JOC Article

Thermodynamic Stability and Reactivity of Silylated Bis(oxy)iminium Ions

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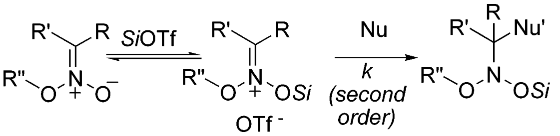

Silylation of various nitronates with trialkylsilyl triflates was investigated by applying NMR techniques. In several cases, a flexible nitronate−bis(oxy)iminium ion (as an ion pair with triflate as counterion) equlibrium was found, and its thermodynamic parameters were determined. Elevation of temperature or dilution shifts this equilibrium toward the reactants. Activation parameters for the C,C-coupling reaction of silylated bis(oxy)iminium ions with a series of reference nucleophiles were determined. Estimated electrophilicity of bis(oxy)iminium ions allows one to count on C,C-coupling when partner nucleophilicity is $N > 4$.

Introduction

Nitroalkanes **1** are important substrates in organic synthesis.[1] While most synthetic applications proceed via nitronate anions **2** generated by deprotonation of nitroalkanes **1** with various bases, we have previously shown[2] that it is possible to convert nitroalkanes into siloxyiminium ions **4**, which are able to react with a variety of nucleophiles and thus can be considered as "umpoled" nitronate anions (Scheme 1).[3]

In order to define the scope and limitations of C,C-coupling of the silyl bis(oxy)iminium ions **4** with nucleophiles, we have investigated the intermediates **4** by NMR (^{1}H, ^{13}C, and ^{29}Si). Now we will report on the study of equilibria **3** $\leftrightarrows$ **4** as well as on the kinetics of the reaction of cations **4** with electron-rich π-systems.

Results and Discussion

Structural Characterization of the Siloxyiminium Ions 4. Procedure. Silylated bis(oxy)iminium triflates **4** were obtained by addition of ca. 2 equiv of the trialkylsilyltriflates **5a** (Si = SiMe$_2$^{t}Bu) or **5b** (Si = SiMe$_3$) to CD$_2$Cl$_2$ solutions of nitronates **3** in a NMR tube at approximately −70 °C using CH$_2$Br$_2$ as internal standard. In order to avoid protonation of **3** by traces of humidity, all reactions were performed under an inert atmosphere in the presence of 2,6-di-*tert*-butyl-4-methylpyridine as a proton trap.

The characteristic signals (NMR) of cations **4** are listed in Table 1. Corresponding signals of initial nitronates **3** are shown for comparison.

The data show that silylation of **3** causes a downfield shift of the α-C-atom's signal (C-3) by about 30 ppm. A downfield shift of 1.5−2.0 ppm is observed for the signal H-C$_\alpha$ (3-H).

The signals of H-C$_\beta$ (4-H) show a smaller downfield shift. All cations **4** have a signal in their ^{29}Si NMR spectra near 50 ppm. It distinctly differs from the signal of the initial silyl triflate near 45 ppm.[4] (For more details of the configuration of cations **4** as well as their conformational analysis, see the Supporting Information.)

Nitronates **3a**−**g** showed only a single set of NMR signals, and their configuration was derived from the $^3J_{\text{H,H}}$ coupling

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(1) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: New York, 2001.

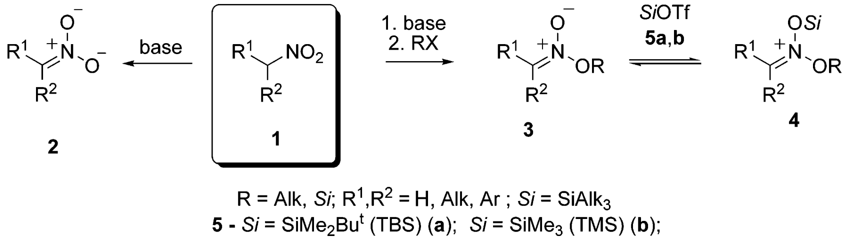
(2) Smirnov, V. O.; Ioffe, S. L.; Tishkov, A. A.; Khomutova, Yu. A.; Nesterov, I. D.; Antipin, M. Yu.; Smit, W. A.; Tartakovsky, V. A. *J. Org. Chem.* **2004**, *69*, 8485−8488.

(3) *N,N*-Bis(hydroxy)iminium ions are discussed as evident intermediates of the Nef reaction (see ref 1 and: Kornblum, N.; Brown, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 1742−1747). For activity of these cations in C,C-coupling reactions, see: Prakash, S.; Schleyer, P. v. R. *Stable Carbocation Chemistry*; John Wiley & Sons: New York, 1997; pp 525−539 and references therein. However, the procedures cited in these papers are very harsh for use in directed organic synthesis.

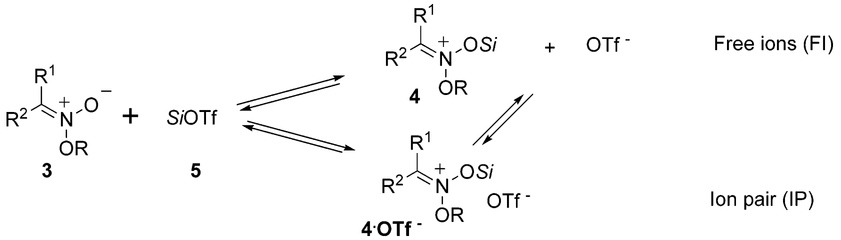
(4) Similar NMR spectra were fixed recently for cations generated by silylation of some nitrones (Chalaye-Mauger, H.; Denis, J.-N.; Averbuch-Pouchot, M.-T.; Vallee, Y. *Tetrahedron* **2000**, *56*, 791−804).

10.1021/jo070633x CCC: $37.00

SCHEME 1. New Reactivity of Aliphatic Nitro Compounds



SCHEME 2



constants[5] and in some cases from NOE experiments. The barriers of ring inversion (I_R) for six-membered cyclic nitronates can be assumed to be around 20−25 kJ/mol.[6] Because such processes are rapid for the NMR time scale, we can observe only averaged conformations of **3a**−**g**. The values of vicinal $^3J_{H,H}$ for protons attached to C-4 and C-6 atoms allow to determine orientation of the substituents on these atoms in nitronates **3a**−**g**[7] (the dominant conformations of **3a**−**g** derived by this analysis are depicted in the Supporting Information).

It should be noted that in general the cations **4a**,**b**,**d**−**g** and corresponding nitronates **3a**,**b**,**d**−**g** adopt analogous conformations (see Table 1 and the Supporting Information). The cation **4c** is an exception: one can observe for this cation two conformers (**4c*a*** and **4c*b***, ratio ≈ 1.5:1) with slow interconversion at −80 to −40 °C.[8] We do not detect line broadening of the NMR signals of these conformers at −40 °C. The low stability of intermediate **4c** does not allow to perform NMR experiments at elevated temperatures in order to determine the barrier for interconvertion of the conformers. The calculation of the I_R barrier for hypothetic model cation **4**, derived from an unsubstituted six-membered cyclic nitronate and containing *SiH$_3$* fragment,[6] does not show an increase of I_R barrier in the comparison to that of the initial nitronate **3** (without taking into account effects of solvent).[9]

Silylation of Nitronates 3 as an Equilibrium Process. Silylation of nitronates **3** with the silyl triflates **5** may either produce free cation **4** and anion TfO$^-$ or the ion pairs **4·TfO$^-$** (Scheme 2).

Since free (**4** + **OTf$^-$**) and paired (**4·OTf$^-$**) iminium triflates cannot be differentiated by their NMR spectra, the degree of ion-pairing was derived from the concentration dependence of the equilibria. The expression of equilibrium constant K_{FI} for formation of the free ions **4** and **OTf$^-$** (eq 1) and the equilibrium constant K_{IP} for formation of the ion pairs **4·OTf$^-$** (eq 2) can be summarized by eq 3, which is transformed into eq 4

$$K_{FI} = [\mathbf{4}][\mathbf{OTf^-}]/([\mathbf{3}][\mathbf{5}]) = [\mathbf{4}]^2/([\mathbf{3}][\mathbf{5}]) \qquad (1)$$

$$K_{IP} = [\mathbf{4{\cdot}OTf^-}]/([\mathbf{3}][\mathbf{5}]) \qquad (2)$$

$$K = [4]^n/([\mathbf{3}][\mathbf{5}]) \qquad (3)$$

$$\log K = n{\cdot}\log[4] - \log([\mathbf{3}]{\cdot}[\mathbf{5}]) \qquad (4)$$

where [*4*] is the concentration of actually observed cationic species (**4** or/and **4·OTf** $^-$). Plot of log([**3**]·[**5**]) versus log[*4*] should give a straight line with slope n and an intercept log ***K***.

For the determination of the equilibrium constants **3** ⇆ ***4*** comparable amounts of nitronate **3** and ***4*** should be observable. In most cases this equilibrium is completely shifted to the right, however, Figure 1 shows an example where the conversion of **3f** to **4f** is incomplete and thus renders the determination of the equlibrium constant.

One can see that the ratio [**4f**]/[**3f**] decreases with increasing dilution. From the slope of 0.96 (Figure 2) one can derive $n = 1$ (eqs 3 and 4) indicating that the silylation of **3f** leads to the exclusive formation of the ion pair[10] **4f·OTf** $^-$ while the concentration of free ions **4f** is negligible under these conditions.

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[5] See Karplus curves for cyclohexanes (Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*; Thieme: Stuttgart, 1995; p 108) and N-containing heterocycles (Lambert, J. B.; Takeuchi, Y., *Cyclic Organonitrogen Stereodynamics*; VCH: New York, 1992; p 170).

[6] Birukov, A. A. Unpublished quantium calculations of I_R for model six-membered cyclic nitronate. See also the data for the I_R barrier of cyclohexene: Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University Press: Oxford, 2001; p 471.

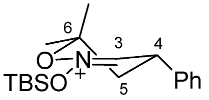
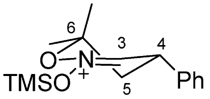
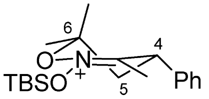
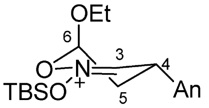
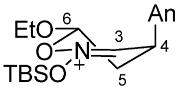
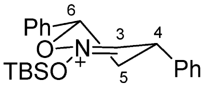
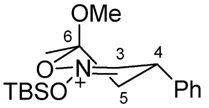
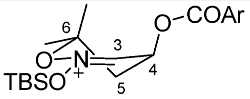
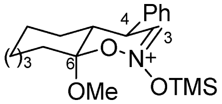
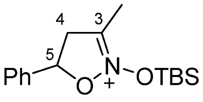
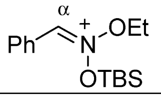
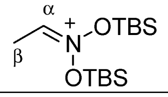
[7] The half-chair conformation of six-membered nitronates in the solid state was established according to X-ray data. (For example, see: Tishkov, A. A.; Lesiv, A. V.; Khomutova, Yu. A.; Strelenko, Yu. A.; Nesterov, I. D.; Antipin, M. Yu.; Ioffe, S. L.; Denmark, S. E. *J. Org. Chem.* **2003**, *68*, 9477−9480). The same conclusion on dominant conformation of cyclic nitronates could be made according to the NMR spectra of their solution.

[8] NOESY technique was applied to confirm that observed species are conformers of cation **4c** and the epimerization at C(6) does not occur. Additive evidence on absence of epimerization is that *cis*-isomer of **4c** in course of C,C-coupling with **6h** give rise to product of other configuration than *trans*-isomer **4c**.[2]

[9] For possible explanation of this fenomena see below.

[10] Within this discussion, we can't distinguish tight ion pair and loose ion pair.

TABLE 1. Characteristic NMR Data for Cations 4 and Initial Nitronates 3 (CD_2Cl_2, 300 MHz, 200 K)

entry	*cation*	*Configuration and conformation of* **4**	*^{1}HNMR, ppm (J (Hz) in parentheses)*		*^{13}CNMR, ppm*		*^{29}Si, ppm*
			initial nitronate	*cation*	*initial nitronate*	*cation*	
1	**4a**		**3a** *3*: **6.36** (d, 2.5); *4*: **3.80** (ddd, 11.0, 7.3, 2.8);	*3:* **8.09** (br s); *4:* **4.59** (dd, 11.5, 7.2);	*3:* **113.5**; *i-Ph:* **139.6**; *6:* **82.4**;	*3:* **141.4** ($^1J_{CH}$ = 198.8 Hz); *i-Ph:* **133.9**; *6:* **93.4**;	50.1
2	**4a′**			*3:* **8.08** (d, 1.8); *4:* **4.55** (ddd, 11.0, 7.2, 1.8);		*3:* **141.5**; *i-Ph:* **134.4**; *6:* **93.9**;	49.9
3	**4b**		**3b** *4:* **3.69** (dd, 10.6, 8.0, 1.3);	*4:* **4.58** (dd, 10.5, 7.5);	*3:* **123.7**; *i-Ph:* **139.9**; *6:* **82.0**;	*3:* **154.2**; *i-Ph:* **135.5**; *6:* **92.0**;	50.2
4	**4c** [a,b]	**4c**[a] 	**3c** *3:* **6.31** (d, 2.0); *6:* **5.38** (br s); *4:* **3.93** (ddd, 11.9, 6.6, 2.0);	*3:* **8.24** (br s); *6:* **6.02** (br s), *4:* **4.44** (dd, 11.3, 6.0);	*3:* **116.6**; *i-An:* **131.2**; *6:* **102.1**;	*3:* **144.7**; *i-An:* **129.9**; *6:* **109.8**;	50.3
		4c[b] 		*3:* **8.02** (br s); *6:* **6.10** (d, 6.6); *4:* **4.68** (t, 6.5);		*3:* **144.6**;	49.3
5	**4d**		**3d** *3:* **6.66** (d, 4.5); *6:* **5.81** (d, 11.5); *4:* **4.16** (dd, 6.6, 4.5);	*3:* **8.00** (br s), 6: **6.12** (d, 11.3); 4: **4.96** (t, 9.5);	*3:* **113.2**; *6:* **81.9**;	*3:* **142.2** ($^1J_{CH}$ = 204.2 Hz); *6:* **89.1**;	50.2
6	**4e** [c]		**3e** *3:* **6.37** (br s); *4:* **3.96** (dd, 12.0, 7.3);	*3:* **8.28** (br s); *4:* **4.50** (dd, 11.9, 7.3);	*3:* **114.3**; *i-Ph:* **139.3**; *6:* **104.4**;	*3:* **143.9**; *i-Ph:* **133.1**; *6:* **115.7**;	49.7
7	**4f** [c,d]		**3f** *3:* **6.65** (d, 2.0); *4:* **5.81** (ddd, 6.6, 4.4, 2.3);	*3:* **8.48** (br s); *4:* **6.18** (dd, 7.3, 3.2);	*3:* **108.1**; *6:* **82.3**;	*3:* **136.3** *6:* **94.0**;	52.5
8	**4g′** [c]		**3g** *3:* **6.21** (d, 2.5); *4:* **3.44** (dd, 10.6, 2.3);	*3:* **8.13** (d, 2.3); *4:* **3.97** (dd, 11.5, 2.3);	*3:* **115.1**; *i-Ph:* **138.6**; *6:* **108.9**;	3: **143.2**; *i-Ph:* **132.8**; *6:* **122.0**;	49.7
9	**4h** [c]		**3h** *4:* **3.45** (dd, 16.2, 8.3); *4’:* **3.02** (dd, 16.2, 8.3); *5:* **5.51** (t, 8.9);	*4:* **4.10** (dd, 19.2, 10.0); *4’:* **3.70** (dd, 19.2, 11.9); *5:* **6.20** (t, 10.6);	*3:* **114.0**; *i-Ph:* **139.2**; *5:* **76.2**;	*3:* **150.5**; *i-Ph:* **133.9**; *5:* **85.2**;	53.0
10	**4i** [c]		**3i** *α:* **7.15** (s);	*α:* **9.40** (s);	*α:* **117.2**; *i-Ph:* **131.0**;	*α:* **138.5**; *i-Ph:* **134.8**;	51.3
11	**4j** [c]		**3j** *α:* **6.18** (q, 7.2); *β:* **1.75** (d, 7.3);	*α:* **8.60** (q, 7.2); *β:* **2.68** (d, 7.3);	*α:* **114.0**; *β:* **12.5**;	*α:* **155.2**; *β:* **17.9**;	50.2, 50.5

[a] **4c**^{a}:**4c**^{b} = 1.5:1, An = *p*-C_6H_4OMe. [b] 215 K. [c] 210 K. [d] Ar = *p*-$C_6H_4NO_2$.

The degree of ionization, i.e., the ratio [**4f**]/[**3f**] decreases as the temperature is increased (Figure 1). The Gibbs plot in Figure 3 indicates that the reaction of **3f** with silyl triflate **5a** is exothermic but has a highly negative reaction entropy, in agreement with observations for other ionization processes. Compensation for the enthalpic and entropic terms occurs at T = 195 K, where K = 1. Similar observations have been made for the reactions of silyl triflate **5a** with some other nitronates **3** (Table 2).

One could draw the conclusion from the thermodynamic parameters of equilibrium nitronate ⇆ iminium ion that the decrease of concentration of reagents and the increase of

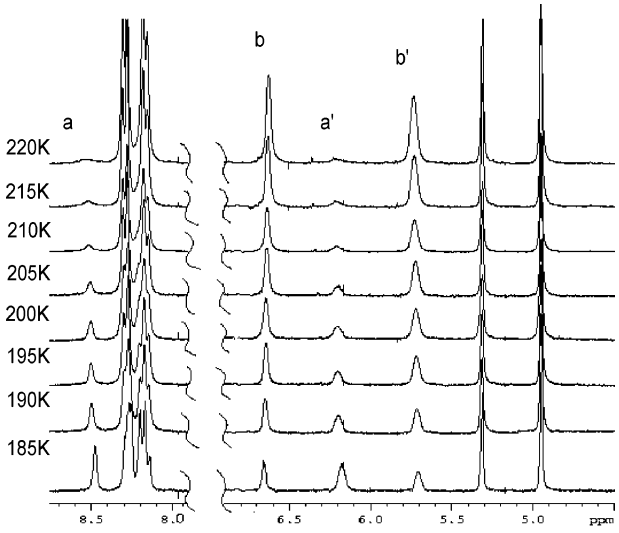


FIGURE 1. Proton NMR spectra of equilibrating system **3f** + **5a** ⇆ **4f·OTf**$^-$ at various temperatures (CD_2Cl_2, 300 MHz). Peaks of cation **4f** marked as "a" (H-3) and "a′" (H-4), peaks of starting nitronate **3f** marked as "b" (H-3) and "b′" (H-4) (see the Supporting Information, pp 52−53).

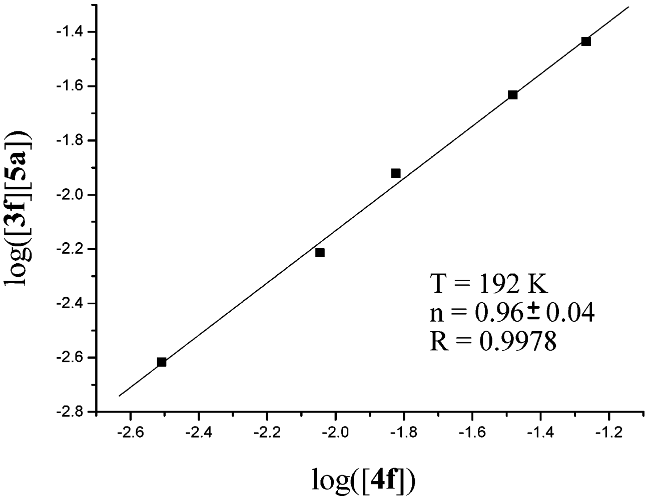


FIGURE 2. Plot of log([**3f**]·[**5a**]) vs log[**4f**] for the equilibrating system **3f** + **5a** ⇆ **4f·OTf**$^-$ at 192 K (see the Supporting Information, pp 52−53).

temperature move substantially the above-mentioned equilibrium toward the initial nitronates.

Taking into account typical concentrations of NMR samples and achievable temperature range, the NMR method can be considered to be the most effective for direct registration of these cationic intermediates.

The existence of cations **4** as ionic pairs could explain the unexpectedly high barrier for I_R processes for these intermediates (cf. $\mathbf{4c}^a \leftrightarrows \mathbf{4c}^b$), because the dissociation of ionic pairs can be crucial for realization of ring inversion.

Kinetic Measurements. In order to define the synthetic potential of the silylated bisoxyiminium ions **4** in C,C-coupling reactions, we tried to determine their electrophilicity parameter *E* according to eq 5 where *s* and *N* are nucleophile-specific parameters.[11]

$$\log(k_{20\,°\mathrm{C}}) = s(N + E) \tag{5}$$

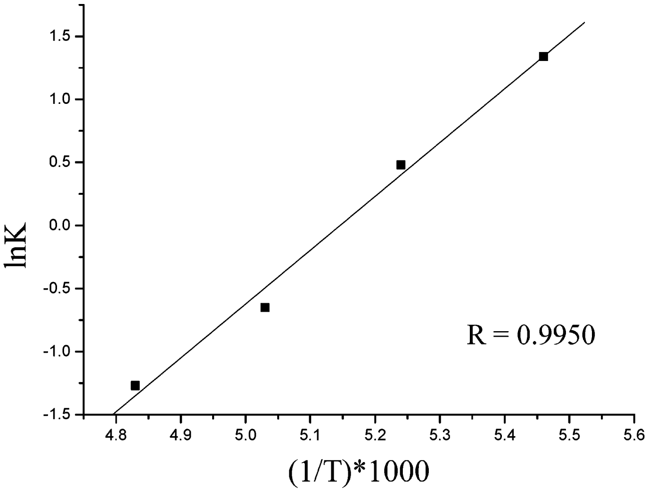


FIGURE 3. Gibbs plot for the equilibrating system **3f** + **5a** ⇆ **4f·OTf**$^-$ (see the Supporting Information, pp 52−53).

For this purpose, we measured the kinetics of the reactions of a few cations **4** with some π-nucleophiles which have been defined as reference compounds in ref 12.[12]

The rates of the reactions of cations **4a**,**b** with nucleophiles were monitored by ^{1}H NMR spectroscopy. For this purpose, the nitronates **3a**,**b** were quantitatively converted into the iminium triflates **(4a,b)·OTf**$^-$ in CD_2Cl_2 by treatment with the silyl triflates **5a**,**b** as described above. These solutions were thermostated in an NMR magnet, and 1.5−2.0 equiv of the neat nucleophiles **6a**−**g** were added. Figure 4 depicts the decrease of the cation **4a** and of the nucleophile **6a** as well as the increase of the product **7a** as the reaction **4a** + **6a** proceeds.

Analogous spectral changes were observed when **(4a,b)·OTf**$^-$ was combined with other reference nucleophiles **6**. Typically, 15 min to 4 h were required to achieve 85% conversion of cationic intermediates **4**. In several cases, it was demonstrated that the rate of the formation of product **7** was identical to the rate of the disappearance of the minor reactant **4** (Scheme 3).

The concentrations of cations **4** could always be precisely derived from their 3-H or 4-H resonances relative to internal standard. The evaluation of the kinetics was generally based on the consumption of **4**, employing the second-order rate law in integrated form (eq 6). This equation could be transformed into eq 7, in which $[\mathbf{4}]_t$ is the only time-dependent variable parameter.

$$\frac{[\mathbf{6}]_t}{[\mathbf{4}]_t} = \frac{[\mathbf{6}]_0}{[\mathbf{4}]_0}\, e^{([\mathbf{6}]_t - [\mathbf{4}]_t)kt} \tag{6}$$

$$ktd = \ln([\mathbf{4}]_t + d) - \ln([\mathbf{4}]_t) - \ln([\mathbf{4}]_0 + d) + \ln([\mathbf{4}]_0) \tag{7}$$

where $[\mathbf{4}]_0$ and $[\mathbf{4}]_\mathrm{t}$ refer to initial and current concentrations of **4**, respectively, and $d = [\mathbf{6}]_t - [\mathbf{4}]_t$ (or $[\mathbf{6}]_0 - [\mathbf{4}]_0$).

The linear correlation between $\ln[([\mathbf{4a}]_t + d)/[\mathbf{4a}]_t]$ and t (Figure 5) shows that second-order kinetics are followed as described by eq 7. (Analogous plots for other C,C-coupling reactions are shown in the Supporting Information.)

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[11] Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66−77.

[12] Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512.

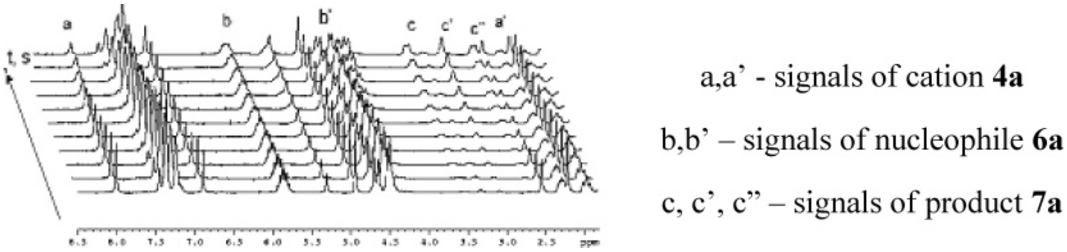
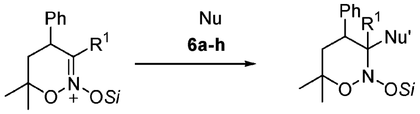


FIGURE 4. Time-dependent proton NMR spectra during the C,C-coupling reaction **4a** + **6a** → **7a** (CD_2Cl_2, 200 K, 300 MHz) (see the Supporting Information, pp 17−20).

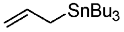
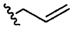
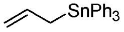
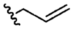
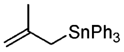
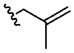
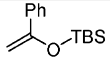
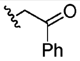
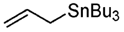
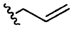
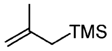
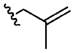
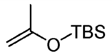
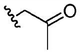
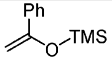
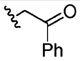
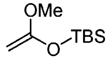
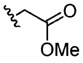
TABLE 2. Thermodynamic Parameters for the Equilibriums 3 + 5a ⇆ 4·OTf⁻

equilibruim	*n* (averaged)	range of *T*, K	ΔG^0_{293}, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/mol·K
3f ⇆ **4f**	0.98 ± 0.05	183 ÷ 207	18.0 ± 1.1	−35.5 ± 0.4	−182.7 ± 2.4
3h ⇆ **4h**	1.04 ± 0.08	190 ÷ 220	1.7 ± 3.3	−29.0 ± 1.3	−104.8 ± 6.7
3i ⇆ **4i**	1.04 ± 0.06	180 ÷ 210	12.2 ± 2.3	−26.4 ± 0.9	−131.7 ± 4.8
3j ⇆ **4j**	0.84 ± 0.05	210 ÷ 240	9.3 ± 2.3	−59.5 ± 1.0	−234.9 ± 4.3

SCHEME 3



4a-b **7a-h**

Cation	R^1	*Si*	Nu	Nu'	Product
4a	H	TBS	 **6a**		**7a**
4a	H	TBS	 **6e**		**7a**
4a	H	TBS	 **6f**		**7c**
4a	H	TBS	 **6g**		**7d**
4a′	H	TMS	 **6a**		**7e**
4a′	H	TMS	 **6b**		**7f**
4a′	H	TMS	 **6c**		**7b**
4a′	H	TMS	 **6d**		**7g**
4b	Me	TBS	 **6h**		**7h**

According to proton NMR spectra (Figure 4), the reaction **4a** and **6a** proceeds without the formation of any side products. Analogously, other reactions **4** and **6** proceed with high selectivity and efficiency.

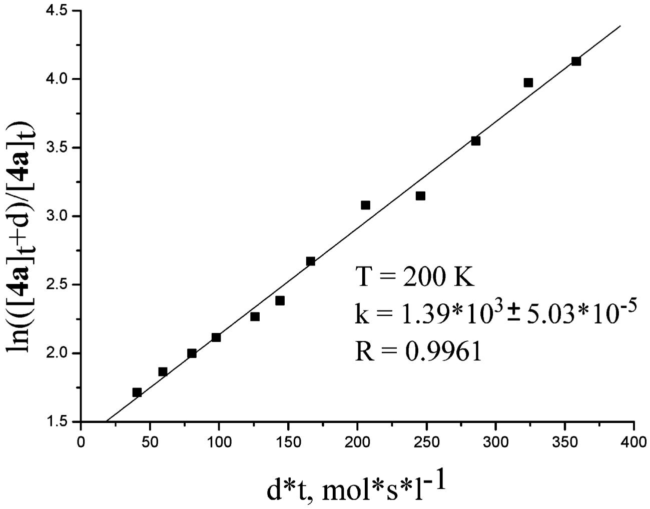


FIGURE 5. Plot of ln{([**4a**]$_t$ + d)/[**4a**]$_t$} vs *dt* (eq 7) for **4a** + **6a** C,C-coupling reaction according to second-order kinetics **(**see the Supporting Information, pp 17−20**)**.

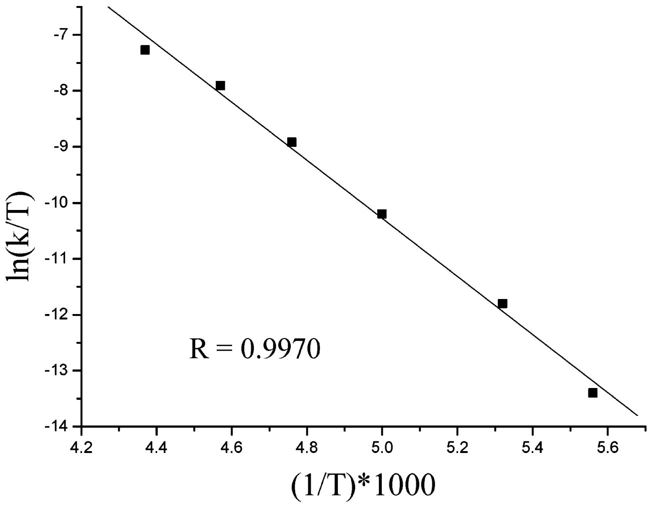


FIGURE 6. Eyring plot for the reaction of **4a** with **6a** **(**see the Supporting Information, pp 17−20**)**.

Because of the decomposition of the cations **4** at elevated temperature, the kinetics could only be determined in the range from −90 to −40 °C. From Eyring plots of ln(*k*/*T*) vs 1/*T* (see Figure 6 and Supporting Information), one can derive the activation parameters listed in Table 3. It is found that $\Delta S^{\ddagger}$ has a large negative value as previously reported for other reactions of cationic electrophiles with neutral π-systems.[12]

Discussion

While the reaction of **4a** with **6g** and **4a′** with **6d** has been studied at variable temperature (Table 3), the reaction of **4a** with **6d** was only investigated at −50 °C. The first two entries of Table 4 show that the variation of the silyl group in the enol ether derived from acetophenone does not affect the kinetics. Therefore, one can conclude that the desilylation of cationic intermediate **A** is not the rate-determining step in the reaction cascade **4** + **6** (Scheme 4).

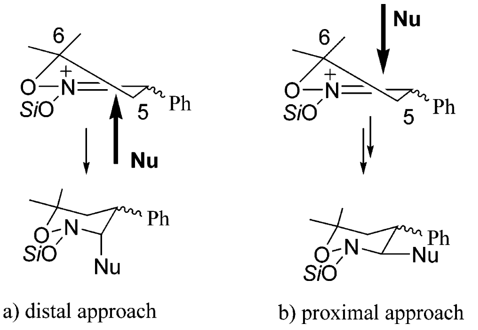
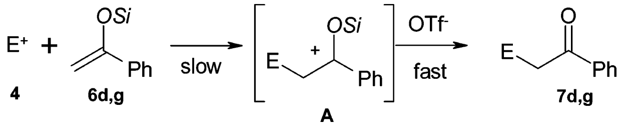


FIGURE 7. Two possible approaches of C-nucleophile **Nu** to dominant conformer of iminium ion **4**.

SCHEME 4



Entries 2 and 3 of Table 4 indicate that nature of the silyl group also does not affect the electrophilicity of the silyl bis(oxy)iminium ions, which allows us to directly compare the rate constants obtained for reactions with **4a** and **4a′**.

The *E* parameters derived for cations **4a,a′** from reactions with different nucleophiles vary by 2.5 units showing that eq 5 does not precisely describe these reactions. However with $E \approx -4$ to -6 one can conclude that, at lowered temperatures, reactions with nucleophiles which have $N > 4$ could be realized.

One could underline also that the selectivity of cation **4a** toward π-systems with triorganostannyl leaving group is rather close to that of benzhydrilium ions, while in the reactions of cation **4a** with silyl-capped π-systems almost no selectivity toward nucleophiles was found.

The analysis of previous results[2] and stereochemical outcome of C,C-coupling products **7** show that the distal approach of the nucleophile (relative to C(6) of cation **4**) is strongly preferable (see Figure 7). It is remarkable that an analogous approach of the dipolarophile was strongly preferable in [3 + 2]-cycloaddition reactions with six-membered cyclic nitronates.[13] Probably, this is connected with the peculiar structure of the cations **4**. Namely, C(6) atom in cations (as well as in the initial nitronates) is more withdrawn from O−N−C(3)−C(4) plane than C(5) on the opposite side.[6,7,14] Correspondingly, the proximal (to C(6)) approach is hampered in comparison to the alternative.

We observed the only example of stereoselectivity violation in C,C-coupling reactions when single conformer of cation **4** was detected. Despite the presence of only one dominant conformation of cation **4a′** (see Table 1, entry 2), its C,C-coupling with $CH_2{=}CMe(OTBS)$ (under the kinetic measurement conditions) gave product contaminated with a slight amount of the alternative diastereomer (for −70 °C dr ≈1:9, for −40 °C dr ≈ 1:4; see the Supporting Information for details).

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(13) Denmark, S. E.; Seierstad, M.; Herbert, B. *J. Org. Chem.* **1999**, *64*, 884−901.

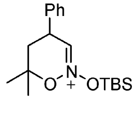
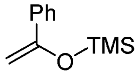
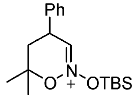
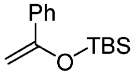
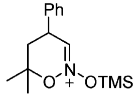
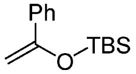
(14) Nesterov, I. D.; Lesiv, A. V.; Ioffe, S. L.; Antipin, M. Yu. *Mendeleev Commun.* **2004**, 281−282.

TABLE 3. Rate Constants and Activation Parameters for the Reactions of 4 with 6

cat. **4**	nucleophile	product	ref *N* and (*s*) parameters[12]	*E*	k$_2$ (20 °C), L•mol^{-1}•s^{-1}	Δ$G^{\ddagger}_{20°C}$, kJ/mol	Δ$H^{\ddagger}$, kJ/mol	Δ$S^{\ddagger}$, J/mol•K
4a	**6a**	**7a**	5.46 (0.89)	−3.69	37.7	62.9 ± 3.7	42.9 ± 1.5	−68.1 ± 7.4
	6e	**7a**	3.09 (0.90)	−3.37	0.55	73.2 ± 4.0	49.5 ± 1.8	−80.7 ± 7.8
	6f	**7c**	5.13 (0.90)[a]	−4.21	6.55	67.1 ± 4.4	45.2 ± 1.9	−74.9 ± 8.6
	6g	**7d**	6.22 (0.96)	−6.08	1.37	70.9 ± 1.7	51.1 ± 0.7	−67.6 ± 3.3
4a′	**6a**	**7e**	5.46 (0.89)	−3.70	36.6	63.0 ± 3.6	41.7 ± 1.5	−72.4 ± 7.2
	6b	**7f**	4.41 (0.96)	−4.54	0.74	72.4 ± 2.3	39.2 ± 1.0	−113.6 ± 4.4
	6c	**7b**	5.41 (0.91)	−5.45	0.92	71.9 ± 2.3	43.9 ± 1.0	−95.6 ± 4.3
	6d	**7g**	6.22 (0.96)	−5.99	1.65	70.5 ± 1.7	51.7 ± 0.7	−64.1 ± 3.1
4b	**6h**	**7h**	10.32 (0.79)	−10.21	1.23	71.2 ± 1.1	31.4 ± 0.5	−135.9 ± 2.3

[a] *s* value for **6f** was estimated the same as for **6a** and **6e** in ref 12.

TABLE 4. Dependence of k_2 Value at −50 °C on the Nature of the Silyl Group in Cation 4 and Nucleophile 6

entry	Cation (E+)	Nucleophile (Nu)	k$_2$ (-50^{0}C), l·mol^{-1}·s^{-1}
1	 **4a**	 **6d**	1.38•10^{-3} ± 2.9•10^{-5}
2	 **4a**	 **6g**	1.40•10^{-3} ± 4.0•10^{-4}
3	 **4a'**	 **6g**	1.41•10^{-3} ± 4.0•10^{-5}

Conclusion

The interaction of iminium ions derived from cyclic six-membered nitronates toward neutral C-centered π-nucleophiles was investigated. NMR was considered to be method of choice for such studies. It was found, that the reactivity of these cations cannot be precisely described by Mayr's equation. In several cases, ion pairing of this type of iminium ion (with a triflate as a counterion) was detected by the concentration dependence of the equilibria with corresponding starting nitronate.

Experimental Section

General Procedure for the Generation of Siloxyiminium Ions 4. A standard sample of neat methanol was used for precise control of the probe temperature. The temperature was measured in the beginning and at the end of each experiment. Starting nitronate **3** (3.0−20.0 mg, 0.03−0.15 mmol) and 2,6-di(*tert*-butyl)-4-methylpyridine (0.5 equiv, 3.0−15.0 mg) were placed into a 5 mm NMR tube which was evacuated and filled with dry argon. Under inert atmosphere, 0.50 mL of CD_2Cl_2 was added, the tube was stoppered with a rubber septum, and 2.0 μL of internal standard (CH_2Br_2) was injected by means of a microsyringe. Then the sample was put into the precooled magnet (T = 200 K). Control spectra (^{1}H, ^{13}C) of initial nitronate **3** were recorded at the temperature of experiment.

After registering the control spectra, the cold sample was taken out from the magnet, and 2 equiv (13−30 μL) of silylation agent (**5a** or **5b**) was quickly injected by means of a microsyringe. The sample was shaken twice and immediately put into the magnet. Then, spectra (^{1}H, ^{13}C, ^{29}Si) of the resulted mixture were registered. The overheating of sample during these manipulations is negligible. It is evident from the spectral picture, that, in most cases, the starting nitronate **3** was fully converted into the siloxyiminium ion **4**. However, for nitronates **3f**,**h**−**j**, there is an temperature-dependent equilibrium **3** + **5** ⇆ **4**.

General Procedure for Kinetic Measurements. The starting siloxyiminium ions **4a-b** were generated as described above. After the registration of cation spectra, the sample was taken out of the magnet, the precise quantity in 0.5−1.0 excess of neat nucleophile **6** (10−20 μL) was injected with a microsyringe, the tube was shaken twice and immediately returned into the magnet. Solid nucleophiles (**6e**,**f**) were placed into the NMR tube after the nitronate and dissolved in CD_2Cl_2 simultaneously during preparation of the NMR sample; the reaction began after addition of silyl triflate **5a**.

Concentrations of cations **4** and nucleophile **6** were measured by the integration of corresponding signals in the proton spectra of that sample and comparison with the integrate intensity of the signal of standard (CH_2Br_2). Precise concentration of standard was determined before addition of silyl triflate **5** by comparison of its signal intensity with signals intensities of nitronates, which were precisely weighted in the course of sample preparation. Kinetic measurements of the C,C-coupling reaction were proceeded until 85% conversion of cation **4** into product **7** was achieved (from 15 min to 4 h), and 12−24 spectra were thus registered. The temperature was calibrated before and after of each experiment with standard sample of neat methanol. The data taken after the second minute of reaction were used for linear correlations. Amounts of reactants for generation of cations **4** and kinetic measurements are specified in the Supporting Information.

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Supporting Information Available: Full experimental procedures for generation of cations **4**, their NMR data, data on equilibrium studies, kinetic data (concentrations and rate constants of the individual kinetic runs), and preparation procedures and characterization for new compounds **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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