atom. Having demonstrated the formation of the anion, some alkylation reactions were performed, the representative examples are shown in Table 1.

Using alkyl, benzyl and allyl bromides or iodides as substrates, the reactions proceeded regioselectively at the carbon atom.[13] After basic ($NaHCO_3$ aq) treatment, the α-silylated amides **3**–**5** were isolated in 60% yield on average starting from the azadiene **1** (Table 1, entries 2–4).[14] The above reactions appeared to be synthetically equivalent to the alkylation of enolates of *secondary* amides (α-silylated). In fact, the zironaoxazoline moiety should be considered as a masked *secondary* amide functionality, since the latter has been restored on hydrolysis.[15] It is noteworthy that, while the metal enolates of *N*,*N*-dialkylamides are easily prepared and C-alkylated, those of *N*-alkylamides are less common. On the other hand, C-silylated *secondary* amides are of potential synthetic utility, as they can undergo fluoride promoted aldolization.[16] These compounds are rather difficult to obtain by direct silylation of *secondary* amides which generally takes place at nitrogen.[11b] Finally, an attempt to silylate the anion with Me_3SiCl succeeded to afford the bis(trimethylsilyl)amide **6**, albeit in a lower yield (Table 1, entry 5).

The Peterson carbonyl alkenation reaction has proven to be of general synthetic utility.[17] Particularly, the use of stabilized α-silylcarbanions has led to a number of versatile transformations. The question arose about the feasibility of the Peterson reaction by using a silyl anion attached to a transition metal residue. We thought that it might be envisaged in our case, as an efficiently stabilized α-silylcarbanion would be involved.[18] Thus, the zirconocene complex was prepared and lithiated as previously, and reacted with benzaldehyde at −78°C to rt for 3 h. After basic ($NaHCO_3$) treatment, the α,β-unsaturated amide **7**, having a unique *E* configuration of the double bond, was obtained (Table 1, entry 6). Some other aldehydes were tested. The Peterson reaction has been demonstrated to occur from the complex and aromatic as well as aliphatic aldehydes to provide the unsaturated amides **7**–**11**. Examination of Table 1 reveals several interesting features: (i) the reaction took place starting from the relatively crowded 2-naphthaldehyde and pivalaldehyde (entries 7 and 9); (ii) it gave a comparatively good yield using an enolizable aldehyde (entry 8); (iii) the use of an α,β-unsaturated aldehyde cleanly led to a 1,2-addition product, i.e. the dienylamide **11** (entry 10);[19] (iv) in all cases, the C–C double bond was formed in a highly stereoselective way, leading predominantly (entry 8) or exclusively (entries 6, 7, 9 and 10) to the (*E*)-configurated products. The above high stereoselectivity is noteworthy, since alkenes formed in Peterson reactions are often mixtures of (*Z*),(*E*)-isomers. The stereochemistry of the reaction can be explained within the context of a rapid spontaneous elimination of β-oxidosilane, often occurring if a stabilized α-silylcarbanion is involved and lithium used as a counter cation. In our case, the *syn* elimination from a markedly less crowded β-silyl alkoxide may predominantly proceed to give the (*E*)-α,β-unsaturated amide (Scheme 3). Finally, as α-silyl carbanions react with acyl chlorides to afford α-silylketones rather than the elimination products,[20] we also tried to perform some acylation reactions. Using acetyl chloride, an almost complete desilylation occurred on hydrolysis to afford the oxoamide **12** (Table 1). Similarly, the amido ester of malonic acid (**13**) was obtained when methyl chloroformate was employed as the electrophile.

In summary, an example of a one-flask procedure for activating a 3-silyloxy 2-azadiene towards the regioselective (at C4) attack of various electrophiles is reported. The reaction begun with an unprecedented zirconium induced retro-Brook rearrangement. Although the resulting organometallic complex could not be isolated, labeling experiments and NMR monitoring was indicative of a 2-(trimethylsilylmethyl)-zirconaoxazoline structure, which was further evidenced by the reactivity pattern. Thus, the intermediate compound could be successively deprotonated and trapped by several electrophiles. This second addition step should be formally regarded to be equivalent to the coupling reactions of a *secondary* amide enolate, since α-substituted (silylated) and α,β-unsaturated *secondary* amides were isolated after hydrolysis. Within this context, the zirconaoxazoline moiety appeared as an organometallic masked *secondary* amide function. A remarkable feature of these alkylation, acylation and even olefination reactions is that they have occurred selectively on the complex, without affecting the transition metal residue. Further studies on the development of these new tandem reactions and their application in synthesis are in progress.

Experimental

All reactions were carried out under Ar using vacuum line techniques. THF was distilled under Ar from sodium-benzophenone ketyl. Zirconocene dichloride was purchased from Strem Chemicals. Other reagents were purchased from Aldrich, and distilled under Ar prior to use. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker AC

250 spectrometer. High and low resolution mass spectra (EI, 70 eV) were performed on a JEOL D300 apparatus. Column flash chromatography was performed on silica gel 40–63 μm or alumina 63–200 μm (Merck). Melting points were determined with a Büchi capillary apparatus and were not corrected.

Reaction of azadiene 1 with zirconocene

To a solution of Cp_2ZrCl_2 (292 mg, 1 mmol) in THF (4 mL) was added *n*-BuLi (0.8 mL, 2 mmol, 2.5 M hexanes solution) at −78°C. After the solution was stirred for 1 h at −78°C, azadiene **1**[1b] (219 mg, 1 mmol) in THF (3 mL) was added slowly via syringe and the reaction mixture was allowed to warm to room temperature for 2 h. At this stage, deuterolysis or electrophilic additions might follow (see below). Alternatively, the reaction mixture was quenched by adding H_2O or D_2O (2 mL) followed by an additional 1 h stirring. Thereafter, the mixture was treated with ice-cold saturated aqueous $NaHCO_3$ (4 mL) and extracted with ether (3×20 mL). The extract was washed with water and dried over Na_2SO_4. Column chromatography on alumina with *n*-hexane/AcOEt=7:3 followed by MeOH as the eluent afforded silylated amide **2** (H_2O quenching) or [^{2}H]-**2** (D_2O quenching).

Metallation—deuterolysis protocol

The solution of the complex (see above) was cooled to −78°C and treated with *n*-BuLi (0.4 mL, 1 mmol, 2.5 M hexanes solution). After stirring for 1 h at −78°C, D_2O (2 mL) was added, and the reaction mixture warmed to rt (1 h). Workup as above afforded bis (deuterated) α-silylated amide [^{2}H,^{2}H]-**2**.

General procedure for the electrophilic addition reactions

The solution of the complex (see above) was cooled to −78°C and treated with *n*-BuLi (0.4 mL, 1 mmol, 2.5 M hexanes solution). After the reaction mixture was stirred for 1 h at −78°C, the solution of electrophile (1 mmol) in THF (2 mL) was added via syringe. The mixture was stirred at this temperature for 3 h. The basic ($NaHCO_3$ aq) workup as above, followed by flash chromatography, afforded compounds **4**–**13** (Table 1).

Selected experimental data

***N*-Benzyl(trimethylsilyl)acetamide (2).** 151 mg (70%); oil; IR (film) ν 1630, 1543 cm^{-1}; ^{1}H NMR δ 7.35–7.20 (m, 5H), 5.45 (m, 1H), 4.42 (d, *J*=5.3 Hz, 2H), 1.80 (s, 2H), 0.12 (s, 9H); ^{13}C NMR δ 171.9 (C=O), 138.7 (C), 128.6 (2 CH), 127.9 (2 CH), 127.4 (CH), 43.8 (CH_2), 29.2 (CH_2), −1.3 (3 CH_3); MS *m/z* (%) 222 (M+1, 76), 221 (72), 206 (53), 205 (27), 164 (22), 147 (18), 115 (22), 107 (100), 106 (62), 105 (57); High Resolution MS: $C_{12}H_{19}NOSi$ requires 221.1236 found 221.1236.

Mono-deuterated *N*-benzyl(trimethylsilyl)acetamide ([^{2}H]-2). Selected data: ^{1}H NMR δ 4.40 (m, 1H); ^{13}C NMR δ 43.5 (CHD).

Bis-deuterated *N*-benzyl(trimethylsilyl)acetamide ([^{2}H], [^{2}H]-2). Selected data: ^{1}H NMR δ 4.31 (m, 1H), 1.75 (m, 1H); ^{13}C NMR δ 43.1 (CHD), 28.4 (CHD).

***N*-Benzyl-2-(trimethylsilyl)propionamide (3).** 144 mg (61%); oil; IR (film) ν 1633, 1541, 1248 cm^{-1}; ^{1}H NMR δ 7.35–7.25 (m, 5H), 5.48 (m 1H), 4.43 (d *J*=5.5 Hz, 2H), 1.80 (q, *J*=7.0 Hz, 1H), 1.22 (d, *J*=7.0 Hz, 3H), 0.07 (s, 9H); ^{13}C NMR δ 175.3 (C=O), 138.8 (C), 128.4 (2CH), 127.8 (2CH), 127.2 (CH), 43.5 (CH_2), 31.9 (CH), 9.8 (CH_3), −3.0 (3CH_3); MS *m/z* (%) 236 (M+1, 33), 235 (46), 220 (18), 179 (26), 164 (27), 163 (20), 147 (27), 129 (16), 120 (100), 119 (32), 117 (36), 107 (90), 106 (47), 105 (28); High Resolution MS: $C_{13}H_{21}NOSi$ requires 235.1392, found 235.1356.

***N*-Benzyl-3-phenyl-2-(trimethylsilyl)propionamide (4).** 187 mg (60%); solid; mp 154°C (from CCl_4); IR (KBr) ν 1630, 1566, 1240 cm^{-1}; ^{1}H NMR δ 7.35–7.15 (m, 8H), 7.06–6.94 (m, 2H), 5.35 (m, 1H), 4.46 (dd, *J*=14.7, 6.4 Hz, 1H), 4.21 (dd, *J*=14.7, 5.2 Hz, 1H), 3.18 (dd, *J*=14.0, 12.0 Hz, 1H), 2.73 (dd, *J*=14.0, 3.0 Hz, 1H), 1.93 (dd, *J*=12.0, 3.0 Hz, 1H), 0.14 (s, 9H); ^{13}C NMR δ 173.6 (C=O), 142.3 (C), 138.6 (C), 128.4 (2CH), 128.3 (4CH), 127.7 (2CH), 127.1 (CH), 125.9 (CH), 43.5 (CH_2), 42.6 (CH), 33.2 (CH_2), −2.6 (3CH_3); MS *m/z* (%) 311 ($M^{+\bullet}$, 64), 296 (17), 239 (19), 238 (100), 220 (21), 164 (17), 106 (26); High Resolution MS $C_{19}H_{25}NOSi$ requires 311.1705 found 311.1687.

***N*-Benzyl-2-trimethylsilyl-pent-4-enamide (5).** 154 mg (59%); oil; IR (film) ν 1705, 1655, 1591 cm^{-1}; ^{1}H NMR δ 7.37–7.23 (m, 5H), 5.86–5.78 (m, 1H), 5.45 (m, 1H), 5.04 (d, *J*=17.2 Hz, 1H), 4.95 (d *J*=9.9 Hz, 1H), 4.48 (dd, *J*=14.6, 5.7 Hz, 1H), 4.37 (dd, *J*=15.0, 5.7 Hz, 1H), 2.59 (m, 1H), 2.16 (m, 1H), 1.75 (dd *J*=11.5, 3.3 Hz, 1H), 0.09 (s, 9H); ^{13}C NMR δ 173.9 (C=O), 138.7 (C), 138.1 (CH), 128.6 (2CH), 128.0 (2CH), 127.4 (CH), 115.1 (CH_2), 43.7 (CH_2), 39.5 (CH), 31.2 (CH_2), −2.6 (3CH_3); MS *m/z* (%) 261 ($M^{+\bullet}$, 5), 246 (5), 190 (17), 189 (100), 188 (20), 172 (6), 164 (10), 160 (12); High Resolution MS $C_{15}H_{23}NOSi$ requires 261.1549 found 261.1557.

***N*-Benzyl-bis(trimethylsilyl)acetamide (6).** 88 mg (30%); oil; IR (film) ν 1616, 1541, 1248 cm^{-1}; ^{1}H NMR δ 7.35–7.20 (m, 5H), 5.51 (m, 1H), 4.37 (d *J*=5.7 Hz, 2H), 1.29 (s, 1H), 0.12 (s, 18H); ^{13}C NMR δ 173.4 (C=O), 139.1 (C), 128.5 (CH), 127.9 (CH), 127.2 (CH), 126.2 (CH), 125.3 (CH), 43.8 (CH_2), 33.2 (CH), 0.1 (6 CH_3); MS *m/z* (%) 293 ($M^{+\bullet}$, 100), 278 (78), 187 (51), 164 (51), 147 (74), 135 (42), 107 (97), 106 (55), 105 (50); High Resolution MS $C_{15}H_{27}NOSi_2$ requires 293.1631 found 293.1631.

***N*-Benzyl-3-phenylacrylamide (7).**[21] 119 mg (50%); eluent: *n*-hexane/AcOEt=85:15, R_f 0.20.

***N*-Benzyl-3-(2-naphthyl)acrylamide (8).** 167 mg (58%); solid; mp 156°C; eluent: *n*-hexane/AcOEt=7:3, R_f=0.60; IR (KBr) ν 1655, 1618, 1543, 1253 cm^{-1}; ^{1}H NMR δ 7.93–7.75 (m, 6H), 7.69–7.59 (m, 1H), 7.56–7.45 (m, 2H), 7.41–7.23 (m, 4H), 6.54 (d, *J*=15.6 Hz, 1H), 4.61 (d, *J*=5.7 Hz, 2H); ^{13}C NMR δ 165.8 (C=O), 141.5 (CH), 138.2 (C), 133.9 (C), 132.2 (C), 129.4 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 127.9 (2 CH), 127.7 (CH), 127.6

(CH), 126.9 (CH), 126.6 (CH), 123.5 (CH), 120.5 (CH), 43.9 (CH_2); MS *m/z* (%) 287 ($M^{+\bullet}$, 55), 182 (100), 181 (88), 154 (42), 153 (59), 152 (70), 127 (19), 106 (61); High Resolution MS $C_{20}H_{17}NO$ requires 287.1310 found 287.1313.

(*E*)-*N*-Benzyl-pent-2-enamide (9a). 83 mg (44%); oil; eluent: *n*-hexane/AcOEt=8:2, R_f=0.30; IR ($CHCl_3$) ν 1667, 1516 cm^{-1}; ^1H NMR δ 7.40–7.20 (m, 5H), 6.92 (dt, *J*=15.3, 6.1 Hz, 1H), 5.96 (m, 1H), 5.79 (dt, *J*=15.3, 1.5 Hz, 1H), 2.20 (m, 2H), 1.05 (t, *J*=7.3 Hz, 3H); ^{13}C NMR δ 166.0 (C=O), 146.5 (CH), 138.3 (C), 128.6 (2CH), 127.8 (2CH), 127.4 (CH), 122.4 (CH), 43.5 (CH_2), 25.0 (CH_2), 12.4 (CH_3); MS *m/z* (%) 190 (M+1, 38), 189 (50), 161 (42), 160 (100), 117 (25), 107 (53), 106 (91); High Resolution MS $C_{12}H_{15}NO$ requires 189.1154 found 189.1165.

(*Z*)-*N*-Benzyl-pent-2-enamide (9b). 15 mg (8%), oil; eluent: *n*-hexane/AcOEt=8:2, R_f=0.40; IR ($CHCl_3$) ν 1666, 1504 cm^{-1}; ^1H NMR δ 7.40–7.20 (m, 5H), 6.02 (dt *J*=11.4, 7.6 Hz, 1H), 5.75 (m, 1H), 5.68 (dt, *J*=11.4, 1.5 Hz, 1H), 2.70 (m, 2H), 1.06 (t, *J*=7.3 Hz, 3H); ^{13}C NMR δ 166.3 (C=O), 147.8 (CH), 138.3 (C), 128.7 (2 CH), 127.9 (2 CH), 127.5 (CH), 121.3 (CH), 43.3 (CH_2), 22.2 (CH_2), 13.8 (CH_3); MS *m/z* (%) 189 ($M^{+\bullet}$, 27), 160 (100), 117 (8), 106 (37), 104 (9); High Resolution MS $C_{12}H_{15}NO$ requires 189.1154 found 189.1159.

***N*-Benzyl-3-*tert*-butylacrylamide (10).** 102 mg (47%) solid; mp 101°C (from hexane); eluent: *n*-hexane/AcOEt=85:15, R_f=0.25; IR (KBr) ν 1667, 1630, 1566 cm^{-1}; ^1H NMR δ 7.38–7.20 (m, 5H), 6.87 (d, *J*=15.6 Hz, 1H), 6.08 (m, 1H), 5.70 (d, *J*=15.6 Hz, 1H), 4.47 (d, *J*=5.7 Hz, 2H), 1.05 (s, 9H); ^{13}C NMR δ 166.3 (C=O), 155.1 (CH), 138.3 (C), 128.7 (2CH), 128.1 (2CH), 127.5 (CH), 118.5 (CH), 43.6 (CH_2), 33.4 (C), 28.8 ($3CH_3$); MS *m/z* (%) 218 (M+1, 10), 217 (11), 209 (9), 161 (19), 160 (100), 117 (9), 111 (30), 106 (24); High Resolution MS $C_{14}H_{19}NO$ requires 217.1467 found 217.1459.

(*E*,*E*)-*N*-Benzyl-4-methyl-5-phenylpenta-2,4-dienamide (11). 105 mg (38%); solid; mp 141°C (from CCl_4); eluent: *n*-hexane/AcOEt=85:15, R_f=0.20; IR (KBr) ν 1655, 1604, 1566 cm^{-1}; ^1H NMR δ 7.48 (d, *J*=15.6 Hz, 1H), 7.40–7.20 (m, 10H), 6.82 (s, 1H), 6.21 (s, 1H), 5.99 (d, *J*=15.6 Hz, 1H), 4.54 (d, *J*=5.7 Hz, 2H), 2.02 (s, 3H); ^{13}C NMR δ 166.1 (C=O), 146.4 (CH), 138.3 (C), 137.9 (CH), 136.9 (C), 133.8 (C), 129.4 (2CH), 128.7 (2CH), 128.2 (2CH), 127.9 (2CH), 127.5 (CH), 127.4 (CH), 119.7 (CH), 43.8 (CH_2), 13.8 (CH_3); MS *m/z* (%) 277 ($M^{+\bullet}$, 16), 141 (37), 128 (100), 115 (64), 104 (52); High Resolution MS $C_{19}H_{19}NO$ requires 277.1467 found 277.1470.

***N*-Benzyl-3-oxobutyramide (12).**[22] 74 mg (39%); eluent: *n*-hexane/AcOEt=1:1, R_f=0.20.

***N*-Benzyl-carbamoylmethylacetate (13).**[23] 125 mg (61%); eluent: *n*-hexane/AcOEt=1:1, R_f=0.30.

References

1. (a) Boger, D. L. *Comprehensive Organic Synthesis*, Vol. 5, Trost, B. M., Fleming, I., Eds. Pergamon, Oxford, 1991, p 451. (b) Ghosez, L.; Bayard, P.; Nshimyumukiza, P.; Gouverneur, V.; Sainte, F.; Beaudegnies, R.; Rivera, M.; Frisque-Hesbain, A.-M.; Wynants, C. *Tetrahedron* **1995**, *51*, 11021. (c) Barluenga, J.; Joglar, J.; González, F. J.; Fustero, S. *Synlett* **1990**, 129. (d) Gouverneur, V.; Ghosez, L. *Tetrahedron* **1996**, *52*, 7585. (e) Ghosez, L.; Jnoff, E.; Bayard, P.; Sainte, F.; Beaudegnies, R. *Tetrahedron* **1999**, *55*, 3387. (f) Jnoff, E.; Ghosez, L. *J. Am. Chem. Soc.* **1999**, *121*, 2617.

2. Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic: London, 1987.

3. (a) Bandini, E.; Martelli, G.; Spunta, G.; Panunzio, M.; Piersanti, G. *Tetrahedron: Asymmetry* **1999**, *10*, 1445. (b) Bongini, A.; Panunzio, M.; Bandini, E.; Martelli, G.; Spunta, G. *J. Org. Chem.* **1997**, *62*, 8911. (c) Barluenga, J.; Carlón, R. P.; Peláez, E.; Joglar, J.; Ortiz, F. L. *Tetrahedron* **1992**, *48*, 9745.

4. (a) Panunzio, M.; Zarantonello, P. *Org. Process Res. Dev.* **1998**, *2*, 49. (b) Lasarte, J.; Palomo, C.; Picard, J. P.; Dunogues, J.; Aizpurua, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 72.

5. (a) Wender, P. A.; Schaus, J. M. *J. Org. Chem.* **1978**, *43*, 782. (b) Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5866.

6. (a) Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 4469. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (c) Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1989**, *111*, 4495.

7. Gandon, V.; Bertus, P.; Szymoniak, J. *Tetrahedron Lett.* **2000**, *41*, 3053.

8. For reviews of 'Cp_2Zr' chemistry, see: (a) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn* **1998**, *71*, 755. (b) Negishi, E.; Kondakov, D. Y. *Chem. Soc. Rev.* **1996**, *26*, 417. (c) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (d) Negishi, E. *Chem. Scripta* **1989**, *29*, 457.

9. Scholz, J.; Kahlert, S.; Görls, H. *Organometallics* **1998**, *17*, 2876.

10. A retro-[1,4]-Brook rearrangement (C4–Si bond forming process) exclusively occurred starting from the more crowded 1,4-diphenyl-3-trimethylsilyloxy-2-aza-1,3-butadiene. In this case, similar structural environment at C1 and C4 in the substrate led to the generally easier Zr–C bond-breaking.

11. (a) Panek, J. S. *Comprehensive Organic Synthesis*, Vol. 1, Trost, B. M., Fleming, I., Eds.; Pergamon, Oxford, 1991, p. 580. (b) Colvin, E. W. *Silicon in Organic Synthesis*, Krieger, R. E. Publishing Company, Malabar, FL, 1985.

12. Meyers, A. I.; Mihelich, E. D. *Angew. Chem.* **1976**, *88*, 321; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 270.

13. This feature corroborates the total regioselectivity of the Meyers C-alkylation of 2-oxazolines, see Ref. 12.

14. The structures of silylated amides were confirmed by removal of the α-trimethylsilyl group, which could be readily accomplished by either brief heating with NaOH–MeOH–H_2O or by treatment with KF in MeOH, see Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1978**, 881.

15. We have proved the complex to be quite inert towards insertion of carbonyl compounds and even isocyanides into the Zr–C bond.

16. Werner, R. M.; Barwick, M.; Davis, J. T. *Tetrahedron Lett.* **1995**, *36*, 7395.

17. Ager, D. J. *Synthesis* **1984**, 384.

18. Lithiated 2-silylmethyl-1,3-oxazines have been demonstrated to react efficiently with aldehydes, see Sachdev, K. *Tetrahedron Lett.* **1976**, 4041.

19. To elaborate the 1,3-diene system via the Peterson reaction,

the reactions of α-silylallylanions with saturated aldehydes are generally employed.
20. Chan, T. H.; Chang, E.; Vinokur, E. *Tetrahedron Lett.* **1970**, 1137.
21. Kazuyoshi, T.; Kanoko, T.; Hiroaki, T.; Rie, S.; Masumi, T.; Haruo, O. *Chem. Pharm. Bull.* **1989**, *37*, 2334.
22. Casadei, M. A.; Cesa, S.; Inesi, A.; Franco, M. *J. Chem. Res.* **1995**, *5*, 1064.
23. Garcia, M. J.; Rebolledo, F.; Gotor, V. *Tetrahedron* **1994**, *50*, 6935.