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Claisen Rearrangement of *N*-Silyl Ketene *N,O*-Acetals Generated from Allyl *N*-Phenylimidates

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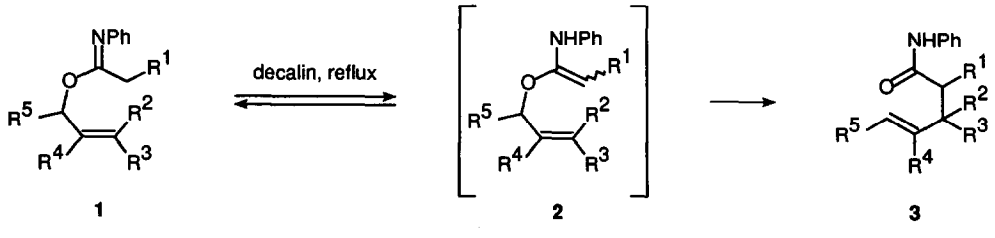
Abstract: Deprotonation and subsequent *N*-silylation of allyl *N*-phenylimidates **1** lead to *N*-silyl ketene *N,O*-acetals **5** which undergo a Claisen rearrangement to yield γ,δ-unsaturated anilides **3** after hydrolytic work-up. The temperature for the rearrangement step is dependent on the nature of the substituent R^2 in **5**. Ketene acetals **5** with $R^2 = H$ rearrange readily at room temperature, while heating at 130 °C is required if $R^2 \neq H$. The degree of simple diastereoselection attainable for the conversion of **1** to **3** is strongly affected by the size of the substituent R^4. With $R^4 > H$ excellent *anti*/*syn* selectivity is caused by efficient suppression of the rearrangement pathway *via* a boat transition state. This rationale is supported by NOE difference data obtained for several allyl *N*-phenylimidates and *N*-silyl ketene *N,O*-acetals.

INTRODUCTION

The thermal isomerization of allyl *N*-phenylimidates **1** *via* ketene *N,O*-acetals **2** constitutes a simple protocol for the synthesis of γ,δ-unsaturated anilides **3** (Scheme 1).[1a] However, due to the non-stereoselective formation of the ketene acetal moiety within intermediates **2**, only a moderate control over the relative configuration of the two newly formed stereogenic centers α and β to the carbonyl group in **3** is achieved.

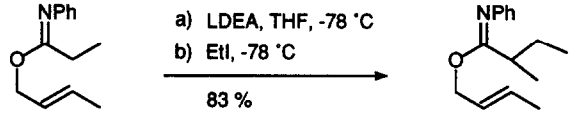
In the course of our studies on rearrangement reactions of allyl imidates,[1] we have developed an alternative procedure for the conversion of **1** to **3** by Claisen rearrangement[2] of *N*-silyl ketene *N,O*-acetals generated from **1** through deprotonation and subsequent *N*-silylation.[1b,3] This method provides a highly diastereoselective access to amides **3** which can be hydrolyzed to the corresponding carboxylic acids without epimerization.[4] Here, we give a full account of our investigations on the title reaction including NOE difference studies of educts and *N*-silyl ketene *N,O*-acetals.



1 **2** **3**

Scheme 1. Claisen rearrangement *via* thermal isomerization of allyl *N*-phenylimidates **1**

In order to find suitable conditions for the deprotonation of allyl *N*-phenylimidates **1**, model substrate **1a**[1a] was treated with a broad range of bases[5] followed by an excess of ethyliodide. Eventually, it turned out that the use of lithium diethylamide[6] allowed for a complete conversion of **1a** and led to a good yield of alkylation product **4** (Scheme 2).[7]



1a **4**

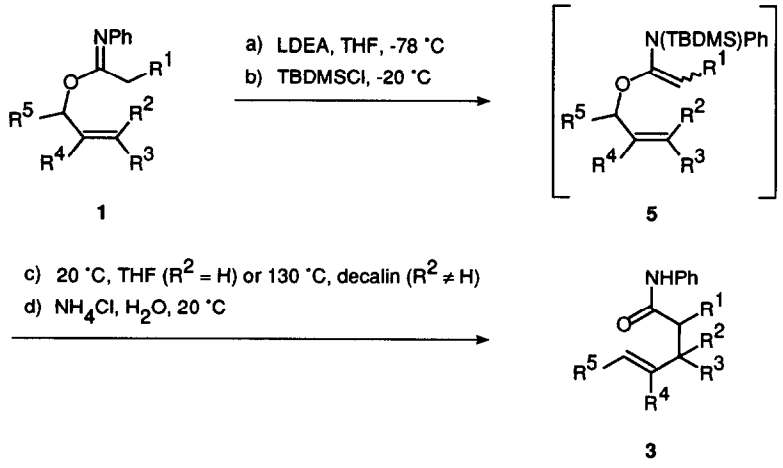
Scheme 2. Deprotonation/alkylation of allyl *N*-phenylimidate **1a**
(LDEA = lithium diethylamide)

RESULTS AND DISCUSSION

General Features of the Deprotonation/Silylation Sequence

Deprotonation of allyl *N*-phenylimidates **1** with lithium diethylamide and silylation of the resultant azaenolates with *tert*-butyldimethylchlorosilane afford *N*-silyl ketene *N,O*-acetals **5**.[8] Without isolation, these intermediates were rearranged to *N*-silylated amides which smoothly hydrolyzed to anilides **3** on aqueous work-up in moderate to good overall yields (Scheme 3, Table 1). Starting from substrates **1** with $R^2 = H$, Claisen rearrangement of the corresponding ketene acetals **5** is complete after 24 h at room temperature, whereas no rearrangement is detectable for substrates with $R^2 \neq H$ under these conditions. The rearrangement step for the latter substrates (entries 3,5,7,8) is best performed by heating the intermediates **5** at 130 °C for 48 h after exchanging the solvent THF against decalin.

In contrast to the thermal isomerization of allyl imidates,[1a] a sterically unfavorable formation of a β-quaternary center is easily accomplished (entry 8), and imidate **1g** (entry 9) derived from a secondary alcohol leads exclusively to (*E*)-configured **3g**, while simple heating of **1g** also produces 2.8 % of the (*Z*)-isomer.[1a]



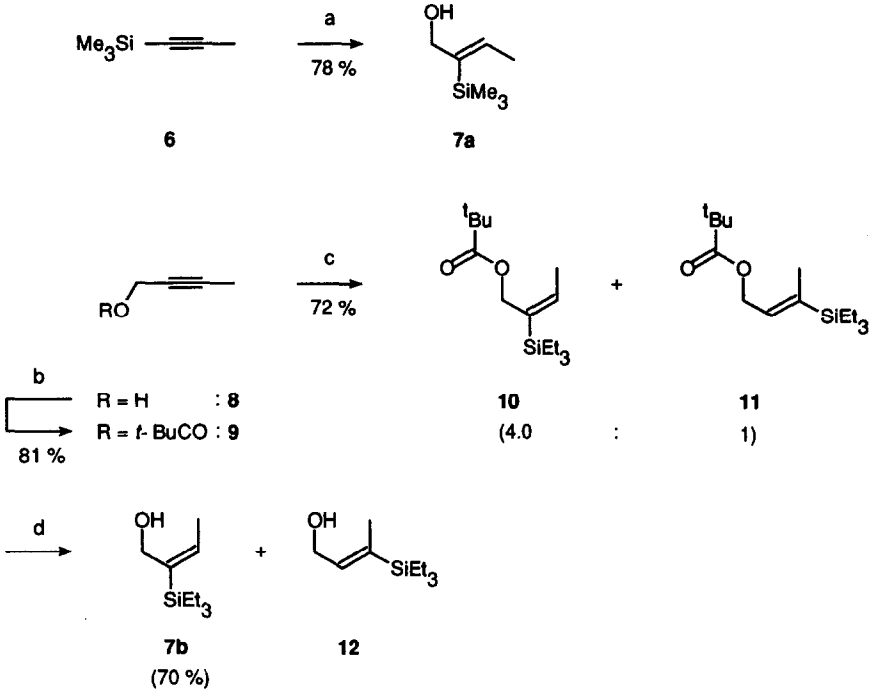
1 **5** **3**

Scheme 3. Claisen rearrangement *via* deprotonation/silylation of allyl *N*-phenylimidates **1**
(LDEA = lithium diethylamide; TBDMSCl = *tert*-butyldimethylchlorosilane)

Table 1. Claisen rearrangement of *N*-silyl ketene *N,O*-acetals **5** generated from allyl *N*-phenylimidates **1**.

entry	1	R^1	R^2	R^3	R^4	R^5	T [°C]	3	Yield [%][a]
1	**a**	Me	H	Me	H	H	20	**a**	67
2	(*E*)-**b**	Me	H	*n*-Pr	H	H	20	**b**	66
3	(*Z*)-**b**	Me	*n*-Pr	H	H	H	130	**b**	63
4	(*E*)-**c**	Me	H	Me	Me	H	20	**c**	59
5	(*Z*)-**c**	Me	Me	H	Me	H	130	**c**	70
6	**d**	Me	H	Me	$SiMe_3$	H	20	**d**	64
7	**e**	Me	Me	H	$SiEt_3$	H	130	**e**	38
8	**f**	Me	Me	Me	H	H	130	**f**	56
9	**g**	Me	H	H	H	Me	20	**g**	55[b]
10	**h**	Ph	H	Me	H	H	20	**h**	47
11	**i**	OMe	H	Me	H	H	20	**i**	54

[a] Yield of anilides **3** after chromatographic purification. [b] Only (*E*)-**3g** by capillary GC analysis of the crude product.

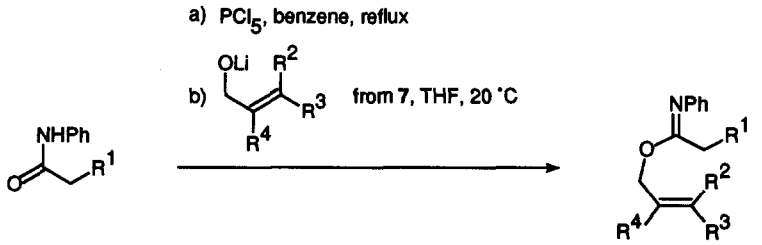


Scheme 4. Preparation of allyl alcohols **7a** and **7b**. a: (i) DIBAH, ether, 35 °C, (ii) MeLi, 20 °C, (iii) $(CH_2O)_x$, ether, 20 °C; b: *t*-BuCOCl, DMAP, Et_3N, CH_2Cl_2, 20 °C; c: Et_3SiH, $H_2PtCl_6 \cdot H_2O$, 100 - 120 °C; d: $LiAlH_4$, ether, reflux
(DIBAH = di-*iso*-butylaluminum hydride; DMAP = 4-*N,N*-(dimethylamino)pyridine)

Scheme 4 illustrates the preparation of trialkylsilyl substituted alcohols **7a** and **7b** required for the synthesis of allyl imidates **1d** and **1e**, respectively. Regio- and stereoselective hydroalumination[9] of alkyne **6** followed by hydroxymethylation[10] directly yielded **7a** as a single isomer, thus providing an efficient alternative to the published multi-step route[11] to this compound. Alcohol **7b** was prepared according to the procedure of Stork and co-workers from alkyne **8** *via* directed hydrosilylation of pivalate **9** and subsequent reduction.[12] In our hands, a mixture of **10** and **11** (4.0 : 1) was obtained in the key step, but pure **7b** was easily isolated by flash chromatography after reductive ester cleavage.

Allyl *N*-phenylimidates **1** were synthesized under standard conditions[1a] from amides **13** and the lithium salts of the requisite allyl alcohols (Table 2).

Table 2. Preparation of allyl *N*-phenylimidates **1**.[a]



13 **1**

13	R^1	**7**	R^2	R^3	R^4	**1**	Yield [%][b]
a	Me	(Z)-**c**[c]	Me	H	Me	(Z)-**c**	62
a	Me	**a**	H	Me	$SiMe_3$	**d**	62
a	Me	**b**	Me	H	$SiEt_3$	**e**	64[d]
b	OMe[e]	**d**[f]	H	Me	H	**i**	44

[a] For the preparation of the other imidates 1 used in this study, see ref 1a. [b] Yield of distilled imidates **1**. [c] Ref 13. [d] Yield after chromatographic purification. [e] Ref 14. [f] Ref 15.

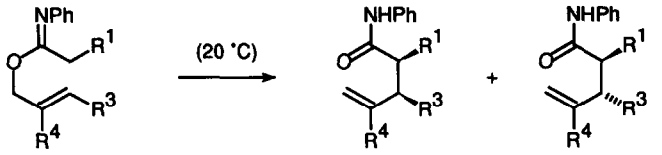
Simple Diastereoselectivity

A central issue of our study was the determination of the simple diastereoselectivity attainable by this new variant of the Claisen rearrangement. The diastereomeric ratios listed in Table 3 exceed the corresponding values for the thermal isomerization of allyl imidates **1** by far and, moreover, they are complementary to the latter.[1a] Thus, (*E*)-configured[16] substrates **1** lead preferably to *anti*-**3**, whereas (*Z*)-configured[16] imidates **1** yield mainly *syn*-**3**.[17]

In the series of (*E*)-configured substrates **1**, a pronounced increase in diastereoselection is noted with increasing size of substituent R^4 along the line **1a** (R^4 = H), (*E*)-**1c** (R^4 = Me), and **1d** (R^4 = $SiMe_3$). Compared to **1a**, *anti* selectivity is decreased for R^1 = Ph (**1h**) though still being in a preparatively useful range, while R^1 = OMe (**1i**) causes a nearly stereorandom reaction.

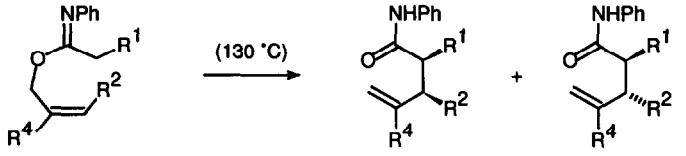
For the Ireland variant of the Claisen rearrangement starting from allyl esters, a change of the solvent during the enolization step can switch the relative configuration of the major rearranged product.[18] To determine whether a similar solvent effect is operative for allyl *N*-phenylimidates **1** as well, **1a** was deprotonated in a mixture of THF and hexamethylphosphoric triamide, too. However, this modification did not alter the *anti*/*syn* ratio of products **3a** recorded in Table 3.

Table 3. Simple diastereoselectivity of the Claisen rearrangement of *N*-silyl ketene *N,O*-acetals generated from allyl *N*-phenylimidates **1**.[a]



1 *anti*-**3** *syn*-**3**

1	R^1	R^3	R^4	*anti*-**3**	:	*syn*-**3**	**3**
a	Me	Me	H	90.7	:	9.3	**a**
(*E*)-**b**	Me	*n*-Pr	H	90.9	:	9.1	**b**
(*E*)-**c**	Me	Me	Me	98.1	:	1.9	**c**
d	Me	Me	$SiMe_3$	99.2	:	0.8	**d**
h	Ph	Me	H	83.2	:	16.8	**h**
i	OMe	Me	H	46.6	:	53.4	**i**



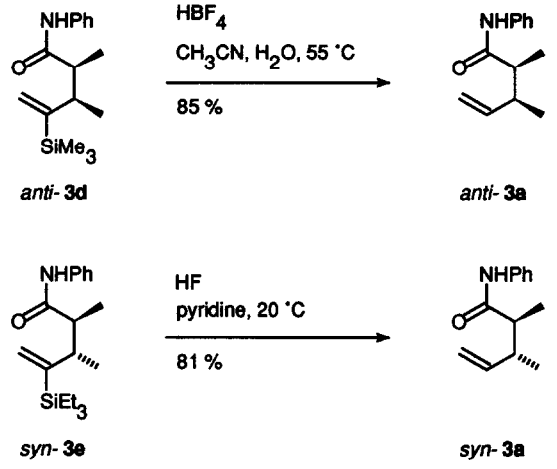
1 *anti*-**3** *syn*-**3**

1	R^1	R^2	R^4	*anti*-**3**	:	*syn*-**3**	**3**
(*Z*)-**b**	Me	*n*-Pr	H	11.5	:	88.5[b]	**b**
(*Z*)-**c**	Me	Me	Me	3.9	:	96.1[b]	**c**
e	Me	Me	$SiEt_3$	1.6	:	98.4	**e**

[a] Determined by capillary GC analysis of the crude anilides **3**. [b] Corrected for 100 % (*Z*)-educt.

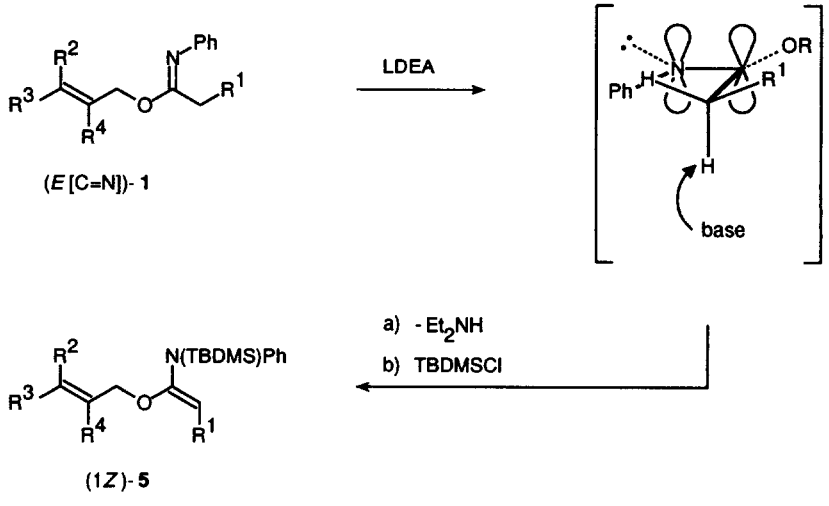
On the other hand, good to excellent *syn* selectivity is observed for (*Z*)-configured substrates **1**. Whereas the extreme reactivity difference between (*E*)- and (*Z*)-configured imidates **1** allows for a chemoselective conversion of the (*E*) isomer from an isomeric mixture at room temperature, high geometrical purity of the (*Z*) substrates **1** is essential to achieve a highly *syn* selective rearrangement. As is inferred from the last three entries in Table 3, the substituent R^4 again has a marked effect on the degree of diastereoselection.

Since anilides *anti*-**3d** and *syn*-**3e** are readily protodesilylated[19] to *anti*-**3a** and *syn*-**3a** without epimerization α to the carbonyl group, respectively, the trialkylsilyl groups in **1d** and **1e** may be regarded as temporary substituents for stereocontrol,[20] eventually providing an access to amides **3** with R^4 = H of very high stereoisomeric purity (Scheme 5). Moreover, in view of the broad synthetic potential of vinylsilanes,[19a] introduction of various groups at C-4 is easily envisioned from **3d** and **3e**.



Scheme 5. Desilylation of anilides *anti*-**3d** and *syn*-**3e**

With the exception of **3i**, the relative configuration of all major product stereoisomers is compatible with a (*Z*)-configuration of the vinylic double bond in the intermediate *N*-silyl ketene *N,O*-acetals **5** and a chair transition state geometry for the rearrangement step.[2] It appeared highly improbable to us, that the substituent R^4 exerts a significant influence on the stereoselectivity of azaenolate formation, i.e. the lower *anti*/*syn* ratio obtained from **1a** compared to (*E*)-**1c** and **1d** should not be due to different proportions of the corresponding intermediates **5** containing an (*E*)-configured ketene *N,O*-acetal moiety. As a more plausible explanation, all *N*-silyl ketene *N,O*-acetals **5** for $R^1 \neq$ OMe are > 99 % (*Z*)-configured and stereochemical differentiation ensues from the participation of both chair and boat transition state geometries.



Scheme 6. Stereoelectronically controlled formation of *N*-silyl ketene *N,O*-acetals
(LDEA = lithium diethylamide; TBDMSCl = *tert*-butyldimethylchlorosilane)

Indeed, if allyl *N*-phenylimidates **1** existed solely as (*E*[C=N]) isomers, as is usually the case for *N*-alkyl imidates,[6,21] a stereoelectronically controlled deprotonation of the conformer of (*E*[C=N])-**1** with minimized $A^{1,3}$-strain would yield (1*Z*)-**5** (Scheme 6).[6,22] For R^1 = OMe, however, generation of an (*E*) azaenolate would enable chelate formation. The striking drop in stereoselectivity observed for Claisen rearrangement starting from **1i** is attributable to a compensation of these two opposing factors.

Since all imidates **1** as well as *N*-silyl ketene *N,O*-acetals **5** containing a (*Z*)-configured allyl moiety are stable species at room temperature, it was possible to verify the assumptions regarding the geometry of the C,N double bond in **1** and the configuration of the vinylic double bond in **5** by NOE difference studies.[21c,23]

According to capillary GC, ^{1}H NMR, and ^{13}C NMR data, imidates **1** are stereochemically homogeneous about the C,N double bond. Figure 1 illustrates the results of NOE difference spectral analyses for (*Z*)-**1b** and **1a**. While irradiation of the methylene protons α to C=N and of the adjacent methyl protons resulted in significant enhancements for the *ortho* phenyl protons, respectively, no corresponding effect was noted for irradiation of the methylene protons adjacent to oxygen. These data strongly support an (*E*[C=N]) configuration.

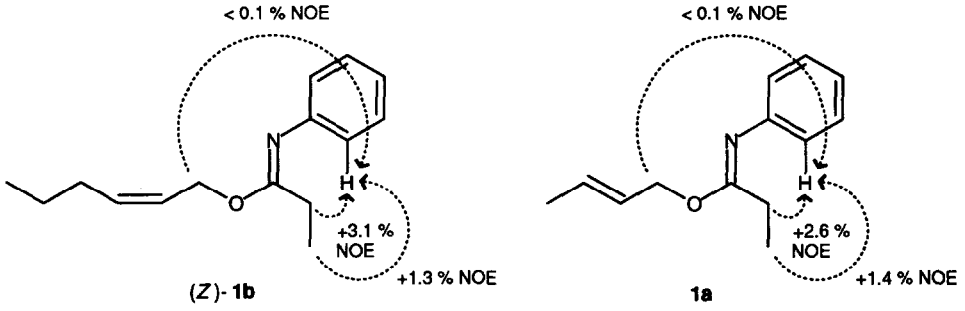


Figure 1. Selected NOE difference data for allyl *N*-phenylimidates (*Z*)-**1b** and **1a**

N-silyl ketene *N,O*-acetals **5** derived from (*E*)-configured allyl alcohols already rearrange at room temperature. Hence, allyl *N*-phenylimidate (*Z*)-**1b** and ethyl *N*-phenylpropanimidate[24] were deprotonated, and after subsequent silylation, *N*-silyl ketene *N,O*-acetals (1*Z*,2'*Z*)-**5b** and (*Z*)-**14** were isolated, respectively. These compounds were homogeneous by ^{1}H and ^{13}C NMR spectroscopy, too. Figure 2 depicts characteristic NOE difference data for (1*Z*,2'*Z*)-**5b** and (*Z*)-**14**.

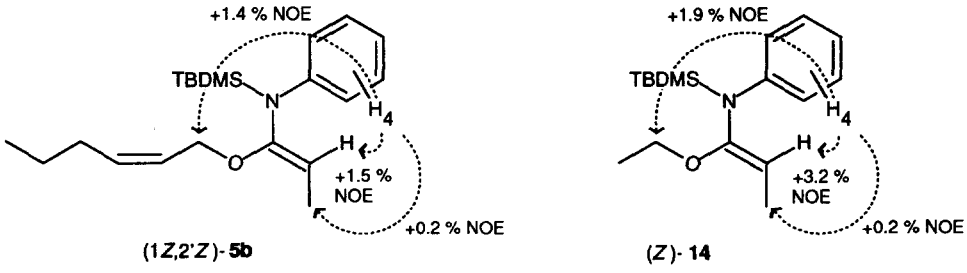


Figure 2. Selected NOE difference data for *N*-silyl ketene *N,O*-acetals (1*Z*,2'*Z*)-**5b** and (*Z*)-**14**

While irradiation of a four proton multiplet of the phenyl group produced enhancements of 1.5 % (3.2 %) for the vinylic hydrogen, enhancements of only 0.2 % were observed for the protons of the vinylic methyl group in these experiments. In addition to these data which clearly indicate a (*Z*)-configured ketene acetal moiety, enhancements of 1.4 % (1.9 %) were recorded for the methylene protons adjacent to oxygen. Thus, rotation around the C-1,N bond of (1Z,2'Z)-**5b** and (*Z*)-**14** is possible.

Since these NOE studies confirm that only *N*-silyl ketene *N,O*-acetals **5** with a (*Z*)-configured vinylic double bond ($R^1 \neq OMe$) are involved in the rearrangement step, a competition between reaction pathways *via* chair transition state **TS(1)** and boat transition state **TS(2)** is responsible for the varying diastereomeric ratios of anilides **3** listed in Table 3 (Figure 3).

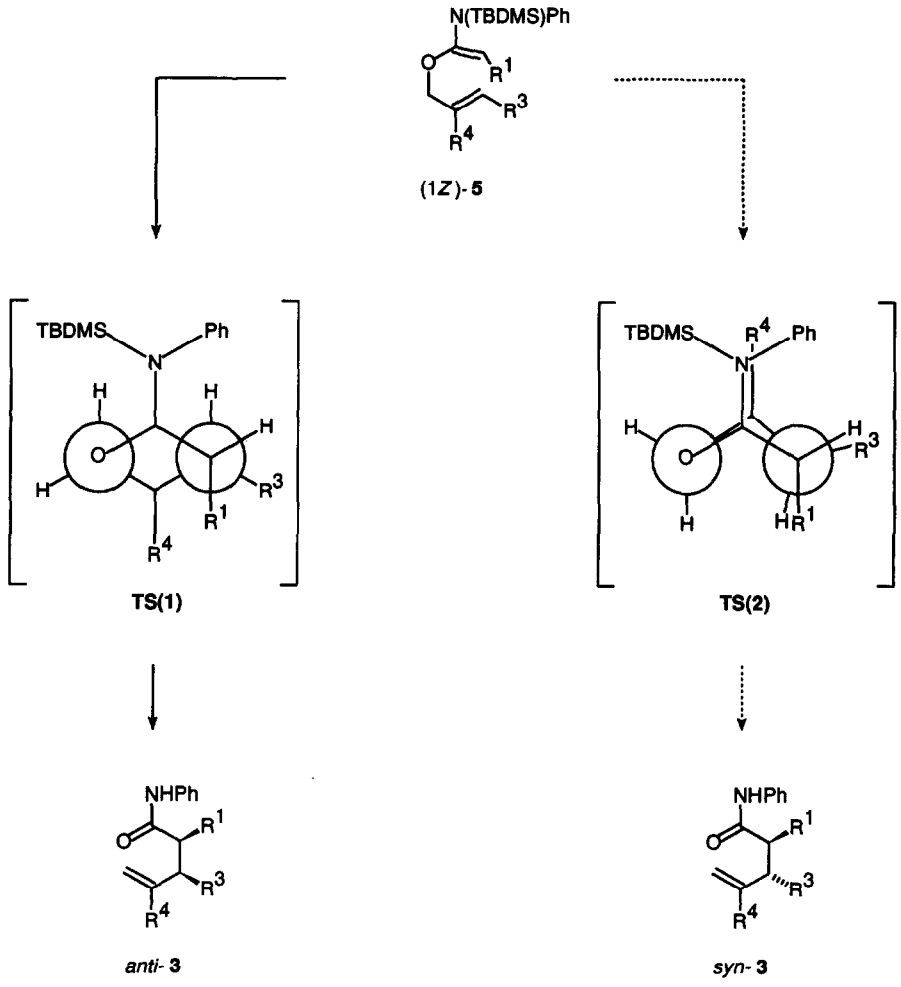


Figure 3. Competing pathways for the Claisen rearrangement of *N*-silyl ketene *N,O*-acetals (1*Z*)-**5**

To what extent a reaction course *via* **TS(2)** intervenes, is significantly influenced by the size of substituent R^4.[25] For R^4 = H (**1a**, (*E*)-**1b**), about 9 % of the intermediates **5** react *via* **TS(2)**,[26] whereas for R^4 = Me ((*E*)-**1c**) and even more pronounced for R^4 = $SiMe_3$ (**1d**), the increased ecliptic interaction between R^4 and the bulky amino substituent causes an efficient suppression of the reaction pathway *via* boat transition state **TS(2)**.[27] While Figure 3 is depicted for (*E*)-configured allyl moieties, the rationale given above also applies to the reaction of the (*Z*)-configured isomers as is easily seen after exchanging R^3 against H and the hydrogen atom geminal to R^3 against R^2.

EXPERIMENTAL

General Remarks

All reactions requiring exclusion of moisture were run under argon using flame-dried glassware. Solvents were dried by distillation from benzophenone ketyl (THF, ether) or else from CaH_2. Flash chromatography was performed on Merck silica gel 60 (40 - 63 µm). Capillary GC analyses were performed with a Shimadzu GC-14APFsc, a Shimadzu C-R6A integrator, an OV 225 CB column, 25 m length, 0.25 mm i. d., 0.25 µm film (column 1), a SE 54 CB column, 25 m length, 0.25 mm i. d., 0.25 µm film (column 2), a FFAP CB column, 50 m length, 0.32 mm i. d., 0.25 µm film (column 3), and a FFAP CB column, 50 m length, 0.20 mm i. d., 0.3 µm film (column 4). HPLC separations were performed with a Knauer 64 pump, a Knauer 51.78 differential refractometer, a Knauer 42.00 recorder, a Rheodyne 7125 injector, and a Knauer Polygosil 60 (5 µm) column, 250 mm length, 32 mm i. d.. Boiling points for bulb-to-bulb distillations refer to bath temperatures. Melting points were determined on a Kofler microscope desk. ^{1}H NMR spectra (300 MHz, $CDCl_3$), NOE difference spectra (300 MHz, $CDCl_3$) and ^{13}C NMR spectra (75.47 MHz, $CDCl_3$) were obtained on a Bruker WM 300 - m_c = multiplet centered at, br. = broad. ^{13}C multiplicities were determined using INEPT or DEPT pulse sequences. IR spectra ($CHCl_3$) were obtained on a Shimadzu IR-408 and a Nicolet 5DXC FT-IR. Mass spectra (70 eV) were recorded with a Varian MAT CH-7A + data system Finnigan MAT 200 (GC/MS), a Finnigan MAT 8230 + data system Finnigan SS 300 (GC/MS), and a Varian MAT CH-7 + data system Varian SS 200. Microanalyses were performed by the analytical laboratory of the Organisch-Chemisches Institut, Universität Münster, and by Mikroanalytisches Laboratorium M. Beller, Göttingen.

Allyl Alcohols **7**

Except for **7a**, the required allyl alcohols were either purchased from Aldrich (capillary GC analysis using column 1, 50 °C isothermal, indicated a (*Z*)/(*E*) ratio of 97.2:2.8 for the alcohol converted to allyl *N*-phenylimidate (*Z*)-**1b**) or prepared according to published procedures (cf. ref 1a; (*Z*)-**7c**: ref 13, (*Z*)/(*E*) = 98:2 by ^{1}H NMR integration).

Preparation of **7a**. 1-(Trimethylsilyl)propyne (**6**; 6.5 ml, 43.9 mmol) is added dropwise at room temperature (water bath) to a solution of di-*iso*-butylaluminum hydride (8.73 ml, 49 mmol) in ether (22 ml). The mixture is heated to 35 °C for 1 h, cooled to 0 °C, and treated with methyllithium (30.3 ml, 1.6 M in ether). After stirring for 10 min at room temperature, the resultant solution is added dropwise to a suspension of paraformaldehyde (10.5 g, 350 mmol) in ether (22 ml) cooled to 0 °C. The mixture is stirred for 24 h at room temperature and poured into ice-cooled 1 N H_2SO_4 (100 ml). After extraction with ether (4 x 70 ml), the organic layers are washed with brine (70 ml), dried over $MgSO_4$, and concentrated *in vacuo* (rotary evaporator, 40 °C bath temperature). Bulb-to-bulb distillation (79 °C/15 Torr) yields **7a** (4.92 g, 78 %) as a colorless liquid. No geometric isomer of **7a** was detected with any of the GC columns applied in this study.

(Z)-2-Trimethylsilyl-2-buten-1-ol (**7a**).[11] ^{1}H NMR δ 0.19 [s, 9 H, $Si(CH_3)_3$], 1.80 (br. d, 3 H, J = 6.9 Hz, CH-CH_3), 4.12 (br. s, 2 H, OCH_2), 6.30 (tq, 1 H, J_t = 1.2 Hz, J_q = 6.9 Hz, CH-CH_3); ^{13}C NMR δ -0.3 (q), 17.3 (q), 68.7 (t), 138.3 (d), 139.8 (s); IR 3609 (O-H) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 129 (M^+ - CH_3,

11), 111 (M^+ - CH_3 - H_2O, 1), 75 [$(CH_3)_2Si{=}OH^+$, 100], 73 [$(CH_3)_3Si^+$, 44]. HRMS Calcd for $C_6H_{13}OSi$ (M^+ - CH_3): 129.0736. Found: 129.0737.

Preparation of **9**. To a solution of 2,2-dimethylpropionylchloride (4.07 ml, 33.1 mmol) in CH_2Cl_2 (20 ml) cooled to 0 °C is added 4-(*N,N*-dimethylamino)pyridine (0.4 g, 3.27 mmol) followed by a solution of 2-butyn-1-ol (**8**; 2.1 g, 30 mmol) and triethylamine (8.36 ml, 60 mmol) in CH_2Cl_2 (10 ml). After stirring the resultant mixture for 1 h at 0 °C and 24 h at room temperature, it is diluted with CH_2Cl_2 (70 ml), washed successively with 2 N HCl (30 ml), sat. aqueous $NaHCO_3$ (30 ml), and brine (30 ml), and dried over $MgSO_4$. The solvent is removed *in vacuo* (rotary evaporator, 20 °C bath temperature), and the crude product is purified by fractional distillation (94 °C/15 Torr) to give **9** (3.74 g, 81 %) as a colorless liquid.

2-Butyn-1-yl 2,2-Dimethylpropionate (**9**).[12] ^1H NMR δ 1.19 [s, 9 H, $C(CH_3)_3$], 1.83 (t, 3 H, J = 2.3 Hz, CH_2-CC-CH_3), 4.59 (q, 2 H, J = 2.3 Hz, OCH_2); MS (GC/MS) *m/e* (relative intensity): 154 (M^+, 3), 85 [$(CH_3)_3C$-CO^+, 19], 57 [$(CH_3)_3C^+$, 100].

Preparation of **10**. A mixture of alkyne **9** (3.1 g, 20.1 mmol), triethylsilane (3.21 ml, 20.1 mmol), and a 10 % aqueous solution of $H_2PtCl_6 \cdot H_2O$ (0.5 g, 0.12 mmol) is stirred under argon for 2 h at 120 °C and 3 h at 100 °C. After cooling to room temperature, the mixture is diluted with ether (120 ml), washed with sat. aqueous $NaHCO_3$ (30 ml) and water (30 ml), filtered, and dried over $MgSO_4$. The solvent is removed *in vacuo*, and the crude product is fractionally distilled (81 - 84 °C/0.53 Torr) to yield a mixture of **10** and **11** (3.92 g, 72 %) as a colorless liquid. Capillary GC analysis using column 1, 50 - 200 °C, 5 °C/min, then 200 °C isothermal, indicated a ratio **10**:**11** = 4.0:1 for the distilled as well as for the crude product.

(E)-2-Triethylsilyl-2-buten-1-yl 2,2-Dimethylpropionate (**10**).[12] ^1H NMR δ 0.61 [q, 6 H, J = 7.8 Hz, $Si(CH_2$-$CH_3)_3$], 0.91 [t, 9 H, J = 7.8 Hz, $Si(CH_2CH_3)_3$], 1.20 [s, 9 H, $C(CH_3)_3$], 1.78 (d, 3 H, J = 6.8 Hz, C=CH-CH_3), 4.66 (s, 2 H, OCH_2) 6.07 (br. q, 1 H, J = 6.8 Hz, C=CH-CH_3); MS (GC/MS) *m/e* (relative intensity): 241 (M^+ - C_2H_5, 17), 187 [$(CH_3)_3C$-CO-O=$Si(C_2H_5)_2^+$, 100], 172 [M^+ - CH_2=C=CH-CH_3 - CH_3, 12], 57 [$(CH_3)_3C^+$, 32].

(E)-3-Triethylsilyl-2-buten-1-yl 2,2-Dimethylpropionate (**11**). ^1H NMR (separable signals) δ 1.72 (s, 3 H, CH=C-CH_3), 5.76 (br. t, 1 H, J = 6 Hz, C=CH); MS (GC/MS) *m/e* (relative intensity): 241 (M^+ - C_2H_5, 10), 187 [$(CH_3)_3C$-CO-O=$Si(C_2H_5)_2^+$, 100], 172 (M^+ - CH_2=C=CH-CH_3 - CH_3, 6), 57 [$(CH_3)_3C^+$, 22].

Preparation of **7b**. A solution of the 4.0:1 mixture of **10** and **11** (5.93 g, 21.9 mmol **10** + **11**; 17.5 mmol **10**) in ether (22 ml) is added dropwise to a suspension of $LiAlH_4$ (831 mg, 21.9 mmol) in ether (90 ml) cooled to 0 °C. After heating at reflux for 2 h, the mixture is cooled to 0 °C, and water (2.3 ml) is added slowly. The ethereal layer is decanted, the residue is extracted inside the reaction flask with ether (3 x 100 ml), and the combined organic layers are dried over $MgSO_4$. Removal of the solvent *in vacuo* and subsequent flash chromatography (ethyl acetate/petroleum ether 1:9, including 1 vol % triethylamine) affords **7b** (2.87 g, 70 % on mixture of **10** + **11**, 88 % on **10**) as a colorless liquid and a small amount of **12**. No geometric isomer of **7b** was detected with any of the GC columns applied in this study.

(E)-2-Triethylsilyl-2-buten-1-ol (**7b**).[12] ^1H NMR δ 0.63 [q, 6 H, J = 7.8 Hz, $Si(CH_2$-$CH_3)_3$], 0.93 [t, 9 H, J = 7.8 Hz, $Si(CH_2CH_3)_3$], 1.79 (d, 3 H, J = 6.8 Hz, C=CH-CH_3), 4.26 (s, 2 H, OCH_2), 5.98 (br. q, 1 H, J = 6.8 Hz, C=CH-CH_3); ^{13}C NMR δ 3.2 (t), 7.4 (q), 14.6 (q), 60.3 (t), 138.4 (s), 139.1 (d); IR 3616 (O-H), 1614 (C=C) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 157 (M^+ - C_2H_5, 4), 129 (M^+ - C_2H_5 - CO, 18), 103 [$(C_2H_5)_2Si{=}OH^+$, 100], 75 (80).

(E)-3-Triethylsilyl-2-buten-1-ol (**12**). ^{1}H NMR δ 0.60 [br. q, 6 H, *J* = 7.9 Hz, Si(C*H*$_2$-CH$_3$)$_3$], 0.92 [t, 9 H, *J* = 7.9 Hz, Si(CH$_2$C*H*$_3$)$_3$], 1.69 (br. s, 3 H, CH=C-C*H*$_3$), 4.28 (br. d, 2 H, *J* = 5.9 Hz, OCH$_2$), 5.86 (qt, 1 H, J_q = 1.7 Hz, J_t = 5.9 Hz, C=C*H*); MS (GC/MS) *m/e* (relative intensity): 186 (M^+, 2), 157 (M^+ - C_2H_5, 82), 129 (M^+ - C_2H_5 - CO, 41), 103 [$(C_2H_5)_2Si{=}OH^+$, 80], 75 (100).

Imidates **1**

The general procedure in ref 1a is followed (for yields, see Table 2). **1e** is purified by chromatography (14 g basic alumina, activity III, for preparation on a 2.22 mmol scale; elution with ethyl acetate/petroleum ether 1:9, including 1 vol % triethylamine).

(*Z*)/(*E*) ratios for (*Z*)-**1b** (97.5:2.5) and (*Z*)-**1c** (98.5:1.5) were determined by capillary GC analysis using column 2, 50 - 200 °C, 5 °C/min, then 200 °C isothermal; for **1e** no geometric isomer was detected with any of the GC columns applied in this study.

(E)-2-Buten-1-yl N-Phenylpropanimidate (**1a**).[1a] Selected NOE difference data: *N*-Ph-*o*-H (6.75 ppm) experiences enhancements of 1.4 % for irradiation of CH$_2$-C*H*$_3$ (1.08 ppm), 2.6 % for irradiation of C*H*$_2$-CH$_3$ (2.17 ppm), and < 0.1 % for irradiation of OCH$_2$ (4.61 ppm), respectively. Irradiation of OCH$_2$ (4.61 ppm) causes no (< 0.2 %) enhancements for C*H*$_2$-CH$_3$ (2.17 ppm) or CH$_2$-C*H*$_3$ (1.08 ppm).

(Z)-2-Hexen-1-yl N-Phenylpropanimidate [(*Z*)-**1b**].[1a] Selected NOE difference data: *N*-Ph-*o*-H (6.76 ppm) experiences enhancements of 1.3 % for irradiation of N=C-CH$_2$-C*H*$_3$ (1.06 ppm), 3.1 % for irradiation of N=C-C*H*$_2$-CH$_3$ (2.16 ppm), and < 0.1 % for irradiation of OCH$_2$ (4.72 ppm), respectively.

(Z)-2-Methyl-2-buten-1-yl N-Phenylpropanimidate [(*Z*)-**1c**]. ^{1}H NMR δ 1.09 (t, 3 H, *J* = 7.6 Hz, CH$_2$-C*H*$_3$), 1.69 (br. d, 3 H, *J* = 6.9 Hz, C=CH-C*H*$_3$), 1.83 (br. s, 3 H, OCH$_2$-C-C*H*$_3$), 2.19 (q, 2 H, *J* = 7.6 Hz, C*H*$_2$-CH$_3$), 4.69 (s, 2 H, OCH$_2$), 5.49 (br. q, 1 H, *J* = 6.9 Hz, C=C*H*-CH$_3$), 6.75 - 7.32 (m, 5 H, H$_{arom}$); ^{13}C NMR δ 11.0 (q), 13.3 (q), 21.5 (q), 23.3 (t), 64.1 (t), 121.1 (d), 122.6 (d), 123.8 (d), 128.8 (d), 131.6 (s), 148.9 (s), 164.4 (s); IR 1661 (C=N), 1596 (C=C) cm^{-1}; MS *m/e* (relative intensity): 217 (M^+, 15), 202 (M^+ - CH$_3$, 11), 188 (M^+ - C_2H_5, 4), 149 (21), 132 [M^+ - CH$_3$-CH=C(CH$_3$)-CH$_2$O, 23], 93 (Ph-NH_2^+, 100), 77 (Ph^+, 21), 69 [CH$_3$-CH=C(CH$_3$)-CH_2^+, 18]. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81. Found: C, 77.18; H, 8.80.

(Z)-2-Trimethylsilyl-2-buten-1-yl N-Phenylpropanimidate (**1d**). ^{1}H NMR δ 0.22 [s, 9 H, Si(CH$_3$)$_3$], 1.08 (t, 3 H, *J* = 7.6 Hz, CH$_2$-C*H*$_3$), 1.85 (d, 3 H, *J* = 6.9 Hz, C=CH-C*H*$_3$), 2.17 (q, 2 H, *J* = 7.6 Hz, C*H*$_2$-CH$_3$), 4.64 (s, 2 H, OCH$_2$), 6.42 (br. q, 1 H, *J* = 6.9 Hz, C=C*H*-CH$_3$), 6.70 - 7.33 (m, 5 H, H$_{arom}$); ^{13}C NMR δ -0.3 (q), 11.0 (q), 17.5 (q), 23.3 (t), 72.3 (t), 121.1 (d), 122.5 (d), 128.8 (d), 136.0 (s), 141.5 (d), 149.0 (s), 164.0 (s); IR (film) 1666 (C=N), 1596 (C=C) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 275 (M^+, 4), 260 (M^+ - CH$_3$, 11), 246 (M^+ - C_2H_5, 2), 202 [M^+ - (CH$_3$)$_3$Si, 11], 132 [M^+ - CH$_3$-CH=C(Si(CH$_3$)$_3$)-CH$_2$O, 54], 93 (Ph-NH_2^+, 33), 77 (Ph^+, 17), 73 [$(CH_3)_3Si^+$, 100]. HRMS Calcd for $C_{16}H_{25}NOSi$ (M^+): 275.1705. Found: 275.1714.

(E)-2-Triethylsilyl-2-buten-1-yl N-Phenylpropanimidate (**1e**). ^{1}H NMR δ 0.66 [q, 6 H, *J* = 7.8 Hz, Si(C*H*$_2$-CH$_3$)$_3$], 0.95 [t, 9 H, *J* = 7.8 Hz, Si(CH$_2$C*H*$_3$)$_3$], 1.08 (t, 3 H, *J* = 7.6 Hz, N=C-CH$_2$-C*H*$_3$), 1.82 (d, 3 H, *J* = 6.6 Hz, C=CH-C*H*$_3$), 2.18 (q, 2 H, *J* = 7.6 Hz, N=C-C*H*$_2$-CH$_3$), 4.81 (s, 2 H, OCH$_2$), 6.05 (br. q, 1 H, *J* = 6.6 Hz, C=C*H*-CH$_3$), 6.75 - 7.33 (m, 5 H, H$_{arom}$); ^{13}C NMR δ 3.3 (t), 7.4 (q), 11.2 (q), 15.0 (q), 23.4 (t), 64.2 (t), 121.2 (d), 122.6 (d), 128.9 (d), 134.4 (s), 139.8 (d), 149.1 (s), 164.6 (s); IR 1660 (C=N), 1596 (C=C) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 317 (M^+, 3), 302 (M^+ - CH$_3$, 6), 288 (M^+ - C_2H_5, 46), 234 (M^+ - C_2H_5 - CH$_2$=C=CH-CH$_3$, 25), 202 [M^+ - $(C_2H_5)_3Si$, 29], 132 [M^+ - CH$_3$-CH=C(Si(C_2H_5)$_3$)-CH$_2$O, 100], 115 [$(C_2H_5)_3Si^+$, 32], 93 (Ph-NH_2^+, 23), 87 (36), 77 (Ph^+, 26), 59 (29). Anal. Calcd for $C_{19}H_{31}NOSi$: C, 71.85; H, 9.84. Found: C, 71.85; H, 9.88.

(E)-2-Buten-1-yl N-Phenylmethoxyacetimidate (**1i**). ^{1}H NMR δ 1.76 (br. d, 3 H, J = 6.0 Hz, CH=CH-C*H*$_3$), 3.31 (s, 3 H, OCH$_3$), 3.93 (s, 2 H, C*H*$_2$-OCH$_3$), 4.68 (d, 2 H, J = 6.1 Hz, OCH$_2$), 5.77 (br. dt, 1 H, J_d = 15.4 Hz, J_t = 6.1 Hz, OCH$_2$-C*H*=CH), 5.87 (br. dq, 1 H, J_d = 15.4 Hz, J_q = 6.0 Hz, CH=C*H*-CH$_3$), 6.75 - 7.33 (m, 5 H, H$_{arom}$); ^{13}C NMR δ 17.8 (q), 59.0 (q), 66.9 (t), 67.3 (t), 120.8 (d), 123.1 (d), 125.6 (d), 128.9 (d), 130.9 (d), 147.4 (s), 158.8 (s); IR 1670 (C=N), 1596 (C=C) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 219 (M$^+$, 16), 204 (M$^+$ - CH$_3$, 3), 174 (M$^+$ - CH$_3$O-CH$_2$, 30), 165 (M$^+$ - CH$_2$=C=CH-CH$_3$, 5), 135 (27), 120 (M$^+$ - CH$_3$O-CH$_2$ - CH$_2$=C=CH-CH$_3$, 21), 106 (33), 92 (25), 77 (Ph$^+$, 20), 55 (CH$_3$-CH=CH-CH$_2^+$, 99), 45 (CH$_3$O=CH$_2^+$, 100). HRMS Calcd for C$_{13}$H$_{17}$NO$_2$ (M$^+$): 219.1259. Found: 219.1265.

Claisen Rearrangement to **3** *via Deprotonation/Silylation of* **1** *- General Procedure*

To a solution of diethylamine (3.2 mmol) in THF (7 ml) cooled to 0 °C is added dropwise *n*-BuLi (3 mmol) in hexane. The resultant solution of LDEA is cooled to -78 °C and allyl *N*-phenylimidate **1** (2 mmol) dissolved in THF (2 ml) is added. After stirring the mixture at -78 °C for 1 h, a solution of TBDMSCl (3.2 mmol) in hexamethylphosphoric triamide (1 ml)/THF (1 ml) is added and stirring is continued for 1 h at -20 °C.

Substrates **1** with R^2 = H (Table 1): the mixture is stirred at room temperature for 24 h.

Substrates **1** with R^2 ≠ H (Table 1): the mixture is warmed to room temperature, decalin (10 ml) is added, and THF is removed by distillation under normal pressure using a Vigreux column. The reaction flask is equipped with a reflux condenser and after heating the mixture to 130 °C for 48 h, it is cooled to room temperature.

Work-up for all substrates **1**: the mixture is poured into sat. aqueous NH$_4$Cl (50 ml) and extracted with CH$_2$Cl$_2$ (3 x 20 ml). The combined extracts are washed successively with water (15 ml) and brine (15 ml), dried over MgSO$_4$, and concentrated *in vacuo*. Flash chromatography (**3d**: ethyl acetate/petroleum ether 1:9; **3e**: CH$_2$Cl$_2$; **3i**: ethyl acetate/petroleum ether 1:6) affords the amides **3** as mixture of *syn/anti* diastereomers (for yields, see Table 1). Complete data of **3a-c** and **3f-h** as well as details for their chromatographic purification are listed in ref 1a. Attempted HPLC separation of *anti*- and *syn*-**3i** failed.

Diastereomeric ratios (Table 3) were determined by capillary GC analysis of the crude products using the following columns, temperatures, and heating rates - **3a**: column 3, 190 °C isothermal; **3b**: column 3, 210 °C isothermal; **3c,d,g**: column 1, 50 - 200 °C, 5 °C/min, then 200 °C isothermal; **3e**: column 2, 50 - 200 °C, 5 °C/min, then 200 °C isothermal; **3h**: column 3, 240 °C isothermal; **3i**: column 2, 150 °C isothermal.

anti-N-Phenyl-2,3-dimethyl-4-trimethylsilyl-4-pentenamide (*anti*-**3d**). m.p. 156 - 157 °C. ^{1}H NMR δ 0.15 [s, 9 H, Si(CH$_3$)$_3$], 1.06 (d, 3 H, J = 6.7 Hz, CH-C*H*$_3$), 1.15 (d, 3 H, J = 6.7 Hz, CH-C*H*$_3$), 2.38 (dq, 1 H, J_d = 9.5 Hz, J_q = 6.7 Hz, C*H*-CH$_3$), 2.60 (dq, 1 H, J_d = 9.5 Hz, J_q = 6.7 Hz, C*H*-CH$_3$), 5.52 (br. s, 1 H, C=CH-*H*), 5.67 (br. s, 1 H, C=CH-*H*), 7.06 - 7.60 (m, 5 H, H$_{arom}$); ^{13}C NMR δ -1.2 (q), 17.2 (q), 20.5 (q), 42.1 (d), 47.8 (d), 119.9 (d), 124.1 (d), 124.4 (t), 128.7 (d), 138.0 (s), 155.6 (s), 174.7 (s); IR 1688 (C=O), 1601 (C=C) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 275 (M$^+$, 3), 260 (M$^+$ - CH$_3$, 14), 202 [M$^+$ - (CH$_3$)$_3$Si, 6], 150 (4), 93 (Ph-NH$_2^+$, 28), 73 [(CH$_3$)$_3$Si$^+$, 100]. HRMS Calcd for C$_{16}$H$_{25}$NOSi (M$^+$): 275.1705. Found: 275.1709.

syn-N-Phenyl-2,3-dimethyl-4-trimethylsilyl-4-pentenamide (*syn*-**3d**). MS (GC/MS) *m/e* (relative intensity): 275 (M$^+$, 2), 260 (M$^+$ - CH$_3$, 15), 202 [M$^+$ - (CH$_3$)$_3$Si, 7], 150 (6), 93 (Ph-NH$_2^+$, 23), 73 [(CH$_3$)$_3$Si$^+$, 100].

anti-N-Phenyl-2,3-dimethyl-4-triethylsilyl-4-pentenamide (*anti*-**3e**). MS (GC/MS) *m/e* (relative intensity): 317 (M$^+$, 2), 288 (M$^+$ - C$_2$H$_5$, 100), 202 [M$^+$ - (C$_2$H$_5$)$_3$Si, 5], 186 [M$^+$ - (C$_2$H$_5$)$_3$SiO, 6], 178 (9), 150 (6), 115 [(C$_2$H$_5$)$_3$Si$^+$, 11], 103 [(C$_2$H$_5$)$_2$Si=OH$^+$, 14], 93 (Ph-NH$_2^+$, 10), 87 (27), 75 (17), 59 (22).

syn-N-Phenyl-2,3-dimethyl-4-triethylsilyl-4-pentenamide (*syn*-**3e**). m.p. 79 - 81 °C. ^{1}H NMR δ 0.62 [q, 6 H, *J* = 7.8 Hz, Si(C*H*$_2$-CH$_3$)$_3$], 0.89 [t, 9 H, *J* = 7.8 Hz, Si(CH$_2$C*H*$_3$)$_3$], 1.02 (d, 3 H, *J* = 7.1 Hz, CH-C*H*$_3$), 1.20 (d, 3 H, *J* = 6.8 Hz, CH-C*H*$_3$), 2.46 (m$_c$, 1 H, C*H*-CH$_3$), 2.70 (m$_c$, 1 H, C*H*-CH$_3$), 5.45 (br. s, 1 H, C=CH-*H*), 5.80 (br. s, 1 H, C=CH-*H*), 7.00 - 7.51 (m, 5 H, H$_{arom}$); ^{13}C NMR δ 3.0 (t), 7.2 (q), 14.5 (q), 17.7 (q), 40.2 (d), 46.6 (d), 119.6 (d), 123.9 (d), 125.0 (t), 128.8 (d), 138.0 (s), 153.6 (s), 174.1 (s); IR 1676 (C=O), 1601 (C=C) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 317 (M$^+$, 2), 288 (M$^+$ - C$_2$H$_5$, 100), 202 [M$^+$ - (C$_2$H$_5$)$_3$Si, 6], 186 [M$^+$ - (C$_2$H$_5$)$_3$SiO, 10], 178 (11), 150 (10), 115 [(C$_2$H$_5$)$_3$Si$^+$, 12], 103 [(C$_2$H$_5$)$_2$Si=OH$^+$, 23], 93 (Ph-NH$_2^+$, 15), 87 (42), 75 (38), 59 (53). Anal. Calcd for C$_{19}$H$_{31}$NOSi: C, 71.85; H, 9.84. Found: C, 71.91; H, 9.84.

anti-N-Phenyl-2-methoxy-3-methyl-4-pentenamide (*anti*-**3i**) and *syn-N-Phenyl-2-methoxy-3-methyl-4-pentenamide* (*syn*-**3i**). ^{1}H NMR δ 1.07 (d, 3 H, *J* = 7.0 Hz, CH-C*H*$_3$, *syn*-**3i**), 1.18 (d, 3 H, *J* = 7.0 Hz, CH-C*H*$_3$, *anti*-**3i**), 2.67 - 2.86 (m, 1 H, C*H*-CH$_3$, *anti*-**3i** and *syn*-**3i**), 3.50 (s, 3 H, CH$_3$O, *syn*-**3i**), 3.52 (s, 3 H, CH$_3$O, *anti*-**3i**), 3.65 (d, 1 H, *J* = 3.9 Hz, C*H*-OCH$_3$, *anti*-**3i**), 3.72 (d, 1 H, *J* = 3.7 Hz, C*H*-OCH$_3$, *syn*-**3i**), 5.01 - 5.19 (m, 2 H, CH=C*H*$_2$, *anti*-**3i** and *syn*-**3i**), 5.82 (ddd, 1 H, *J* = 7.8, 10.3, 17.3 Hz, C*H*=CH$_2$, *anti*-**3i**), 5.92 (ddd, 1 H, *J* = 7.2, 10.4, 17.4 Hz, C*H*=CH$_2$, *syn*-**3i**), 7.05 - 7.65 (m, 5 H, H$_{arom}$, *anti*-**3i** and *syn*-**3i**); ^{13}C NMR δ 13.8 (q), 16.5 (q), 40.7 (d), 41.2 (d), 59.67 (q), 59.74 (q), 86.3 (d), 87.0 (d), 115.2 (t), 115.8 (t), 119.67 (d), 119.74 (d), 124.4 (d), 129.0 (d), 137.08 (s), 137.11 (s), 138.1 (d), 139.8 (d), 169.5 (s), 169.7 (s); IR 1675 (C=O), 1595 (C=C) cm^{-1}; MS (GC/MS, *anti*-**3i**) *m/e* (relative intensity): 219 (M$^+$, 19), 204 (M$^+$ - CH$_3$, 3), 189 (M$^+$ - CH$_2$=O, 4), 188 (M$^+$ - CH$_3$O, 4), 187 (M$^+$ - CH$_3$OH, 14), 165 (M$^+$ - CH$_2$=C=CH-CH$_3$, 7), 150 (M$^+$ - CH$_3$ - CH$_2$=C=CH-CH$_3$, 5), 136 (21), 132 (14), 99 [CH$_2$=CH-CH(CH$_3$)-CH=OCH$_3^+$, 100], 93 (Ph-NH$_2^+$, 16), 77 (Ph$^+$, 17), 67 [CH$_2$=CH-CH(CH$_3$)-CH=OCH$_3^+$ - CH$_3$OH, 48]; MS (GC/MS, *syn*-**3i**) *m/e* (relative intensity): 219 (M$^+$, 13), 204 (M$^+$ - CH$_3$, 2), 189 (M$^+$ - CH$_2$=O, 3), 188 (M$^+$ - CH$_3$O, 5), 187 (M$^+$ - CH$_3$OH, 21), 165 (M$^+$ - CH$_2$=C=CH-CH$_3$, 6), 150 (M$^+$ - CH$_3$ - CH$_2$=C=CH-CH$_3$, 5), 136 (21), 132 (12), 99 [CH$_2$=CH-CH(CH$_3$)-CH=OCH$_3^+$, 100], 93 (Ph-NH$_2^+$, 15), 77 (Ph$^+$, 15), 67 [CH$_2$=CH-CH(CH$_3$)-CH=OCH$_3^+$ - CH$_3$OH, 51]. HRMS Calcd for C$_{13}$H$_{17}$NO$_2$ (M$^+$): 219.1259. Found: 219.1265.

Deprotonation / Alkylation of **1a**

Allyl *N*-phenylimidate **1a** (1 mmol) is deprotonated with LDEA as described above. Ethyliodide (3 mmol) is added at -78 °C, and stirring is continued for 2 h at -78 °C. The mixture is warmed to room temperature, poured into sat. aqueous NH$_4$Cl (40 ml), and extracted with ether (3 x). After washing with brine, drying over Na$_2$SO$_4$, and removal of the solvent *in vacuo*, pure **4** (83 %) is obtained as a colorless oil.

(E)-2-Buten-1-yl N-Phenyl-2-methylbutanimidate (**4**). ^{1}H NMR δ 0.81 (t, 3 H, *J* = 7.4 Hz, CH$_2$-C*H*$_3$), 1.08 (d, 3 H, *J* = 6.9 Hz, N=C-CH-C*H*$_3$), 1.19 - 1.40 (m, 1 H, CH$_3$-CH-*H*), 1.52 - 1.69 (m, 1 H, CH$_3$-CH-*H*), 1.75 (br. d, 3 H, *J* = 6.1 Hz, CH=CH-C*H*$_3$), 2.35 - 2.50 (m, 1 H, N=C-C*H*-CH$_3$), 4.60 (br. d, 2 H, *J* = 5.8 Hz, OCH$_2$), 5.70 (br. dt, 1 H, J_d = 15.4 Hz, J_t = 5.8 Hz, OCH$_2$-C*H*=CH), 5.81 (br. dq, 1 H, J_d = 15.4 Hz, J_q = 6.1 Hz, CH=C*H*-CH$_3$), 6.70 - 7.30 (m, 5 H, H$_{arom}$); ^{13}C NMR δ 12.0 (q), 17.8 (q), 18.3 (q), 27.1 (t), 36.0 (d), 65.9 (t), 121.1 (d), 122.4 (d), 126.3 (d), 128.8 (d), 129.4 (d), 148.9 (s), 165.5 (s); IR (film) 1655 (C=N), 1595 (C=C) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 231 (M$^+$, 11), 216 (M$^+$ - CH$_3$, 4), 203 (M$^+$ - CH$_2$=CH$_2$, 3), 202 (M$^+$ - C$_2$H$_5$, 2), 174 (M$^+$ - C$_2$H$_5$-CH-CH$_3$, 6), 162 (M$^+$ - CH$_3$ - CH$_2$=C=CH-CH$_3$, 15), 149 (M$^+$ - CH$_2$=CH$_2$ - CH$_2$=C=CH-CH$_3$, 31), 147 (37), 93 (Ph-NH$_2^+$, 57), 77 (Ph$^+$, 29), 57 (C$_2$H$_5$-CH-CH$_3^+$, 91), 55 (CH$_3$-CH=CH-CH$_2^+$, 100). Anal. Calcd for C$_{15}$H$_{21}$NO: C, 77.89; H, 9.15. Found: C, 77.77; H, 9.35.

Isolation of N-Silyl Ketene N,O-Acetals - General Procedure

(*Z*)-2-Hexen-1-yl *N*-phenylpropanimidate [(*Z*)-**1b**] and ethyl *N*-phenylpropanimidate,[24] respectively, are deprotonated on a 2 mmol scale with LDEA at -78 °C and subsequently treated with *tert*-butyldimethylchlorosilane at -20 °C as described above. After stirring the resultant mixture at room temperature overnight, the solvent is removed *in vacuo* at room temperature. The residue is extracted inside the flask with pentane (3 x 20 ml), the combined pentane solutions are evaporated *in vacuo* at room temperature, and an

analytical sample of the remaining crude *N*-silyl ketene *N,O*-acetal is dissolved in $CDCl_3$. After passing a slow stream of argon through this solution for several minutes, it is analyzed by NMR spectroscopy. Aside from small amounts of the educt imidate and hexamethylphosphoric triamide, only a single *N*-silyl ketene *N,O*-acetal isomer is observed, respectively. (1Z,2'Z)-**5b** is obtained from (*Z*)-**1b**, and (*Z*)-**14** is obtained from ethyl *N*-phenylpropanimidate.

(Z)-Methylketene-O-[(Z)-2-hexen-1-yl]-N-(tert-butyldimethylsilyl)-N-phenylacetal [(1Z,2'Z)-**5b**]. ^{1}H NMR δ 0.24 [s, 6 H, $Si(CH_3)_2$], 0.80 [s, 9 H, $C(CH_3)_3$], 1.20 - 1.35 (m, 2 H, CH_3-CH_2), 1.59 (d, 3 H, J = 6.7 Hz, C=CH-CH_3), 1.80 - 1.95 (m, 2 H, C_2H_5-CH_2), 4.15 (d, 2 H, J = 5.1 Hz, CH_2O), 4.40 (q, 1 H, J = 6.7 Hz, C=CH-CH_3), 5.33 - 5.46 (m, 2 H, CH=CH), 6.92 (tt, 1 H, J = 1.7, 6.8 Hz, *N*-Ph-*p*-H), 7.08 - 7.25 (m, 4 H, *N*-Ph-*o*-H, *N*-Ph-*m*-H); selected NOE difference data: irradiation of the 4 H multiplet for *N*-Ph-*o*-H and *N*-Ph-*m*-H (7.08 - 7.25 ppm) causes enhancements of 0.2 % for C=CH-CH_3 (1.59 ppm), 1.4 % for CH_2O (4.15 ppm), and 1.5 % for C=CH-CH_3 (4.40 ppm); ^{13}C NMR δ -1.9 (q), 10.5 (q), 13.4 (q), 20.0 (s), 22.4 (t), 27.3 (q), 29.3 (t), 62.5 (t), 98.0 (d), 122.4 (d), 123.9 (d), 125.8 (d), 128.4 (d), 132.7 (d), 146.9 (s), 151.2 (s).

(Z)-Methylketene-O-ethyl-N-(tert-butyldimethylsilyl)-N-phenylacetal [(*Z*)-**14**]. ^{1}H NMR δ 0.22 [s, 6 H, $Si(CH_3)_2$], 0.80 [s, 9 H, $C(CH_3)_3$], 1.04 (t, 3 H, J = 7.0 Hz, CH_3-CH_2), 1.58 (d, 3 H, J = 6.7 Hz, C=CH-CH_3), 3.63 (q, 2 H, J = 7.0 Hz, CH_2O), 4.37 (q, 1 H, J = 6.7 Hz, C=CH-CH_3), 6.92 (tt, 1 H, J = 1.6, 6.9 Hz, *N*-Ph-*p*-H), 7.07 - 7.25 (m, 4 H, *N*-Ph-*o*-H, *N*-Ph-*m*-H); selected NOE difference data: irradiation of the 4 H multiplet for *N*-Ph-*o*-H and *N*-Ph-*m*-H (7.07 - 7.25 ppm) causes enhancements of 0.2 % for C=CH-CH_3 (1.58 ppm), 1.9 % for CH_2O (3.63 ppm), and 3.2 % for C=CH-CH_3 (4.37 ppm); ^{13}C NMR δ -2.0 (q), 10.5 (q), 15.0 (q), 19.9 (s), 27.3 (q), 62.3 (t), 97.7 (d), 122.4 (d), 124.0 (d), 128.4 (d), 147.1 (s), 151.4 (s).

Desilylation

Of Anilide anti-**3d**. A mixture of *anti*-**3d** (71.0 mg, 0.258 mmol; *anti*-**3d**:*syn*-**3d** = 99.5:0.5 by capillary GC analysis), acetonitrile (2.6 ml), and 50 % aqueous HBF_4 (0.47 g, ca. 10 equiv.) is heated at 55 °C for 48 h. The mixture is cooled to room temperature, diluted with CH_2Cl_2 (50 ml), washed with sat. aqueous $NaHCO_3$ (10 ml) and brine (10 ml), and dried over $MgSO_4$. TLC (ethyl acetate/petroleum ether 1:6) indicated only a small amount of educt *anti*-**3d** aside from product *anti*-**3a**. After concentration *in vacuo*, a residue (52.2 mg) is obtained which consists solely of 85.5 % *anti*-**3a** (yield 85 %, 96 % on conversion) and 14.5 % educt *anti*-**3d** according to capillary GC analysis (column 3, 210 °C isothermal).

Of Anilide syn-**3e**. A mixture of *syn*-**3e** (102.0 mg, 0.321 mmol; *syn*-**3e**:*anti*-**3e** = 98.1:1.9 by capillary GC analysis - column 1, 50 - 200 °C, 5 °C/min, then 200 °C isothermal) and 65 % HF in pyridine (1.1 ml, 40.7 mmol HF) is stirred in a plastic vial for 1 h at room temperature. Another portion of HF solution is added (1.1 ml), and stirring is continued for 1 h at room temperature. The mixture is diluted with CH_2Cl_2 (10 ml), neutralized with 2 N NaOH at 0 °C and after addition of more CH_2Cl_2 (90 ml), it is washed with water (30 ml), brine (30 ml), and dried over $MgSO_4$. Removal of the solvent *in vacuo* and subsequent flash chromatography (ethyl acetate/petroleum ether 1:6) yields *syn*-**3a** (52.8 mg, 81 %; *syn*-**3a**:*anti*-**3a** = 98.0:2.0 by capillary GC analysis - column 4, 220 °C isothermal) as a colorless solid.

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