

Nucleophilic Reactivities of Silyl Ketene Acetals and Silyl Enol Ethers Containing $(\text{C}_6\text{F}_5)_3\text{SiO}$ and $(\text{C}_6\text{H}_5)_3\text{SiO}$ Groups

Alexander D. Dilman^{*[a]} and Herbert Mayr^[b]

Keywords: Silicon / Perfluorinated ligands / Silyl ketene acetals and enol ethers / Kinetics / Substituent effects

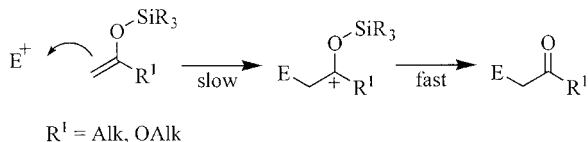
The kinetics of the reactions of tris(pentafluorophenyl)silyl and triphenylsilyl ketene acetals and enol ethers with benzhydrylium cations have been measured photometrically. The second-order rate constants ($\log k_2$) have been used to determine the nucleophilicity parameters of these π systems, which provide a quantitative comparison of their reactivities with those of other types of nucleophiles. A change from trimethylsilyloxy to triphenylsilyloxy reduces reactivity by only

a factor of ten, while replacement of triphenylsilyloxy with tris(pentafluorophenyl)silyloxy decreases the nucleophilicity of the enolate C=C double bond by three to four orders of magnitude. The cation-stabilizing ability of the tris(pentafluorophenyl)silyloxy group is thus similar to that of a methyl group.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

Silyl ketene acetals and silyl enol ethers have found widespread use as nucleophilic reagents in aldol,^[1] Michael,^[2] and Mannich^[3] reactions. In these processes, electrophilic attack at the carbon–carbon double bond is followed by rapid desilylation (Scheme 1). In accord with this mechanism, the reactivity of the double bond is primarily determined by the substituent R^1 adjacent to the silyloxy group, as has been demonstrated by extensive investigations of trialkylsilyl derivatives.^[4,5] The silyl group serves mainly as a positively charged leaving group serving to quench the carbocationic center, thus preventing the polymerization of the π system.^[6]



Scheme 1.

Recently, one of us introduced a new type of enol ethers containing tris(pentafluorophenyl)silyl groups, and these compounds smoothly undergo uncatalyzed aldol reac-

tions.^[7] This observation stands in sharp contrast with the behavior of conventional trialkylsilyl enol ethers, which do not react with aldehydes in the absence of additional activators.^[1a,1c] For the efficient elaboration of methods for aldol and related reactions it is therefore important to understand the magnitude of the electronic influence of substituents at silicon on the reactivity of the enolate C=C double bond.

In this study we have quantitatively evaluated the effect of silicon substitution on the nucleophilicity of silyl ketene acetals **1a** and **1b** and the silyl enol ethers **2a**, **2b**, **3a**, and **3b** by studying the kinetics of their reactions with benzhydrylium ions (Table 1). The reactivities of $(\text{C}_6\text{F}_5)_3\text{SiO}$ - and $(\text{C}_6\text{H}_5)_3\text{SiO}$ -substituted C=C double bonds were then compared with those of Me_3SiO -, Me-, and H-containing derivatives.

Table 1. Nucleophilic π systems.

X			
$\text{OSi}(\text{C}_6\text{F}_5)_3$	1a	2a	3a
$\text{OSi}(\text{C}_6\text{H}_5)_3$	1b	2b	3b
OSiMe_3	1c	2c	3c
H	1d	2d	3d

Results and Discussion

Our approach is based on previous work by the München group that demonstrates that the reactions of car-

[a] N. D. Zelinsky Institute of Organic Chemistry, 119991 Moscow, Leninsky prosp. 47, Russian Federation
Fax: +7-095-135-5328
E-mail: adil25@mail.ru

[b] Department Chemie und Biochemie der Ludwig-Maximilians-Universität, München, Butenandtstr. 5–13 (Haus F), 81377 München, Germany
Fax: +49-89-2180-77717
E-mail: Herbert.Mayr@cup.uni-muenchen.de

Supporting information for this article is available on the WWW under <http://www.eurjoc.org> or from the author.

bocations with π nucleophiles can be analyzed by Equation (1)

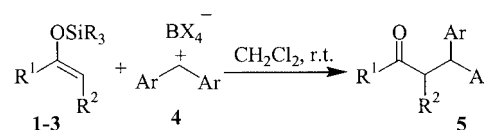
$$\log k = s(N + E) \quad (1)$$

where k is the second-order rate constant of a reaction at 20 °C, N is the nucleophilicity parameter, E is the electrophilicity parameter, and s is a nucleophile-specific slope parameter.^[8] As reference electrophiles we employed the benzhydrylium cations **4a–h**,^[9] either employed as stable tetrafluoroborates (**4a–g**·BF₄) or generated in situ from the precursor **4h**-Cl and BCl₃^[10] (Table 2).

Table 2. Benzhydrylium ions **4** used as reference electrophiles.

Ar ₂ CH ⁺		E
(lil) ₂ CH ⁺	4a	-10.04
(jul) ₂ CH ⁺	4b	-9.45
(ind) ₂ CH ⁺	4c	-8.76
(pyr) ₂ CH ⁺	4d X = N(CH ₂) ₄	-7.69
(dma) ₂ CH ⁺	4e X = NMe ₂	-7.02
(mor) ₂ CH ⁺	4f X =	-5.53
(dpa) ₂ CH ⁺	4g X = NPh ₂	-4.72
(ani) ₂ CH ⁺	4h X = OMe	0.00

Analogously with previously described reactions,^[4,5] cations **4** reacted readily with compounds **1–3** in dichloromethane, affording the corresponding products **5**. This reaction course was investigated for the combinations listed in Scheme 2.



Nu	Ar ₂ CH ⁺	5	yield, %
1a	(dma) ₂ CH ⁺	5a	71
1b	(jul) ₂ CH ⁺	5b	36
2a	(ani) ₂ CH ⁺	5c	67
2b	(dma) ₂ CH ⁺	5d	61
3a	(ani) ₂ CH ⁺	5e	82

Scheme 2.

The kinetics of the reactions of the benzhydrylium ions **4** with the nucleophiles **1–3** (>10 equiv.) in dichloromethane at 20 °C were monitored by UV/Vis spectroscopy with the instrumentation described previously.^[9,11] From the exponential decays of the carbenium ions' absorbances we derived the pseudo-first-order rate constants, which were plotted against nucleophile concentrations to afford second-order rate constants (Table 3). For some reactions of compounds **1a**, **1b**, **2a**, and **2b**, activation parameters were determined from experiments at variable temperature. Plotting of the logarithms of the second-order rate constants against

Table 3. Second-order rate constants and activation parameters for the reactions of benzhydrylium ions **1** with nucleophiles **1–3** (CH₂Cl₂) and calculated nucleophilicity (N) and slope (s) parameters for **1–3**.

Nucleophile	N	s	Ar ₂ CH ⁺	k_2 , L mol ⁻¹ s ⁻¹	$\Delta H^\ddagger$, kJ mol ⁻¹	$\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹
	1a 8.16	0.67	(mor) ₂ CH ⁺	6.031×10^1	30.4 ± 0.6	-107.3 ± 2.2
			(dma) ₂ CH ⁺	5.546		
			(pyr) ₂ CH ⁺	2.173		
	1b 11.28	0.91	(ind) ₂ CH ⁺	2.153×10^2	29.1 ± 0.7	-115.0 ± 2.5
			(jul) ₂ CH ⁺	3.992×10^1		
			(lil) ₂ CH ⁺	1.471×10^1		
	2a (1.38)	(0.93) ^[a]	(ani) ₂ CH ⁺	1.941×10^1	16.3 ± 0.3	-164.7 ± 1.1
	2b 5.76	1.02	(dpa) ₂ CH ⁺	1.196×10^1	25.8 ± 0.9	-136.5 ± 3.2
			(mor) ₂ CH ⁺	1.596		
			(dma) ₂ CH ⁺	5.328×10^{-2}		
	3a (0.58)	(0.91) ^[a]	(ani) ₂ CH ⁺	3.344		
	1d 4.37	0.90	(dpa) ₂ CH ⁺	4.764×10^{-1}		
			(mor) ₂ CH ⁺	9.312×10^{-2}		
			(dma) ₂ CH ⁺	3.996×10^{-3}		

[a] Assumed slope as for analogous trimethylsilyl derivative.^[4,8a]

the electrophilicity parameters of benzhydrylium ions^[9] (Figure 1) allows one to derive nucleophilicity (*N*) and slope (*s*) parameters of nucleophiles **1–3** by using Equation (1).

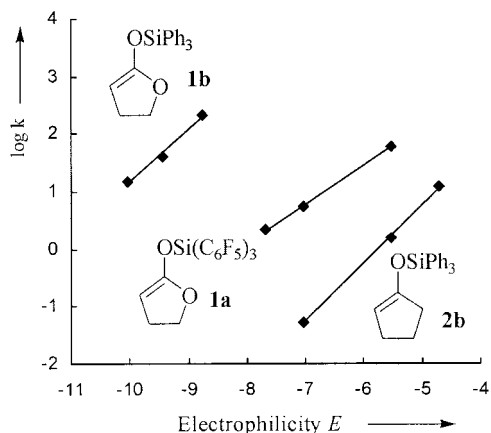
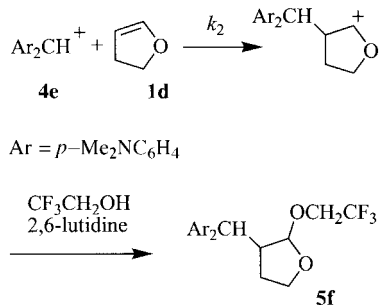


Figure 1. Correlation of the rate constants ($\log k_2$, at 20 °C, in CH_2Cl_2) for the reactions of nucleophiles with the benzhydrylium ions (**4**) in relation to their electrophilicity parameters *E*.

In order to compare the effects of R_3SiO groups with that of hydrogen we also studied the nucleophilicity of 2,3-dihydrofuran **1d**. However, alkyl enol ethers readily polymerize when treated with electrophiles,^[6] and for that reason trifluoroethanol and 2,6-lutidine were added to the reaction mixtures when the kinetics of electrophilic additions to 2,3-dihydrofuran were studied (Scheme 3).^[12] Because of the stabilizing anomeric interaction of two alkoxy groups, the intermediate carboxonium ion shows a higher selectivity for alcohols (compared to π nucleophiles) than the initial benzhydrylium ion. On a preparative scale the product **5f** was isolated as a 1.3:1 mixture of diastereoisomers in 38% yield from the reaction of **1d** with **4e-BF₄**. The kinetics of the reaction of **1d** with the bis(*p*-chloro) benzhydrylium ion were studied previously, giving the rate constant of $1.3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$.^[13] This point was not taken for the calculation of *N* and *s* because of the proximity of the diffusion limit. Nevertheless, the rate constant of the reaction of **1d** with (*p*-ClC₆H₄)₂CH⁺ as calculated by Equation (1) with the parameters of **1d** determined here affords the value of $2.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, which is very close to that found experimentally.



Scheme 3.

Figure 2 illustrates the influence of different silyloxy groups on the reactivity of different π systems. Comparison of the pairs **1c/1b**, **2c/2b**, and **3c/3b** shows that substitution of Me_3SiO by Ph_3SiO leads to a decrease in double bond reactivity by a factor of approximately ten. Perfluorination of the phenyl rings diminishes the nucleophilicity by three to four orders of magnitude, (cf. **1a/1b**, **2a/2b**, and **3a/3b**), due to the significant electron-withdrawing influence of fluorine.^[14] This inductive effect is so strong that it largely compensates for the electron-donating ability of oxygen, thus making the tris(pentafluorophenyl)silyloxy group behave more like an alkyl substituent (cf. **2a** with 1-methylcyclopentene and **3a** with isobutylene).

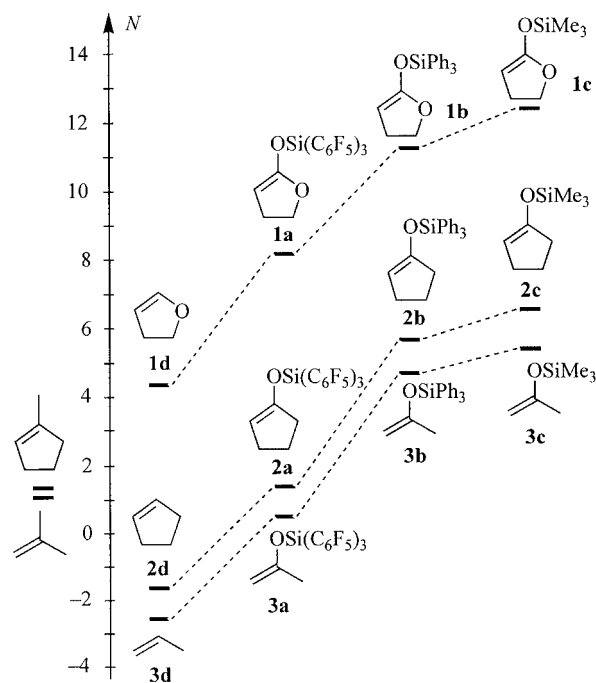
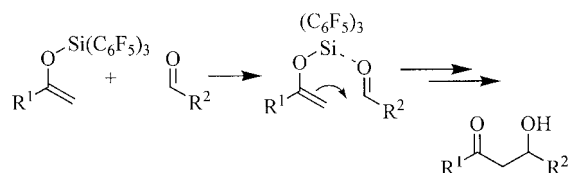


Figure 2. Relative nucleophilicities of silyl ketene acetals, enol ethers, and alkenes. *N* parameters of **1c**,^[9] **2c**,^[4] **3b**, **3c**,^[4] and alkenes^[8a,9] are taken from the literature.

In view of the low nucleophilicities of the tris(pentafluorophenyl)silyl enol ethers **2a** and **3a**, their uncatalyzed coupling with aldehydes is remarkable.^[7a] Obviously, the Lewis acidity of the silyl moiety plays an important role in the rate-determining step of the aldol reaction (Scheme 4). Since the three pentafluorophenyl groups have been shown in this work to reduce the nucleophilicity of the $\text{C}=\text{C}$ double bond significantly, it must be concluded that in reactions with aldehydes this effect is overcompensated by the increased Lewis acidity of the silicon atom.



Scheme 4.

In summary, the reactivity of silyl ketene acetals and silyl enol ethers may be considerably affected by the nature of the silyl group substituents. While replacement of methyl by phenyl (that is, *sp*³ by *sp*²) has a weak effect, the reactivity decreases dramatically with incorporation of fluorine atoms in the phenyl ring.

Experimental Section

General Remarks: The benzhydrylium cations^[9] used in this work and the tris(pentafluorophenyl)silyl ketene acetal **1a**^[7b] and enol ethers **2a** and **3a**^[7b] were prepared by literature procedures. NMR spectra were recorded on a Bruker ARX 300 instrument in CDCl₃ distilled from CaH₂ and stored over MS (4A).

Kinetics: Measurements were performed with a J&M TIDAS diode array spectrophotometer connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) through fiber optic cables using standard SMA connectors. All kinetic measurements were conducted in Schlenk flasks with the exclusion of moisture, and the temperature of the solutions during the kinetic measurements was maintained by circulating bath cryostats within ± 0.1 °C (water/glycol bath for *T* > -10 °C; ethanol bath for *T* < -10 °C) and monitored with a thermocouple probe inserted into the reaction mixture.

5-(Triphenylsilyloxy)-2,3-dihydrofuran (1b):^[15] Butyllithium (5.3 mL of a 2.5 M solution in hexane, 13.2 mmol) was added to a solution of *i*Pr₂NH (2.0 mL, 14.5 mmol) in THF (30 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C and cooled to -78 °C, followed by dropwise addition of butyrolactone (0.91 mL, 11.9 mmol). After the system had been stirred for 10 min, a solution of Ph₃SiCl (4.28 g, 14.5 mmol) in THF (7 mL) was rapidly injected. The mixture was allowed to warm to room temperature over 3 h. The solvent was removed under vacuum, and the residue was diluted with hexane (20 mL) and filtered through celite under nitrogen. The filter cake was washed with dry dichloromethane, with the filtrate being collected into a separate flask. Evaporation of dichloromethane afforded 2.28 g of **1b** containing ca. 15% of 3-(triphenylsilyl)tetrahydrofuran-2-one, ca. 56% yield (this sample was used for kinetic experiments). M.p. 83–101 °C. ¹H NMR (CDCl₃): δ = 2.38 (td, *J* = 2.1, 8.7 Hz, 2 H, CH₂CH), 3.51 (t, *J* = 2.1 Hz, 1 H, CH), 4.06 (t, *J* = 8.7 Hz, 2 H, CH₂O), 7.21–7.31 (m) and 7.54–7.59 (m) (15 H, 3 Ph) ppm. ¹³C NMR (CDCl₃): δ = 28.9 (CH₂C), 68.5 (CH₂O), 70.4 (CH), 128.4 (CH_{Ph}), 130.9 (CH_{Ph}), 133.2 (C_{Ph}), 135.9 (CH_{Ph}), 158.7 (CO₂) ppm. Evaporation of the hexane filtrate gave 2.50 g containing **1b**, 10% of 3-(triphenylsilyl)tetrahydrofuran-2-one, and 10% of other unidentified impurity. Attempted distillation failed due to decomposition of **1b**.

1-(Triphenylsilyloxy)cyclopentene (2b):^[16] Triethylamine (0.88 mL, 6.4 mmol), cyclopentanone (470 μ L, 5.3 mmol), and a solution of NaI (0.79 g, 5.3 mmol) in MeCN (7 mL) were successively added to a solution of Ph₃SiCl (1.56 g, 5.3 mmol) in MeCN/benzene (12 mL/2 mL) at room temperature. The mixture was stirred for 1.5 h and extracted with hexane (3 $\times$ 20 mL). The combined hexane solution was concentrated under vacuum, diluted with hexane, filtered, concentrated, and the residue was distilled (bulb-to-bulb, 230–245 °C/3.9 $\times$ 10⁻² mbar), followed by recrystallization from hexane (ca. 5 mL, with cooling to -10 °C) to furnish **2b** (1.15 g, 63% yield) as white crystals. M.p. 73–79 °C. ¹H NMR (CDCl₃): δ = 1.61–1.72 (m, 2 H, CH₂), 2.01–2.09 (m, 2 H, CH₂), 2.12–2.20 (m, 2 H, CH₂), 4.47 (quintet, *J* = 2.1 Hz, 1 H, CH), 7.22–7.32 (m) and 7.54–7.60 (m) (15 H, 3 Ph) ppm. ¹³C NMR (CDCl₃): δ = 21.8 (CH₂), 29.1

(CH₂), 38.8 (CH₂), 104.7 (CH), 128.3 (CH_{Ph}), 130.6 (CH_{Ph}), 134.4 (C_{Ph}), 135.9 (CH_{Ph}), 155.1 (CO) ppm. HRMS (EI): calcd. *m/z* for C₂₃H₂₂O_{Si}, 342.1440; found 322.1447.

3-{Bis[4-(dimethylamino)phenyl]methyl}tetrahydrofuran-2-one (5a): A solution of **1a** (420 mg, 0.68 mmol) in CH₂Cl₂ (5 mL) was added to a solution of (dma)₂CH·BF₄ (194 mg, 0.57 mmol) in CH₂Cl₂ (5 mL) at room temperature. The mixture was stirred for 30 min, quenched with a solution of NH₄F (42 mg) and AcOH (102 mg) in MeOH (2.5 mL)/H₂O (0.5 mL), stirred for an additional 15 min, filtered through celite (solution in CH₂Cl₂), dried (CaSO₄), and concentrated under vacuum. Flash column chromatography on silica gel (ether/pentane/NEt₃ from 1:1:0.01 to 3:1:0.01) gave a sample containing traces of butyrolactone, which was removed by heating at 90–100 °C/0.03 mbar for 2 h to afford **5a** (137 mg, 71%) as a greenish oil. *R*_f (ether/pentane, 1:1) = 0.26. ¹H NMR (CDCl₃): δ = 2.08 (dq, *J* = 8.2, 12.9 Hz, 1 H), 2.27–2.39 (m, 1 H), 2.81 (s, 6 H, NMe₂), 2.84 (s, 6 H, NMe₂), 3.23 (ddd, *J* = 4.4, 8.1, 9.4 Hz, 1 H), 3.69 (td, *J* = 5.1, 8.5 Hz, 1 H), 4.02 (dt, *J* = 7.6, 8.7 Hz, 1 H), 4.48 (d, *J* = 4.4 Hz, 1 H, CHAr₂), 6.54 (d, *J* = 8.8 Hz, 2 H, Ar), 6.61 (d, *J* = 8.7 Hz, 2 H, Ar), 6.93 (d, *J* = 8.8 Hz, 2 H, Ar), 7.04 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. ¹³C NMR (CDCl₃): δ = 26.2 (CH₂CH), 40.96 (NMe₂), 41.04 (NMe₂), 44.3 and 49.0 (CHCH), 66.9 (CH₂O), 112.9 and 113.0 (2 CH_{Ar}), 129.2 and 130.1 (2 CH_{Ar}), 129.9 and 131.1 (2 C_{Ar}), 149.6 and 149.8 (2 C_{Ar}), 179.4 (C=O) ppm. IR (film, cm⁻¹): $\tilde{\nu}$ = 2985, 2886, 2801, 1766, 1614, 1520, 1481, 1445, 1349, 1210, 1161, 1061, 1026, 948, 810, 734, 573. MS (EI): *m/z* (%) = 338 (8) [M]⁺, 254 (19), 253 (100) [**4e**], 237 (12). HRMS (EI): calcd. *m/z* for C₂₁H₂₆N₂O₂, 338.1994; found 338.1972.

3-[Bis(julolidin-9-yl)methyl]dihydrofuran-2-one (5b): A solution of (jul)₂CH·BF₄ (163 mg, 0.37 mmol) in CH₂Cl₂ (5 mL) was added to a solution of **1b** (147 mg, 0.37 mmol) in CH₂Cl₂ (2 mL). After stirring for 30 min, the mixture was quenched by addition of a solution of KF (1 g) and AcOH (1 mL) in MeOH (6 mL)/H₂O (1 mL), stirred for 30 min, poured into ether (70 mL), washed with water (2 $\times$ 30 mL), dried (CaSO₄), and concentrated under vacuum with heating at ca. 100 °C. Flash column chromatography on silica gel (hexane/ethyl acetate/NEt₃ 4:1:0.01) afforded **5b** (59 mg, 36% yield).^[9]

2-{Bis[*p*-(dimethylamino)phenyl]methyl}cyclopentanone (5d): A solution of (dma)₂CH·BF₄ (173 mg, 0.51 mmol) in CH₂Cl₂ (6 mL) was added to a solution of **2b** (183 mg, 0.54 mmol) in CH₂Cl₂ (3 mL). After stirring for 1 h, the mixture was quenched by addition of concentrated aq. ammonia (10 mL), poured into ether (50 mL), washed with water (4 $\times$ 20 mL), dried (CaSO₄), and concentrated under vacuum. Flash column chromatography on silica gel (hexane/ether/NEt₃ 5:2:0.01) afforded **5d** (105 mg, 61% yield).^[4]

Reactions of Bis(4-methoxyphenyl)methyl Chloride with Tris(pentafluorophenyl)silyl Enol Ethers (Compounds 5c, 5e): Gaseous BCl₃ (60 mL) was bubbled through a solution of (ani)₂CHCl (160 mg, 0.61 mmol) in CH₂Cl₂ (5 mL), followed by addition of a solution of silyl enol ether **2a** or **3a** (0.67 mmol) in CH₂Cl₂ (3 mL). After stirring for 10 min the mixture was quenched with a solution of NH₄F (250 mg) and AcOH (560 mg) in MeOH (2.5 mL)/H₂O (0.5 mL), stirred for an additional 15 min, filtered through celite (solution in CH₂Cl₂), dried (CaSO₄), and concentrated under vacuum. The product was purified by flash column chromatography on silica gel with elution with hexane/ethyl acetate.

2-Bis(4-methoxyphenyl)methylcyclopentanone (5c): 67% yield. *R*_f (hexane/ethyl acetate, 3:1) = 0.25. ¹H NMR (CDCl₃): δ = 1.53–1.90 (m, 4 H, CH₂CH₂), 2.09–2.25 (m, 2 H, CH₂CO), 2.74–2.83 (m, 1 H, CHCO), 3.67 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 4.47 (d, *J* = 4.8 Hz, 1 H, CHAr₂), 6.68 (d, *J* = 8.7 Hz, 2 H, Ar), 6.75 (d, *J* =

8.7 Hz, 2 H, Ar), 6.90 (d, J = 8.7 Hz, 2 H, Ar), 7.10 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (CDCl_3): δ = 20.9 (CH_2), 27.6 (CH_2), 38.8 (CH_2), 48.8 (CH), 53.6 (CH), 55.5 (OMe), 55.6 (OMe), 114.0 and 114.1 (2 CH_{Ar}), 129.6 and 130.5 (2 CH_{Ar}), 135.4 and 136.3 (2 C_{Ar}), 158.3 and 158.4 (2 C_{Ar}), 224.1 (C=O) ppm. IR (film, cm^{-1}): $\tilde{\nu}$ = 2959, 2836, 1737, 1609, 1510, 1464, 1248, 1178, 1034, 837, 582. HRMS (EI): calcd. m/z for $\text{C}_{20}\text{H}_{22}\text{O}_3$, 310.1569; found 310.1542.

4-Bis(4-methoxyphenyl)-2-butanone (5e): 82% yield.^[17]

3-{Bis[4-(dimethylamino)phenyl]methyl}-2-(2,2,2-trifluoroethoxy)tetrahydrofuran (5f): A solution of $(\text{dma})_2\text{CH}\cdot\text{BF}_4$ (299.3 mg, 0.88 mmol) in CH_2Cl_2 (10 mL) was added to a solution of 2,3-dihydrofuran (1.00 mL, 13.1 mmol), $\text{CF}_3\text{CH}_2\text{OH}$ (360 μL , 5.28 mmol), and 2,6-lutidine (307 μL , 2.64 mmol) in CH_2Cl_2 (2 mL) at room temperature. After stirring for 1 h, the mixture was poured into ether (50 mL), washed with water (2×25 mL), dried (CaSO_4), and concentrated under vacuum. The crude sample contained a 1.3:1 mixture of isomers. Column chromatography on silica gel in hexane/ethyl acetate (6:1) afforded two fractions with a 38% combined yield: the upper fraction contained the major isomer (75.3 mg): R_f = 0.26. ^1H NMR (CDCl_3): δ = 1.45–1.57 (m, 1 H), 1.98 (qt, J = 5.2, 7.9 Hz, 1 H, $\text{CH}_2\text{CH}_2\text{O}$), 2.789 (s, 6 H, NMe_2), 2.794 (s, 6 H, NMe_2), 3.03 (dddd, J = 0.9, 4.4, 7.9, 12.4 Hz, 1 H, CHCH_2), 3.42 (d, J = 12.4 Hz, 1 H, CHO_2), 3.55 (dq, $J_{\text{H,F}}$ = 8.7, $J_{\text{H,H}}$ = 12.1 Hz, 1 H, $\text{CH}_A\text{H}_B\text{CF}_3$), 3.77 (dq, $J_{\text{H,F}}$ = 9.0, $J_{\text{H,H}}$ = 12.1 Hz, 1 H, $\text{CH}_A\text{H}_B\text{CF}_3$), 3.81–3.97 (m, 2 H, CH_2O), 4.73 (s, 1 H, CHAr_2), 6.56 (d, J = 8.8 Hz, 2 H, Ar), 6.57 (d, J = 8.8 Hz, 2 H, Ar), 7.01 (d, J = 8.8 Hz, 2 H, Ar), 7.07 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (CDCl_3): δ = 29.5 ($\text{CH}_2\text{CH}_2\text{O}$), 47.07 (NMe_2), 47.11 (NMe_2), 50.3 and 52.5 (CHAr_2 and CHCHO_2), 64.4 (q, $J_{\text{C,F}}$ = 34.3 Hz, CH_2CF_3), 67.8 (CH_2O), 108.1 (CHO_2), 113.3 and 113.4 (2 CH_{Ar}), 124.4 (q, $J_{\text{C,F}}$ = 278.2 Hz, CF_3), 128.7 and 128.8 (2 CH_{Ar}), 132.8 and 132.9 (2 C_{Ar}), 149.48 and 149.52 (2 C_{Ar}) ppm. IR (film, cm^{-1}): $\tilde{\nu}$ = 2947, 2889, 1614, 1520, 1480, 1446, 1348, 1279, 1223, 1163, 1118, 1058, 987, 949, 805, 571. MS (EI): m/z (%) = 422 (14) $[\text{M}]^+$, 254 (19), 253 (100) **[4e]**, 237 (13). HRMS (EI): calcd. m/z for $\text{C}_{23}\text{H}_{29}\text{F}_3\text{N}_2\text{O}_2$, 422.2181; found 422.2209. Lower fraction contained the minor isomer along with 20% of the major isomer (65.5 mg): R_f = 0.26. ^1H NMR (CDCl_3): δ = 1.63–1.84 (m, 2 H, $\text{CH}_2\text{CH}_2\text{O}$), 2.79 (s, 6 H, NMe_2), 2.80 (s, 6 H, NMe_2), 2.77–2.89 (m, 1 H), 3.51 (dq, $J_{\text{H,F}}$ = 8.7, $J_{\text{H,H}}$ = 11.9 Hz, 1 H, $\text{CH}_A\text{H}_B\text{CF}_3$), 3.79 (dq, $J_{\text{H,F}}$ = 9.0, $J_{\text{H,H}}$ = 11.9 Hz, 1 H, $\text{CH}_A\text{H}_B\text{CF}_3$), 3.80–3.88 (m, 3 H), 4.58 (d, J = 4.0 Hz, 1 H, CHAr_2), 6.56 (d, J = 8.8 Hz, 2 H, Ar), 6.58 (d, J = 8.8 Hz, 2 H, Ar), 7.09 (d, J = 8.8 Hz, 4 H, Ar) ppm. ^{13}C NMR (CDCl_3): δ = 28.7 ($\text{CH}_2\text{CH}_2\text{O}$), 41.1 (NMe_2), 41.2 (NMe_2), 49.3 and 50.4 (CHAr_2 and CHCHO_2), 64.3 (q, $J_{\text{C,F}}$ = 34.6 Hz, CH_2CF_3), 68.3 (CH_2O), 104.1 (CHO_2), 113.2 and 113.3 (2 CH_{Ar}), 124.5 (q, $J_{\text{C,F}}$ = 278.2 Hz, CF_3), 128.6 and 128.7 (2 CH_{Ar}), 133.2 and 133.6 (2 C_{Ar}), 149.39 and 149.44 (2 C_{Ar}) ppm.

Supporting Information (see also footnote on the first page of this article): Concentrations and rate constants of the individual kinetic runs.

Acknowledgments

This work was supported by INTAS (fellowship to A.D., project # 2003-55-1185) and by the Ministry of Science of the Russian Federation (project MK-2352.2003.03).

- [1] a) T. Mukaiyama, *Org. React.* **1982**, 28, 203–331; b) E. M. Carreira, in: *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto, Springer-Verlag: Heidelberg) **1999**, Vol. 3, pp. 997–1065; c) C. Chuit, R. J. P. Corriu, C. Reye, *J. Organomet. Chem.* **1988**, 358, 57–66; d) R. Mahrwald, *Chem. Rev.* **1999**, 99, 1095–1120.
- [2] a) D. A. Evans, K. A. Scheidt, J. N. Johnston, M. C. Willis, *J. Am. Chem. Soc.* **2001**, 123, 4480–4491; b) M. Miyashita, T. Yanami, T. Kumazawa, A. Yoshikoshi, *J. Am. Chem. Soc.* **1984**, 106, 2149–2156; c) M. Santelli, J.-M. Pons, *Lewis Acids and Selectivity in Organic Synthesis* CRC Press, Boca Raton, **1996**.
- [3] a) A. G. Wenzel, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, 124, 12964–12965; b) S.-I. Murahashi, Y. Imada, T. Kawakami, K. Harada, Y. Yonemushi, N. Tomita, *J. Am. Chem. Soc.* **2002**, 124, 2888–2889; c) M. Sugiura, S. Kobayashi, *Org. Lett.* **2001**, 3, 477–480; d) M. Arend, B. Westermann, N. Risch, *Angew. Chem.* **1998**, 110, 1096–1122; *Angew. Chem. Int. Ed.* **1998**, 37, 1044–1070.
- [4] J. Burfeindt, M. Patz, M. Müller, H. Mayr, *J. Am. Chem. Soc.* **1998**, 120, 3629–3634.
- [5] T. Tokuyasu, H. Mayr, *Eur. J. Org. Chem.* **2004**, 2791–2796.
- [6] Alkyl vinyl ethers and dialkoxyalkenes are prone to polymerization in the presence of electrophilic reagents, see: a) P. R. Johnson, H. M. Barnes, S. M. McElvain, *J. Am. Chem. Soc.* **1940**, 62, 964–972; b) J. V. Crivello, Y.-L. Lai, R. Malik, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, 34, 3103–3120; c) Z. Wu, L. Cao, C. U. Pittmann, Jr., *J. Polym. Sci., Part A: Polym. Chem.* **1998**, 36, 861–871; d) Z. Wu, C. U. Pittmann, Jr., *J. Polym. Sci., Part A: Polym. Chem.* **1998**, 36, 873–881.
- [7] a) A. D. Dilman, P. A. Belyakov, A. A. Korlyukov, V. A. Tartakovsky, *Tetrahedron Lett.* **2004**, 45, 3741–3744; b) V. V. Levin, A. D. Dilman, P. A. Belyakov, A. A. Korlyukov, M. I. Struchkova, V. A. Tartakovsky, *Eur. J. Org. Chem.* **2004**, 5141–5148.
- [8] a) H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, 36, 66–77; b) H. Mayr, M. Patz, *Angew. Chem.* **1994**, 106, 990–1010; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 938–957; c) H. Mayr, M. Patz, M. F. Gotta, A. R. Ofial, *Pure Appl. Chem.* **1998**, 70, 1993–2000.
- [9] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, 123, 9500–9512.
- [10] R. Schneider, H. Mayr, P. H. Plesch, *Ber. Bunsen-Ges. Phys. Chem.* **1987**, 91, 1369–1374.
- [11] H. Mayr, R. Schneider, C. Schade, J. Bartl, R. Bederke, *J. Am. Chem. Soc.* **1990**, 112, 4446–4454.
- [12] *p*-Amino-substituted benzhydrylium ions are stable in trifluoroethanol, see: S. Minegishi, S. Kobayashi, H. Mayr, *J. Am. Chem. Soc.* **2004**, 126, 5174–5181.
- [13] J. Bartl, S. Steenken, H. Mayr, *J. Am. Chem. Soc.* **1991**, 113, 7710–7716.
- [14] According to Taft's constants the pentafluorophenyl group ($\sigma^* = 1.50$) is a much stronger acceptor than phenyl ($\sigma^* = 0.60$) and lies between 3,5-dinitrophenyl ($\sigma^* = 1.37$) and difluoromethyl ($\sigma^* = 2.00$) groups, see: T. Korenaga, K. Kadowaki, T. Ema, T. Sakai, *J. Org. Chem.* **2004**, 69, 7340–7343.
- [15] Jpn. Kokai Tokkyo Koho, 1983, JP 58162585 (*Chem. Abstr.* **1984**, 100:68153r). For **1b** neither procedure nor spectroscopic data were reported.
- [16] a) M. Penso, D. Albanese, D. Landini, V. Lupi, *J. Mol. Cat. A: Chem.* **2003**, 204–205, 177–185; b) D. Albanese, D. Landini, M. Penso, S. Petricci, *Synlett* **1999**, 199–200.
- [17] C. Jia, W. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie, Y. Fujiwara, *J. Am. Chem. Soc.* **2000**, 122, 7252–7263.

Received: October 7, 2004