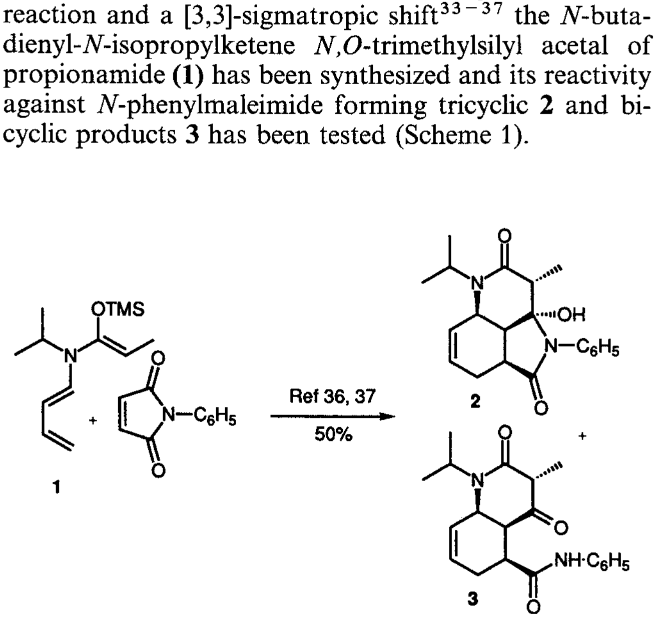
Preparation of *N*-Alkylketene-*N*-Butadienyl-*N,O*-Silyl Acetals

Andreas Franz, Pierre-Yves Eschler, Manuel Tharin, Helen Stoeckli-Evans, Reinhard Neier*
Institut de Chimie de l'Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland
Fax +41(38)232511; E-mail reinhard.neier@ich.unine.ch

Received 20 December 1995; revised 30 April 1996

The synthesis of a series of dienamides **5a–j** using Oppolzer's method is described. Using Rathke's method the ketene *N,O*-silyl acetals **6a–j** can be obtained in good yield from the corresponding dienamides. The ketene acetals are obtained free of base and free of salts. They are stable and can be stored at −20°C. The new dienes are useful reagents for tandem reactions.

Processes combining two or more reaction steps are known as tandem reactions, domino reactions or cascade reactions[1–18] according to a recently proposed systematic nomenclature.[5,9,10] The synthetic power of this methodology has been widely used in the synthesis of complex natural products.[19–32] Cycloadditions and especially the Diels–Alder reaction have been successfully incorporated into tandem processes.[1,10,11] In connection with our studies of tandem reactions combining a Diels–Alder reaction and a [3,3]-sigmatropic shift[33–37] the *N*-butadienyl-*N*-isopropylketene *N,O*-trimethylsilyl acetal of propionamide (**1**) has been synthesized and its reactivity against *N*-phenylmaleimide forming tricyclic **2** and bicyclic products **3** has been tested (Scheme 1).



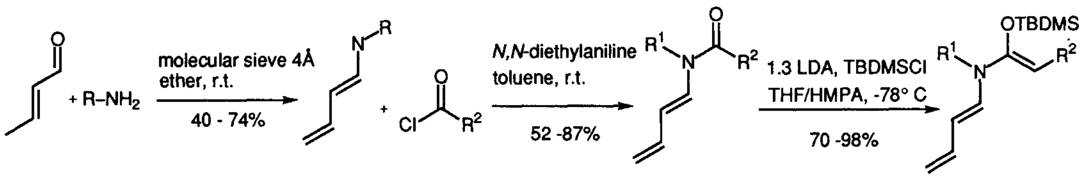
Scheme 1

The sensitivity of the ketene trimethylsilyl acetals towards hydrolysis and the presence of the diisopropylamine in the reaction mixture are the two main disadvantages of this procedure. The trimethylsilyl acetals have to be created in situ for application in the tandem reaction.[36–37] We report the convenient synthesis of a series of *N*-alkyl-*N*-butadienylamides and their transformation into the corresponding ketene *N,O*-silyl acetals. We envisioned the use of the more sterically hindered silyl groups like *tert*-butyldimethylsilyl, triisopropylsilyl or *tert*-butyldiphenylsilyl, which should allow the isolation of ketene *N,O*-silyl acetals free from the base.[38–39] On the other hand, the more hindered silyl groups will reduce the reactivity for the acylation process.

The *N*-alkyl-*N*-butadienylamides were synthesised starting from crotonaldehyde, the alkylamine and the corresponding acid chloride using the two-step procedure: imine formation **4a–e** catalysed by molecular sieves[40] followed by base-catalysed acylation with the corresponding acid chloride[41–44] (Scheme 2). Mixing of the amine and crotonaldehyde in diethyl ether at 0°C in the presence of molecular sieves and then stirring the reaction mixture at room temperature for 6 hours led to good yields of the imines **4a–e** (Scheme 2; Tables 1 and 2). The imines **4a–d** could be purified by distillation. Some losses due to polymerisation occurred. In the case of the imine **4e** purification by distillation was not necessary. The acylation of the imines led, in good to excellent yields, to the *N*-alkyl-*N*-butadienylamides **5a–j** (Scheme 2; Tables 3 and 4). To a solution of the corresponding acid chloride and *N,N*-diethylaniline in toluene the imine **4a–e** was added slowly. The reaction mixture was stirred overnight. The hydrochloride of *N,N*-diethylaniline was removed by filtration. Usual workup gave the raw material, which was purified by distillation (**5a–d**) or by filtration over a short silica column (**5e** and **5i**). In some cases the amide could be recrystallized (**5f, 5h** and **5j**). The synthesis of **5d** starting from the isopropylimine **4a** and the 4 : 1 mixture of (*E*)- and (*Z*)-crotonyl chloride yielded only the (*E*) diastereomer in 66% yield.

The ^{1}H NMR spectra of the dienamides **5a–j** were in accordance with the proposed structure (Table 4). The peaks for the butadienyl system correlate very well within the series of dienamides containing an isopropyl substituent **5a–e** or a benzyl substituent **5f–i** on the N atom. The shift difference between the compounds containing the isopropyl or the benzyl substituent on the N atom is roughly +0.6 ppm for HC(1) and −0.4 ppm for HC(2). This shift difference can be attributed to the deshielding compared to the shielding due to the aromatic ring. The peaks of HC(2) of the diene system and of the substituents directly bonded to the nitrogen were in general broadened because of the slow rotation around the amide bond. Measuring the spectra at 100°C in d_6-DMSO allowed resolved spectra to be obtained. The ^{1}H NMR spectrum of the anthranyl derivative **5j** in contrast showed sharp signals even at room temperature in $CDCl_3$. The X-ray analysis of **5j** indicated that the aromatic anthranyl system is almost orthogonal to the amide function and the butadienyl system.[45] Assuming that the solution structure is similar to the structure in the crystal, the rotation around the amide bound will be strongly hindered by the *peri*-protons. Due to this steric hindrance, one conformer should be strongly preferred explaining the well-resolved spectrum obtained from **5j**.

We decided to replace the trimethylsilyl group of *N*-butadienyl-*N*-isopropylketene *N,O*-trimethylsilyl acetal of propionamide by the *tert*-butyldimethylsilyl group. The *tert*-butyldimethylsilyl derivatives should be considerably more stable towards hydrolysis. The in situ deprotona-



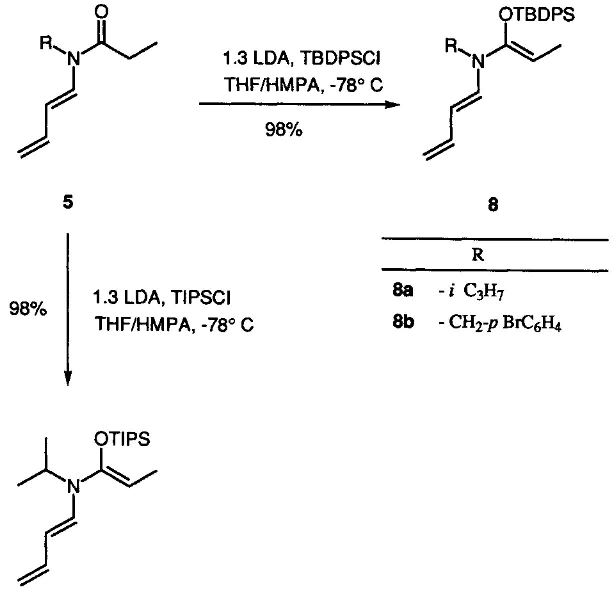
4 5 6

4	R
a	- i C_3H_7
b	- $CH_2C_6H_5$
c	- CH_2-p BrC_6H_4
d	- CH_2-p $CH_3OC_6H_4$
e	- Anthranylmethyl

5, 6	R^1	R^2
a	- i C_3H_7	- CH_3
b	- i C_3H_7	- C_2H_5
c	- i C_3H_7	- $CH_2C_6H_5$
d	- i C_3H_7	- CH=CH-CH_3
e	- i C_3H_7	- CH_2-p $CH_3OC_6H_4$
f	- $CH_2C_6H_5$	- C_2H_5
g	- CH_2-p BrC_6H_4	- C_2H_5
h	- CH_2-p BrC_6H_4	- CH_2-p BrC_6H_4
i	- CH_2-p $CH_3OC_6H_4$	- CH_2-p $CH_3OC_6H_4$
j	- Anthranylmethyl	- C_2H_5

Scheme 2

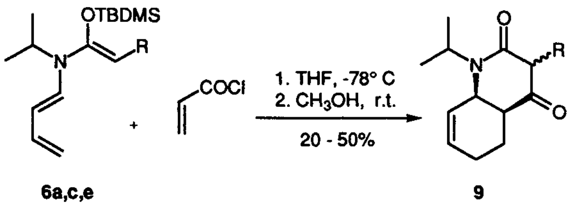
tion silylation[46] which had been applied successfully for the synthesis of the *N*-butadienyl-*N*-isopropylketene *N,O*-trimethylsilyl acetal of propionamide **1**[36–37] could not be used for the synthesis of the ketene *N,O-tert*-butyldimethylsilyl acetal. Only when we applied the method described by Rathke[47] were good and reproducible yields of the *N*-butadienyl-*N*-isopropylketene *N,O-tert*-butyldimethylsilyl acetal of propionamide **6a–j** obtained (Scheme 2, Tables 5 and 6). Deprotonation of the amides **5a–j** with LDA in the solvent mixture THF/HMPA = 10 : 1 at −78 °C followed by the addition of a solution of *tert*-butyldimethylsilyl chloride in THF and warming the reaction mixture to room temperature allowed isolation, after the usual workup, of the *N*-butadienyl-*N*-isopropylketene *N,O-tert*-butyldimethylsilyl acetal of propionamide **6a–j** in almost quantitative yield and in high purity as judged from the ^1H and ^{13}C spectra (Table 6). The deprotonation/silylation of the *N*-(*p*-bromobenzyl) **6h** and *N*-anthranylmethyl derivative **6j** proved to be more difficult. Even though a 30 % excess of LDA was usually used for the deprotonation, the *N*-(*p*-bromobenzyl) derivative **6h** was only 70 % silylated. Submitting this reaction mixture a second time to the deprotonation, silylation conditions allowed the transformation of the starting material completely but the ketene *N,O-tert*-butyldimethylsilyl acetal **6h** was of unsatisfactory purity. In the case of the *N*-anthranylmethyl derivative only 70 % of the ketene-*N,O-tert*-butyldimethylsilyl acetal **6j** could be isolated. Increasing the amount of LDA did not lead to an increased yield of the ketene *N,O-tert*-butyldimethylsilyl acetal **6k**. The relatively low yield could be due either to the competitive deprotonation in the benzylic position or to an electron transfer from the enolate anion to the aromatic system. The other *tert*-butyldimethylsilyl acetals **6a–g** and **6i** were obtained in excellent yield and high purity, free of diisopropylamine. The *tert*-butyldimethylsilyl acetals **6a–j** could be purified via extraction and could be stored for months in the refrigerator. However attempts to purify the ketene *N,O*-acetals **6a–j** via chromatography led to complete hydrolysis. Even the use of deactivated silica gel or aluminium oxide allowed only the isolation of the hydrolysed starting material. It has been reported that the triisopropylsilyl group and the *tert*-butyldiphenylsilyl group are more stable towards hydrolysis than the *tert*-butyldimethylsilyl group. Using the conditions successfully applied to synthesize the ketene *N,O-tert*-butyldimethylsilyl acetals, the corresponding more bulky *N,O*-acetals **7,8a,b** could be isolated in high purity and excellent yield (Scheme 3). Neither triisopropylsilyl **7** nor the *tert*-butyldiphenylsilyl derivatives **8a,b** were stable enough to allow purification by chromatography on silica gel, on silica gel deactivated with triethylamine, or on aluminium oxide.



	R
8a	- i C_3H_7
8b	- CH_2-p BrC_6H_4

Scheme 3

The ^1H NMR spectra of ketene acetals were well resolved and the spectra could be completely assigned (Table 6). The chemical shifts of the compounds **6a–e**, **6f–i** and **6j** showed similar behaviour to that observed for the corresponding amides. Changing the substituents on the silyl group from trimethylsilyl to *tert*-butyldimethyl **6a–6j** to triisopropyl **7** has no strong influence. The *tert*-butyldiphenylsilyl group in contrast induces shift differences of 0.5 ppm for HC(1) and 0.2 ppm for HC(2) and HC(3).



9	R
a	$-CH_3$
b	$-C_6H_5$
c	$-p\,CH_3OC_6H_4$

Scheme 4

Table 1. Imines **4**

Product	R	Yield (%)	bp (°C/Torr)
4a	*i*-C_3H_7	68	29/11
4b	$CH_2C_6H_5$	47	100/0.04
4c	CH_2-*p* BrC_6H_4	60	120/0.02
4d	CH_2-*p* $CH_3OC_6H_4$	40	110/0.02
4e	Anthranylmethyl	74	–[a]

[a] Could not be distilled

Table 3. Dienamides **5**

Product	R^1	R^2	Yield (%)	bp (°C/Torr)
5a	*i*-C_3H_7	CH_3	67	39/0.03
5b	*i*-C_3H_7	C_2H_5	65	51/0.03
5c	*i*-C_3H_7	$CH_2C_6H_5$	52	107/0.02
5d	*i*-C_3H_7	$CH{=}CHCH_3$	66	67/0.05
5e	*i*-C_3H_7	CH_2-*p*$CH_3OC_6H_4$	62	–[a]
5f	$CH_2C_6H_5$	C_2H_5	60	47[b]
5g	CH_2-*p*BrC_6H_4	C_2H_5	80	94–95[b]
5h	CH_2-*p*BrC_6H_4	CH_2-*p*BrC_6H_4	87	97–98[b]
5i	CH_2-*p*$CH_3OC_6H_4$	CH_2-*p*$CH_3OC_6H_4$	82	–[a]
5j	Anthranylmethyl	C_2H_5	73	123[b]

[a] **5e** and **5i** were obtained as oils. They were not distilled.

[b] **5f–5h** and **5j** were recrystallized. The mp of the crystalline material is indicated.

In conclusion, a series of *N*-alkyl-*N*-butadienylamides **5a–j** have been synthesised and a method has been developed to obtain the stable, storable ketene *N,O-tert*-butyldimethylsilyl acetals **6a–j** in excellent yield. These are free of LiCl and diispropylamine. They can be stored for prolonged periods of time at −20 °C. The reported synthesis will allow the study of the tandem reaction under a larger variety of reaction conditions. Preliminary investigations showed that the tandem reaction between the ketene acetals **6a, 6c** and **6e** and acryloyl chloride allowed the isolation of the bicyclic products **9a–c** (Scheme 4). The absence of diisopropylamine facilitated the isolation of the products because diisopropylacryloylamide was not present as a side product. Studies on the reaction of the ketene acetals **6a–j** with fullerenes have been started in a collaborative effort with the group of

Table 2. Spectroscopic Data of the Imines **4a–e**

Product	IR (neat)[a] ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS (70 eV) m/z (%)
4a	2970, 2940, 2830, 1660, 1625, 1465, 1450, 1380, 1320, 1160, 980, 960, 930	7.85 (d, 1 H, $J = 7.7$), 6.22–6.13 (m, 2 H), 3.30 (sept, 1 H, $J = 6.2$), 1.91 and 1.88 (d, 3 H, $J = 5.2$), 1.17 (d, 6 H, $J = 6.3$)	159.9, 139.7, 132.2, 60.9, 24.1, 18.2	112 (16, M$^+$ + 1), 96 (100), 94 (10), 79 (14), 68 (27), 55 (25)
4b	3085–3025, 2965, 2925, 2840, 1655, 1630, 1605, 1495, 1455, 1370, 1170, 1150, 1075, 1030, 970, 735, 700	7.94 (d, 1 H, $J = 8.1$), 7.34–7.24 (m, 5 H), 6.30–6.25 (m, 2 H), 4.69 and 4.63 (s, 2 H), 1.91 and 1.89 (d, 3 H, $J = 5.2$)	163.5, 140.9, 139.5, 133.4, 129.5, 129.1, 126.9, 65.0, 18.4	159 (10, M$^+$), 144 (49), 92 (23), 91 (100), 80 (15), 65 (37)
4c	3020, 2965, 2915, 2840, 1660, 1625, 1590, 1485, 1445, 1400, 1375, 1170, 1100, 1070, 1010, 800	7.93 (dm, 1 H, $J = 8.2$), 7.46–7.43 (m, 2 H), 7.16–7.13 (m, 2 H) 6.29–6.25 (m, 2 H), 4.61 and 4.56 (s, 2 H), 1.91 and 1.89 (d, 3 H, $J = 5.0$)	164.5, 142.0, 139.1, 132.6, 132.2, 130.3, 121.4, 64.8, 19.1	240 (25), 239 (31), 238 (38, M$^+$), 237 (27), 224, 222 (81), 171, 169 (100), 89 (21)
4d	3035, 3000, 2955, 2935, 2910, 2835, 1660, 1625, 1610, 1510, 1465, 1440, 1300, 1250, 1175, 1040, 970	7.94–7.92 (dm, 1 H, $J = 8.3$), 7.19 (m, 2 H), 6.85 (d, 2 H), 6.24 (m, 2 H), 4.61 and 4.56 (s, 2 H), 3.79 and 3.71 (s, 3 H), 1.88 (d, 3 H, $J = 5.2$)	163.2, 158.7, 140.8, 132.2, 131.6, 129.3, 113.9, 64.4, 55.3, 18.4	190 (100, M$^+$ + 1), 189 (100, M$^+$), 188 (39), 174 (100), 134 (20), 122 (70), 121 (100), 91 (80), 89 (40), 78 (70), 77 (85)
4e	3060, 1550, 1310, 1255, 1215, 1140, 1100, 1000, 980, 885	8.45 and 8.42 (s, 1 H), 8.25 (d, 2 H), 8.01 (d, 2 H), 7.86–7.82 (dm, 1 H, $J = 8.7$), 7.51 (m, 4 H), 6.28 (dd, 1 H, $J = 15.6, 8.7$), 6.01 (dq, 1 H, $J = 15.5, 6.6$), 5.76 and 5.67 (s, 2 H), 1.79 (d, 3 H, $J = 6.8$)	163.2, 140.8, 132.4, 131.6, 130.7, 129.9, 129.2, 128.4, 127.6, 126.3, 125.0, 124.5, 55.2, 18.4	260 (100, M$^+$ + 1), 259 (96, M$^+$), 244 (2), 192 (40), 191 (30), 190 (12), 189 (25)

[a] The IR of **4d** and **4e** were measured in CCl_4

Table 4. Spectroscopic Data of the Dienamides **5a–j**

Product[d]	IR (CCl_4)[a] ν (cm^{-1})	^1H NMR (d_6-DMSO/TMS/373 K)[b] δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS)[c] δ	MS (70 eV) m/z (%)
5a	2975, 2940, 1680, 1635, 1605, 1430, 1400, 1370, 1320, 1300, 1255, 1240, 1175, 1020, 1000, 890	6.79 (d, 1 H, *J* = 14.0), 6.49 (dt, 1 H, *J* = 16.9, 10.3, 10.3), 6.17 (br s, 1 H, H-C(2)), 5.27 (d, 1 H, *J* = 16.9), 5.09 (d, 1 H, *J* = 10.1), 4.58 (br s, 1 H), 2.21 (s, 3 H), 1.32 (d, 6 H, *J* = 6.9)	170.1, 134.9, 129.9, 124.9, 117.1, 46.9, 24.0, 20.6	154 (32, M$^+$ + 1), 153, (33, M$^+$), 112 (21), 111 (27), 97 (67), 96 (100), 70 (39), 69 (64), 68 (44), 43 (90)
5b	2980, 2940, 2880, 1680, 1635, 1605, 1460, 1430, 1400, 1380, 1365, 1340, 1290, 1250, 1220, 1170, 1130, 1075, 1000, 925, 890	6.43 (d, 1 H, *J* = 13.7), 6.33 (dt, 1 H, *J* = 16.9, 10.4, 10.1), 6.00 (br s, 1 H), 5.20 (d, 1 H, *J* = 16.9), 5.08 (d, 1 H, *J* = 10.1), 4.66 (br s, 1 H), 2.39 (q, 2 H, *J* = 7.3), 1.24 (d, 6 H, *J* = 6.9), 1.12 (t, 3 H, *J* = 7.3)	172.4, 134.4, 128.8, 123.0, 115.8, 46.5, 28.0, 19.8, 9.2	168 (22, M$^+$ + 1), 167 (M$^+$), 112 (25), 111 (33), 97 (75), 96 (100), 70 (27), 69 (46), 68 (33), 58 (23), 57 (45), 44 (40), 43 (52)
5c	3085, 3065, 3030, 2975, 2935, 1745, 1665, 1635, 1600, 1495, 1455, 1425, 1400, 1345, 1220, 1170, 1000	7.36–7.21 (m, 5 H), 6.41–6.22 (br m, 2 H), 6.04–5.92 (br t, 1 H), 5.19 (d, 1 H, *J* = 16.9), 5.12 (d, 1 H, *J* = 11.1), 4.68 (br sept, 1 H, *J* = 6.6), 3.75 (br s, 2 H), 1.19 (d, 6 H, *J* = 6.9)	170.6, 135.2, 134.0, 129.4, 129.1, 129.0, 127.2, 117.8, 47.4, 42.7, 20.5	229 (42, M$^+$), 111 (44), 96 (71), 91 (100), 65 (18), 41 (14)
5d	2975, 2940, 1665, 1630, 1445, 1425, 1400, 1330, 1295, 1250, 1205, 1170, 1130, 1085, 1000, 970, 930, 895, 855	6.89 (dq, 1 H, *J* = 15.0, 6.9), 6.36 (dt, 1 H, *J* = 17.0, 10.4, 10.3), 6.32 (d, 1 H, *J* = 13.6), 6.21 (dd, 1 H, *J* = 15.1, 1.7), 5.96 (dd, 1 H, *J* = 13.7, 10.8), 5.2 (d, 1 H, *J* = 16.7), 5.09 (d, 1 H, *J* = 10.0), 4.73 (sept, 1 H, *J* = 6.9), 1.84 (dd, 3 H, *J* = 6.9, 1.6), 1.19 (d, 6 H, *J* = 6.9)	166.4, 141.8, 134.8, 128.9, 127.7, 124.6, 117.5, 47.1, 20.8, 18.8	179 (5, M$^+$), 164 (4), 111 (14), 96 (63), 69 (100), 68 (15), 41 (30)
5e	3065, 2965, 2935, 2835, 1740, 1640, 1625, 1585, 1555, 1515, 1465, 1425, 1340, 1300, 1250, 1180, 1035, 1000, 810	7.30 and 7.24 (m, 2 H), 6.97 (m, 2 H), 6.73 (d, 1 H, *J* = 14.0), 6.50 (dt, 1 H, *J* = 17.0, 10.5, 10.3), 6.17 (dd, 1 H, *J* = 14.0, 10.5), 5.30 (dd, 1 H, *J* = 17.0, 1.8), 5.15 (dd, 1 H, *J* = 10.2, 1.8), 4.64 and 3.98 (sept, 1 H, *J* = 6.9), 3.87 and 3.86 (s, 3 H), 3.82 and 3.45 (s, 2 H), 1.32 and 1.20 (d, 6 H, *J* = 6.8)	169.4, 168.9, 157.8, 157.7, 134.5, 129.4, 129.3, 129.3, 127.1, 121.8, 114.9, 113.6, 113.4, 54.7, 46.4, 41.3, 40.0, 21.8, 19.3	260 (72, M$^+$ + 1), 259 (73, M$^+$), 122 (56), 121 (84), 112 (36), 111 (89), 97 (20), 96 (100), 91 (32), 89 (11), 78 (32), 77 (34), 68 (12), 43 (35)
5f	3080, 3030, 2980, 2940, 2875, 1670, 1635, 1455, 1430, 1375, 1345, 1310, 1255, 1190, 1165, 1075, 995, 925, 890, 745, 705	7.45–7.25 (m, 5 H), 7.35 (d, 1 H, *J* = 17.2), 6.46 (dt, 1 H, *J* = 16.5, 10.3, 10.2), 5.81 (dd, 1 H, *J* = 13.9, 10.4), 5.07 (dd, 1 H, *J* = 16.9, 1.8), 4.99 (s, 2 H), 4.97 (dd, 1 H, *J* = 10.2, 1.9), 2.69 (br q, 2 H , *J* = 7.1), 1.21 (t, 3 H, *J* = 7.3)	172.4, 137.1, 135.4, 130.9, 128.3, 126.6, 126.1, 113.2, 112.5, 48.5, 26.3, 8.8	216 (24, M$^+$ + 1), 215 (83, M$^+$), 159 (76), 144 (100), 91 (100), 68 (20), 65 (52), 57 (44)
5g	3070–3010, 2980, 2935, 2915, 1900, 1790, 1670, 1645, 1600, 1480, 1460, 1430, 1420, 1395, 1380, 1320, 1300, 1215, 1175, 1065, 1020, 1010, 970, 960, 890	7.61 (m, 2 H), 7.33 (m, 1 H), 7.26 (d, 2 H), 6.46 (dt, 1 H, *J* = 17.0, 10.2, 10.2), 5.82 (dd, 1 H, *J* = 13.9, 10.2), 5.12 (dd, 1 H, *J* = 17.0, 1.2), 5.00 (d, 1 H, *J* = 10.2), 4.95 (s, 2 H), 2.69 (q, 2 H, *J* = 7.3), 1.21 (t, 3 H, *J* = 7.3)	172.1, 136.4, 134.9, 130.9, 130.4, 128.2, 119.4, 113.1, 112.4, 25.9, 8.5	295, 293 (60, M$^+$ + 1), 239, 237 (100), 224, 222 (83), 171, 169 (73), 90 (13), 89 (13), 57 (15)
5h	3090, 2920, 2850, 1675, 1640, 1490, 1410, 1375, 1160, 1075, 1015	7.61–7.59 (m, 4 H), 7.39 (d, 1 H, *J* = 13.8), 7.34–7.32 and 7.27–7.24 (m, 4 H), 6.46 (dt, 1 H, *J* = 17.2, 10.3, 10.2), 5.86 (dd, 1 H, *J* = 13.8, 10.3), 5.12 (dd, 1 H, *J* = 17.0, 1.6), 5.01 (dd, 1 H, *J* = 10.2, 1.6), 4.98 (s, 2 H), 4.08 (s, 2 H)	175.5, 142.5, 140.4, 141.1, 137.4, 137.2, 137.0, 136.8, 134.6, 125.9, 125.8, 120.0, 119.7, 52.1, 45.2	437, 435, 433 (2, 3, 1, M$^+$), 266, 264 (5), 239, 237 (50), 224, 222 (34), 171, 169 (90), 91, 89 (49)
5i	3070, 3035, 3000, 2955, 2935, 2910, 2835, 1675, 1640, 1615, 1585, 1515, 1465, 1440, 1425, 1380, 1325, 1300, 1250, 1180, 1160, 1040	7.42 (d, 1 H, *J* = 14.0), 7.31 and 7.25 (m, 4 H), 7.01 (m, 4 H), 6.47 (dt, 1 H, *J* = 16.9, 10.3, 10.2), 5.89 (dd, 1 H, *J* = 13.9, 10.3), 5.13 (dd, 1 H, *J* = 16.9, 1.7), 5.01 (dd, 1 H, *J* = 10.2, 1.7), 4.96 (s, 2 H), 4.02 (s, 2 H), 3.88 and 3.87 (s, 6 H)	169.7, 158.1, 157.9, 134.9, 130.8, 129.6, 128.7, 127.3, 126.5, 113.7, 113.6, 113.1, 112.8, 54.7, 45.7, 38.9	337 (1, M$^+$), 189 (2), 121 (100), 91 (11), 78 (15), 77 (17)
5j	3090, 3050, 3015, 2980, 2940, 1675, 1635, 1525, 1460, 1450, 1420, 1380, 1340, 1285, 1245, 1195, 1165, 1030, 990, 920, 885, 735	8.38 (s, 1 H), 8.25 (d, 2 H), 7.99 (d, 2 H), 7.44 (m, 4 H), 6.18 (br d, 1 H, *J* = 13.1), 5.90–5.80 (m, 1 H), 5.85 (s, 2 H), 5.67 (dd, *J* = 13.6, 10.8), 4.72 (d, 1 H, *J* = 10.0), 4.63 (d, 1 H, *J* = 16.8), 2.47 (q, 2 H, *J* = 7.3), 1.23 (t, 3 H, *J* = 7.3)	174.0, 134.5, 131.9, 131.5, 130.1, 129.9, 128.9, 128.5, 126.9, 125.5, 124.6, 122.9, 116.8, 41.5, 28.6, 10.2	316 (25, M$^+$ + 1), 264 (9), 193 (13), 192 (100), 191 (96), 190 (26), 189 (38)

[a] The IR of **5c, 5f, 5g** and **5j** were measured in KBr and the IR of **5d** and **5e** were measured neat.

[b] The ^1H NMR of **5b, 5c, 5d**, and **5j** were measured at r.t. in $CDCl_3$.

[c] The ^{13}C NMR of **5e–5i** were measured at 373 K in d_6-DMSO.

[d] Satisfactory HRMS or microanalysis was obtained C ± 0.04, H ± 0.04, N ± 0.08.

Y. Rubin at UCLA.[48] The results of these studies will be reported later.

All reagents were of commercial quality if not specially mentioned. The reactions were carried out under Ar. Solvents were dried by distillation using the following drying agents: THF (Na), Et_2O (CaH_2), CH_2Cl_2 (CaH_2), MeOH (Mg), EtOH (Mg). Silica Gel 60 (Merck) was used for flash-chromatography (FC). Mps were determined in open capillary tubes on a Kofler melting point apparatus (Thermovar, C. Reichert AG, Vienna) and are uncorrected. IR spectra were obtained using a Perkin–Elmer 1720 X FT IR spectrophotometer (liquid films using KBr discs or in $CHCl_3$ or CCl_4 solution). ^1H and ^{13}C NMR spectra were measured on a Bruker AMX 400 (400 and 100 MHz) or on a VARIAN Gemini 200 (200 and 50 MHz). If not otherwise mentioned, spectra were measured in $CDCl_3$ with $CHCl_3$ as internal standard. *J* values are given in Hz. Mass spectra were recorded on a Vacuum Generator Micromass 7070E for the HRMS and on a NERMAG R30-10 at 70 eV for the rest of the mass spectra; relative peak intensities are given in % of the base peak (= 100 %). Microanalyses were performed in the microanalytical laboratories of CIBA-GEIGY Ltd., Marly/Fribourg.

N-4-Bromobenzyl-(E)-but-2-ene-1-imine (4c); Typical Procedure

To a cold (0 °C) solution of crotonaldehyde (1.25 g, 17.8 mmol) and 4-bromobenzylamine (3.0 g, 16.2 mmol) in Et_2O (30 mL) was added in small portions molecular sieves 4 Å (20 g). The mixture was stirred for 4 h at r. t., filtered and the molecular sieves were washed with Et_2O (4 x 60 mL). Concentration of the filtrate and Kugelrohr distillation (120 °C/0.02 Torr) of the crude product afforded the imine **4c** (2.31 g, 60 %) as a colorless oil. The imines **4a–d** were purified by distillation whereas the imine **4e** was used directly.

(E)-1-Amino-N-isopropyl-N-phenacetylbuta-1,3-diene (5c); Typical Procedure:

To a solution of phenacetyl chloride (12.5 g, 80 mmol) and *N,N*-diethylaniline (14.9 g, 80 mmol) in anhyd toluene (40 mL) was added dropwise at r.t. a solution of imine **4a** (9.0 g, 0.1 mol) in toluene (30 mL) under Ar. The mixture was stirred overnight at this temperature, filtered over Celite and the residue was washed with toluene (2 x 50 mL). The combined organic layers were combined and washed with 1 M aq HCl (2 x 100 mL), sat. aq $NaHCO_3$ (2 x 100 mL) and H_2O (2 x 100 mL). The organic phase was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by distillation (107 °C/0.02 Torr) to give **5a** (9.43 g, 52 %) as a light yellow oil. The dienamides **5a–d** were purified by distillation. The dienamides **5e** and **5i** were filtered over silica gel to give a light yellow oil. The dienamides **5f–h** and **5j** were filtered over silica gel and then recrystallized.

Table 5. *N*-Alkyl-*N*-Butadienylketene *N,O-tert*-Butyldimethylsilyl Acetals **6**

Product	R^1	R^2	Yield (%)
6a	i-C_3H_7	CH_3	98
6b	i-C_3H_7	C_2H_5	92
6c	i-C_3H_7	$CH_2C_6H_5$	97
6d	i-C_3H_7	$CH=CHCH_3$	98
6e	i-C_3H_7	CH_2-$p$$CH_3OC_6H_4$	98
6f	$CH_2C_6H_5$	C_2H_5	98
6g	CH_2-$p$$BrC_6H_4$	C_2H_5	96
6h	CH_2-$p$$BrC_6H_4$	CH_2-$p$$BrC_6H_4$	97[a]
6i	CH_2-$p$$CH_3OC_6H_4$	CH_2-$p$$CH_3OC_6H_4$	98
6j	Anthranylmethyl	C_2H_5	70

[a] For the synthesis of **6h** a second equivalent of BuLi and TBDMSCl had to be added.

(Z)-N-[(E)-Buta-1,3-dienyl]-N-isopropyl-1-[(tert-butyldimethylsilyl)oxy]prop-1-enamine (6a); Typical Procedure:

In a flame dried three-necked flask fitted with magnetic stirrer, septum, Ar bubbler and thermometer, 1.6 M BuLi (hexane, 3.0 mL, 4.2 mmol) was added dropwise to a solution of anhyd (i-Pr)$_2$NH (0.6 mL, 4.3 mmol) in anhyd THF (10 mL) at – 78 °C. After addition was complete the mixture was allowed to reach 0 °C and stirred for 30 min at this temperature. The mixture was cooled to – 78 °C and freshly distilled HMPA (1.0 mL) was added quickly. Afterwards a solution of the dienamide **5a** (0.47 g, 3.0 mmol) in anhyd THF (2 mL) was added slowly at the same temperature and stirring was continued for 10 min at – 78 °C. To this solution was added dropwise a solution of TBDMSCl (0.51 g, 3.4 mmol) in anhyd THF (2 mL) at – 78 °C. The mixture was warmed to r. t. and stirred for 2 h. NMR analysis of the reaction mixture using **5h** as starting material showed that the transformation was not complete. The temperature was lowered to – 78 °C and a 1.6 M solution of BuLi (hexane, 3.0 mL, 4.2 mmol) was added dropwise followed by a solution of TBDMSCl (0.51 g, 3.4 mmol) in THF (2 mL). Pentane was added (30 mL) and the resulting solution was washed with water (2 x 10 mL) and with brine (2 x 10 mL). The organic phase was dried (Na_2SO_4) and the solvent was removed to give spectroscopically pure silyl enol ether **6a** (0.86 g).

We acknowledge financial support from Swiss National Science Foundation.

(1) Ho, T.L. *Tandem Organic Reactions*; Wiley: New York, 1992.
(2) Thebtaranonth, C.; Thebtaranonth, Y. *Cyclization Reactions*; CRC Press: Boca Raton, 1994.
(3) Posner, G.H. *Chem. Rev.* **1986**, *86*, 831.
(4) Corey, E.J.; Cheng, X.M. *The Logic of Chemical Synthesis*; Wiley: New York 1989, p. 31.
(5) Tietze, L.F.; Beifuss, U. *Angew. Chem.* **1993**, *105*, 137; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131.
(6) Wender, P.A.; Miller, B.L. In *Organic Synthesis Theory and Applications*; Hudlicky, T., Ed.; JAI Press: Greenwich, Co, 1993, Vol 2; p. 27.
(7) Hall, N. *Science* **1994**, *266*, 32.
(8) Hudlicky, T. *Chem. Rev.* **1996**, *96*, 3.
(9) Tietze, L. *Chem. Rev.* **1996**, *96*, 115.
(10) Denmark, S.E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137.
(11) Winkler, J.D. *Chem. Rev.* **1996**, *96*, 167.
(12) Ryu, I.; Sonoda, N.; Curran, D.P. *Chem. Rev.* **1996**, *96*, 177.
(13) Parsons, P.J.; Penkett, C.S.; Shell, A.J. *Chem. Rev.* **1996**, *96*, 195.
(14) Wank, K.K. *Chem. Rev.* **1996**, *96*, 207.
(15) Padwa, A.; Weingarten, M.D. *Chem. Rev.* **1996**, *96*, 223.
(16) Malacria, M. *Chem. Rev.* **1996**, *96*, 289.
(17) Molander, G.A.; Harris, C.R. *Chem. Rev.* **1996**, *96*, 307.
(18) Negishi, E.; Copéret, C.; Ma, S.; Liou, S.-Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 177.
(19) Ruggeri, U.; McClure, K.F.; Heathcock, C.H. *J. Am. Chem. Soc.* **1989**, *111*, 1530.
(20) Heathcock, C.H. *Angew. Chem.* **1992**, *104*, 675; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 665.
(21) Knight, S.D.; Overman, L.E.; Pairaudeau, G. *J. Am. Chem. Soc.* **1993**, *115*, 9293.
(22) Tietze, L.F.; von Kiedrowski, G.; Berger, B. *Angew. Chem.* **1982**, *94*, 222; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 221.
(23) Tietze, L.F.; Denzer, H.; Holdgrün, X.; Neumann, M. *Angew. Chem.* **1987**, *99*, 1309; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 1295.

Table 6. Spectroscopic Data of the Ketene *N,O*-Silyl Acetals **6a–j**

	IR (CCl_4)[a] ν (cm^{-1})	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS (70 eV) *m/z* (%)
6a	3085, 3045, 2960, 2930, 2860, 1670, 1630, 1470, 1460, 1320, 1255, 1050, 995	6.23 (dt, 1 H, J = 16.5, 10.6, 10.5), 6.18 (d, 1 H, J = 14.1), 5.32 (dd, 1 H, J = 13.7, 10.6), 4.75 (dd, 1 H, J = 16.8, 2.2), 4.53 (dd, 1 H, J = 10.3, 2.1), 4.33 (q, 1 H, J = 6.7), 3.59 (sept, 1 H, J = 6.7), 1.56 (d, 3 H, J = 6.7), 1.22 (d, 6 H, J = 6.7), 0.93 (s, 9 H), 0.1 (s, 6 H)	147.9, 138.1, 138.0, 106.6, 104.1, 99.6, 50.5, 26.4, 20.9, 18.8, 11.7, −3.5	282 (13, $M^+ + 1$), 281 (19, M^+), 267 (16), 266 (22), 115 (8), 75 (13), 74 (17), 73 (100)
6b	3085, 3040, 2960, 2930, 2890, 2860, 1635, 1470, 1465, 1425, 1390, 1365, 1300, 1255, 1000, 835, 815	6.39 (d, 1 H, J = 14.0), 6.27 (dt, 1 H, J = 16.7, 10.2, 10.2), 5.42 (dd, 1 H, J = 14.1, 10.2), 4.81 (dd, 1 H, J = 16.7, 1.7), 4.61 (dd, J = 10.2, 1.8), 3.84 (sept, 1 H, J = 6.9), 3.76 and 3.72 (d, 2 H, J = 1.7), 1.25 (d, 6 H, J = 6.9), 0.94 (s, 9 H), 0.19 (s, 6 H)	154.0, 137.2, 135.7, 107.1, 104.9, 79.8, 48.5, 25.7, 19.9, 18.0, −4.8	270 (4), 269 (2), 268 (10, $M^+ + 1$), 267 (15, M^+), 266 (13), 147 (10), 114 (11), 96 (17), 94 (18), 75 (50), 73 (100), 59 (13), 57 (15)
6c	3025, 2960, 2930, 2885, 2860, 1630, 1470, 1465, 1390, 1255, 1165, 1115, 840	7.53–7.48 (m, 2 H), 7.30–7.22 (m, 2 H), 7.16–7.08 (m, 1 H), 6.31 (dt, 1 H, J = 16.9, 10.7, 10.2), 6.28 (d, 1 H, J = 13.6), 5.46 (dd, 1 H, J = 13.7, 10.6), 5.33 (s, 1 H), 4.81 (dd, 1 H, J = 16.9, 2.0), 4.63 (dd, 1 H, J = 10.2, 1.9), 3.75 (sept, 1 H, J = 6.7), 1.29 (d, 6 H, J = 6.7), 0.92 (s, 9 H), 0.1 (s, 6 H)	147.6, 137.1, 136.2, 136.1, 128.3, 127.9, 125.6, 107.3, 105.6, 104.3, 50.5, 25.9, 20.4, 18.2, −3.8	344 (1, $M^+ + 1$), 266 (1), 118 (3), 115 (23), 114 (12), 96 (13), 91 (33), 90 (13), 75 (23), 74 (11), 73 (100)
6d	3085, 3045, 2960, 2930, 2860 1630, 1470, 1420, 1390, 1330, 1280, 1250, 1170, 1040, 995, 840	6.55 (dt, 1 H, J = 17.1, 10.6, 10.4), 6.26 (dt, 1 H, J = 16.9, 10.4, 10.3), 6.21 (d, 1 H, J = 13.9), 5.46 (dd, 1 H, J = 13.5, 10.5), 5.07 (d, 1 H, J = 10.8), 4.95 (dd, 1 H, J = 17.2, 2.0), 4.85 (dd, 1 H, J = 16.8, 1.6), 4.79 (dd, 1 H, J = 10.4, 2.0), 4.64 (dd, 1 H, J = 10.2, 1.7 Hz), 3.76 (sept, 1 H, J = 6.8 Hz), 1.23 (d, 6 H, J = 6.8 Hz), 0.97 (s, 9 H), 0.11 (s, 6 H)	149.3, 137.6, 135.2, 132.8, 111.5, 108.5, 107.8, 103.7, 50.8, 26.4, 20.9, 18.9, −3.6	293 (11, M^+), 278 (7), 252 (14), 237 (18), 114 (16), 73 (100)
6e	3045, 2960, 2930, 2900, 2860, 1740, 1630, 1610, 1585, 1575, 1560, 1510, 1465, 1420, 1390, 1365, 1295, 1250, 1175, 1115, 1025, 1005, 840	7.46 (m, 2 H), 6.81 (m, 2 H), 6.32 (dt, 1 H, J = 16.9, 10.7, 10.5 Hz), 6.31 (d, 1 H, J = 13.7 Hz), 5.43 (dd, 1 H, J = 13.8, 10.5 Hz), 5.29 (s, 1 H), 4.80 (dd, 1 H, J = 16.8, 1.9 Hz), 4.60 (dd, 1 H, J = 10.4, 1.8 Hz), 3.80 (s, 3 H), 3.73 (sept, 1 H, J = 6.7), 1.27 (d, 6 H, J = 6.7), 0.97 (s, 9 H), 0.06 (s, 6 H)	158.3, 147.1, 137.7, 137.2, 130.1, 129.4, 114.1, 107.6, 105.8, 105.1, 51.1, 26.6, 20.9, 18.8, −3.2	374 (16, $M^+ + 1$), 261 (38), 260 (100), 259 (67), 121 (32), 111 (61), 97 (12), 96 (80), 91 (32), 78 (24), 77 (28), 75 (12), 73 (31)
6f	3080–3010, 2960, 2950, 2885, 2860, 1670, 1635, 1460, 1425, 1385, 1360, 1330, 1255, 1200, 1060, 995, 885, 840	7.35–7.19 (m, 5 H), 6.66 (d, 1 H, J = 13.7), 6.26 (dt, 1 H, J = 16.7, 10.6, 10.2), 5.19 (dd, 1 H, J = 13.7, 10.6), 4.75 (dd, 1 H, J = 16.7, 1.8), 4.60 (dd, 1 H, J = 10.2, 1.8), 4.49 (s, 2 H), 4.23 (q, 1 H, J = 6.7), 1.58 (d, 3 H, J = 6.7), 1.02 (s, 9 H), 0.17 (s, 6 H)	149.6, 138.4, 137.6, 137.4, 129.1, 127.5, 127.3, 108.1, 104.0, 91.0, 50.5, 26.4, 18.9, 11.7, −3.8	329 (17, M^+), 314 (23), 288 (9), 238 (9), 159 (11), 91 (100), 75 (23), 73 (78), 65 (18)
6g	3080–3010, 2960, 2930, 2885, 2860, 1670, 1635, 1490, 1360, 1260, 1200, 1165, 1060, 995, 840	7.42 (m, 2 H), 7.07 (m, 2 H), 6.60 (d, 1 H, J = 13.8), 6.22 (dt, J = 16.8, 10.3, 10.3), 5.11 (dd, 1 H, J = 13.8, 10.4), 4.73 (dd, 1 H, J = 16.8, 1.8), 4.60 (dd, 1 H, J = 10.2, 1.6), 4.39 (s, 2 H), 4.17 (q, 1 H, J = 6.7), 1.55 (d, 3 H, J = 6.7), 0.98 (s, 9 H), 0.13 (s, 6 H)	149.4, 137.4, 137.3, 137.1, 132.4, 129.3, 121.3, 108.6, 104.3, 91.3, 49.9, 26.4, 18.9, 11.6, −3.8	409 (10, M^+), 394 (3), 238 (4), 171, 169 (46), 75 (13), 73 (100)
6h	3030, 2960, 2930, 2860, 1630, 1490, 1470, 1360, 1260, 1160, 1075, 1010, 995, 915	7.49–7.11 (m, 8 H), 6.85 (d 1 H, J = 13.8), 6.26 (dt, 1 H, J = 16.8, 10.6, 10.3), 5.24 (dd, 1 H, J = 13.8, 10.4), 5.07 (s, 1 H), 4.85 (dd, 1 H, J = 16.9, 1.7), 4.70 (dd, 1 H, J = 10.2, 1.7), 4.57 (s, 2 H), 0.92 (s, 9 H), 0.1 (s, 6 H)	150.3, 136.7, 136.6, 136.1, 135.2, 132.4, 132.3, 131.6, 130.4, 121.5, 118.9, 110.4, 106.6, 94.4, 50.5, 26.3, 18.7, −2.9	549 (1, M^+), 5.48 (1), 547 (1), 239 (8), 237 (8), 224 (8), 222 (8), 171 (44), 169 (46), 90 (27), 89 (24), 75 (15), 73 (100)
6i	3000, 2955, 2930, 2860, 2835, 1635, 1510, 1465, 1365, 1250, 1175, 1160, 1040, 840	7.35–7.16 (m, 4 H), 6.89–6.75 (m, 5 H), 6.28 (dt, 1 H, J = 16.9, 10.4, 10.1), 5.28 (dd, 1 H, J = 13.8, 10.5), 5.15 (s, 1 H), 4.82 (dd, 1 H, J = 16.9, 1.7), 4.66 (dd, 1 H, J = 10.2, 1.8), 4.54 (s, 2 H), 3.79 (s, 6 H), 1.00 (s, 9 H), 0.02 (s, 6 H)	158.6, 157.2, 148.3, 136.6, 135.8, 129.4, 129.2, 128.1, 114.1, 113.4, 108.4, 104.7, 95.6, 55.3, 49.8, 25.9, 18.3, −4.2	452 (4, $M^+ + 1$), 451 (1, M^+), 235 (4), 122 (7), 121 (24), 91 (18), 77 (24), 73 (100)
6j	3060, 2960, 2930, 2860, 1680, 1635, 1550, 1255, 1215, 1165, 1005, 980	8.41 (s, 1 H), 8.28 (m, 2 H), 8.01 (m, 2 H), 7.55–7.41 (m, 4 H), 6.22 (d, 1 H, J = 13.6), 6.12 (dt, 1 H, J = 16.6, 10.4, 10.3), 5.61 (dd, 1 H, J = 13.4, 10.4), 5.17 (s, 2 H), 4.81 (dd, 1 H, J = 16.7, 2.0 Hz), 4.54 (dd, 1 H, J = 10.1, 1.9), 4.28 (q, 1 H, J = 6.7), 1.38 (d, 3 H, J = 6.7), 0.91 (s, 9 H), 0.08 (s, 6 H)	147.9, 139.4, 137.5, 132.1, 132.0, 131.9, 129.7, 126.6, 125.6, 125.5, 125.4, 107.9, 105.2, 97.8, 46.9, 26.4, 18.8, 11.4, −3.65	430 (56, $M^+ + 1$), 429 (5, M^+), 264 (14), 263 (23), 192 (43), 191 (37), 189 (14), 106 (11), 75 (28), 74 (17), 73 (100), 57 (20)

[a] The IR of **6b** was measured in KBr and the IR of **6d** was measured neat.

(24) Tietze, L.F.; Glüsenkamp, K.-H.; Holla, W. *Angew. Chem.* **1982**, 793; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 863.

(25) Tietze, L.F.; Bachmann, J.; Wichmann, J.; Burckhardt, O. *Angew. Chem.* **1988**, *100*, 983; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 971.

(26) Tietze, L.F.; Bachmann, J.; Wichmann, J.; Burckhardt, O. *Synthesis* **1994**, 1185.

(27) van Tamelen, E.E.; Willet, J.; Clayton, R.B.; Lord, K.E. *J. Am. Chem. Soc.* **1966**, *88*, 4752.

(28) van Tamelen, E.E. *Acc. Chem. Res.* **1968**, *1*, 111.

(29) Johnson, W.S. *Acc. Chem. Res.* **1968**, *1*, 1.

(30) Robinson, R. *J. Chem. Soc.* **1917**, 762.

(31) Robinson, R. *J. Chem. Soc.* **1917**, 876.

(32) Schöpf, C.; Lehmann, G.; Arnold, W. *Angew. Chem.* **1937**, *50*, 779.

(33) Huber, S.; Stamouli, P.; Neier, R. *J. Chem. Soc., Chem. Comm.* **1985**, 533.

(34) Schoepfer, J., Eichenberger, E.; Neier, R. *J. Chem. Soc., Chem. Commun.* **1993**, 246.

(35) Huber, S.; Stamouli, P.; Jenny, T.; Neier, R. *Helv. Chim. Acta*, **1986**, *69*, 1898.

(36) Baak, M.; Rubin, Y.; Franz, A.; Stoeckli-Evans, H.; Bigler, L.; Nachbaur, R.; Neier, R. *Chimia* **1993**, *47*, 233.

(37) Baak, M. Inaugural-Dissertation, No. 1000 Institut für Organische Chemie, Universität Fribourg, 1991.

(38) Sommer, L.H. *Stereochemistry, Mechanism and Silicon*; MacGraw Hill: New York, 1965, p. 127.

(39) Corey, E.J.; Rückert, C.; Hua, D.A. *Tetrahedron Lett.* **1981**, *22*, 3455.

(40) Taguchi, K.; Westheimer, F.H. *J. Org. Chem.* **1971**, *36*, 1570.

(41) Oppolzer, W.; Bieber, L.; Francotte, E. *Tetrahedron Lett.* **1979**, *19*, 981.

(42) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 590.

(43) Oppolzer, W.; Bieber, L.; Francotte, E. *Tetrahedron Lett.* **1979**, *19*, 4537.

(44) Oppolzer, W.; Flashkamp, E. *Helv. Chim. Acta* **1977**, *60*, 204.

(45) Stoeckli-Evans, H. unpublished results.

(46) Corey, E.J.; Gross, A.W. *Tetrahedron Lett.* **1984**, *25*, 495.

(47) Woodbury, R.; Rathke, M. *J. Org. Chem.* **1977**, *43*, 881.

(48) An, Y.Z.; Franz, A.; Ganapathi, P.; Neier, R.; Rubin, Y. manuscript in preparation.