Electrophilic Reactivity of a 2-Azaallenium and of a 2-Azaallylium Ion

Guido M. Böttger,[a] Roland Fröhlich,[a] and Ernst-Ulrich Würthwein*[a]

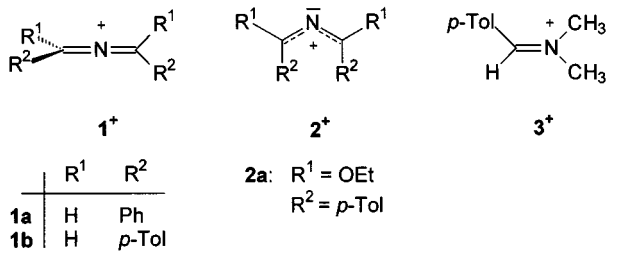
Dedicated to Professor Paul v. R. Schleyer on the occasion of his 70th birthday

Keywords: 2-Azaallenium ion / 2-Azaallylium ion / Iminium ion / Kinetics / Linear Free Energy Relationships / Ab initio calculations

The rate constants for the reactions of the 2-azaallenium ion **1b**$^+$, the 2-azaallylium ion **2a**$^+$ and the iminium ion **3**$^+$ with different nucleophiles were determined by ^{1}H NMR spectroscopy. By correlation with the Linear Free Enthalpy Relationship (LFER) lg $k_{20°C} = s\,(E + N)$, developed by Mayr and Patz, the electrophilicity parameters E(**1b**$^+$) = –3.7, E(**2a**$^+$) ≈ –16 and E(**3**$^+$) = –10.43 were obtained. They show that the relative reactivities of these ions are approximately 10^{12}:1:10^6. Quantum chemical calculations (ab initio, *DFT*) of the methyl anion affinities for the ions **1b**$^+$, **2a**$^+$ and **3**$^+$ are in agreement with the experimental E values. The X-ray structure of **3**$^+$·$CF_3SO_3^-$ is reported for the first time; it shows no strong interaction between the cation and the anion.

Introduction

2-Azapropenylium ions may exist in two valence isomeric forms: as linear orthogonal 2-azaallenium ions **1**$^+$ or as bent-planar 2-azaallylium ions **2**$^+$ (Scheme 1). The actual structure of the respective ion depends on the substitution pattern.[3] Electron donor groups favor the structural type **2**$^+$, whereas geometry **1**$^+$ is found if aliphatic and aromatic groups are present. 2-Azaallenium ions **1**$^+$, positively charged aza analogues of allenes, show considerable electrophilic reactivity towards nucleophiles.[4] Thus, high reactivity in aminoalkylation reactions was observed, especially in comparison to other nitrogen containing electrophiles, e.g. iminium salts. On the other hand, 2-azaallylium ions **2**$^+$ have found interest in synthetically useful C–C bond formations, in spite of their much lower reactivity.[5] Recently, the reactivity of the 1,3-diphenyl-2-azaallenium ion **1a**$^+$, which was generated by protonation of a transient nitrile ylide, towards water, methanol and several aqueous solutions of anionic nucleophiles was studied.[6]



Scheme 1. Molecular structures of cations **1**$^+$–**3**$^+$

However, until now, no comparative kinetic information is available for the two closely related 2-azaallenium- and 2-azaallylium ions **1**$^+$ and **2**$^+$. This would provide a more quantitative characterization of their electrophilic reactivities as a consequence of their electronic structure and would allow a comparison with other nitrogen-containing electrophiles.

Mayr and Patz have shown that the Linear Free Enthalpy Relationship (LFER) lg$k_{20°C} = s\,(E + N)$ holds for a large number of electrophile-nucleophile reactions.[7] From this relationship, it is possible to compare electrophiles of very different electrophilicity on a common reactivity scale. Fortunately, the rate constants for the reactions of classical iminium ions with several nucleophiles have recently been determined by Mayr and Ofial.[8] They used several carbon nucleophiles and hydride transfer reagents with known nucleophilicity parameters N and s to obtain the appropriate electrophilicity parameters E for three different Mannich reagents and for the Vilsmeier–Haack ion. These data provide a welcome basis for the classification of the ions **1**$^+$ and **2**$^+$ relative to other nitrogen-containing electrophiles.

Results

Kinetic Studies

In order to determine the reactivity of a typical, sufficiently stable 2-azaallenium ion, the rate constants for the reaction of 1,3-bis(*p*-tolyl)-2-azaallenium trifluoromethylsulfonate[9] **1b**$^+$·$CF_3SO_3^-$ and hexachloroantimonate **1b**$^+$·$SbCl_6^-$ with excess (5–10 fold) 1,4-cyclohexadiene as hydride donor have been measured by ^{1}H NMR spectroscopy (Table 1). In these hydride transfer reactions the decrease in intensity of the 2-azaallenium =CH– signal and the increase in intensity of the CH_2 signal of the iminium salt which is formed were used for the evaluation of the rate constants. The simultaneous formation of benzene as a second product was also observed. There were no indications

[a] Institut für Organische Chemie der Westfälischen Wilhelms-Universität Münster,
Corrensstrasse 40, D-48149 Münster, Germany
Fax: (internat.) + 49-251/83-39772

  1434–193X/00/0408–1589 $ 17.50+.50/0

Table 1. Rate constants k determined by ^{1}H NMR spectroscopy for the 2-azaallenium ion **1b**$^+$, the 2-azaallylium ion **2a**$^+$ and the iminium ion **3**$^+$

Entry	Electrophile	Nucleophile	Temp. [°C]	k [L·Mol^{-1}·s^{-1}]
1	**1b**$^+$·$CF_3SO_3^-$	1,4-Cyclohexadiene	26	$(1.28\pm0.01)\cdot10^{-4}$ [a]
2	**1b**$^+$·$SbCl_6^-$	1,4-Cyclohexadiene	26	$(1.61\pm0.01)\cdot10^{-4}$ [b]
3	**1b**$^+$·$CF_3SO_3^-$	*E,E*-2,5-Heptatriene	20	$(1.05\pm0.04)\cdot10^{-4}$
4	**2a**$^+$·BF_4^-	Pyridine	20	$(5.37\pm0.02)\cdot10^{-5}$ [a]
5	**3**$^+$·$CF_3SO_3^-$	H_2O	20	$(1.97\pm0.16)\cdot10^{-4}$ [a]

[a] Mean value from three runs. – [b] Mean value from two runs.

for counter-ion effects on the reactivity; the trifluoromethylsulfonate **1b**$^+$·$CF_3SO_3^-$ and the hexachloroantimonate **1b**$^+$·$SbCl_6^-$ [10] ions showed rather similar kinetic behavior. Similarly, the hydride transfer from *E,E*-2,5-heptatriene to **1b**$^+$·$CF_3SO_3^-$ was monitored. Plots of the experimentally obtained kt versus t-values indicate that these reactions obey second order kinetics, first order with respect to the nucleophile and first order with respect to the electrophile.

From our structural investigations on the 2-azaallenium – 2-azaallylium ion valence isomerism[3] the bent, rather than planar, structure of 1,3-diethoxy-1,3-diphenyl-2-azaallylium tetrafluoroborate **2a**$^+$·BF_4^- [11] in the solid state was already known. Preliminary experiments have indicated that this system is indeed relatively unreactive, which limits considerably the choice of suitable nucleophiles for kinetic studies. Pyridine was the only nucleophile whose reaction could be monitored by ^{1}H NMR spectroscopy by integration of the decreasing methylene signals of the ethoxy groups of **2a**$^+$·BF_4^- and the increase of corresponding signals of the newly formed pyridine adduct. However, its plot is characterized by a relatively short linear kt versus t range.

For a better comparison with regard to the special substitution pattern of **1b**$^+$ the corresponding iminium salt, the *p*-tolyl derivative **3**$^+$·$CF_3SO_3^-$ was included in this experimental study. However, its rather low reactivity made a reliable kinetic investigation difficult. The only nucleophilic system which was found to react on an accessible time scale was an excess of water, which, due to its hydrogen bonding capacity, is probably not a very representative nucleophile.[12] Integration of the methyl group intensities of the *p*-tolyl moieties of the starting material and the hydrolysis product was used for the determination of the rate constant. The rates obtained for these reactions are summarized in Table 1.

Electrophilicity Parameters E

For the comparison of electrophilic reactivities of different cations towards known nucleophiles the LFER $\lg k_{20°C} = s\,(E + N)$ developed by Mayr and Patz[7] has proven to be of great interpretive and predictive value. After extrapolation of the rate constant for the reaction of **1b**$^+$·$CF_3SO_3^-$ with 1,4-cyclohexadiene to 20 °C from temperature dependent rate measurements (Arrhenius plot; activation parameters: $\Delta H^{\ddagger} = 71 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -80 \pm 10$ J·mol^{-1}·K^{-1}) the appropriate E values were calculated for the electrophile-nucleophile combinations considered (Table 2). As seen from Table 2, an E parameter of –4.27 for **1b**$^+$·$CF_3SO_3^-$ (from 1,4-cyclohexadiene reactions) could be derived from the kinetic measurements. From the reaction with *E,E*-2,5-heptadiene an E value of –3.12 is obtained, resulting in an average E value of –3.7 for both nucleophiles. The electrophilicity of **1b**$^+$·$CF_3SO_3^-$ is thus significantly higher than that reported for simple iminium salts (–7.0 and –8.0).[8] The successful reaction of **1b**$^+$·$CF_3SO_3^-$ with anisole, for instance, is predicted from the tables of Mayr and Patz,[7] a reaction which was indeed observed experimentally.[13] For the rather electrophilic chloromethylene iminium salt (Vilsmeier–Haack ion) Mayr and Ofial[8] report an E parameter of –4.8, which indicates that this cation is about four times less reactive than the cumulene ion **1b**$^+$. From the rate constants of the UV measurements by Mattay et al.[6] we derived a higher electrophilicity parameter ($E \approx 0$) for **1a**$^+$ than for **1b**$^+$. This value is somewhat higher than expected and cannot be explained by just the substituent effect of the two *p*-methyl groups present in **1b**$^+$. These authors used water, methanol and aqueous solutions of salts as nucleophiles. From Mayr's work[7,8] it is known that such nucleophiles sometimes react unusually fast with nitrogen-containing electrophiles, in comparison to hydride transfer reagents or C-nucleophiles, probably due to extra stabilization in the transition states (see also[12]).

Table 2. Derived electrophilicity parameters E for the 2-azaallenium ion **1b**$^+$, the 2-azaallylium ion **2a**$^+$ and the iminium ion **3**$^+$ (N and s from ref.[7])

Nucleophile	N	s	$k_{20\,°C}$ [L·mol^{-1}·s^{-1}]	E
1,3-Bis(p-tolyl)-2-aza-allenium triflate (**1b**$^+$·$CF_3SO_3^-$)				
1,4-Cyclohexadiene	0.09	1.00	$6.66\cdot10^{-5}$	–4.27
E,E-2,5-Heptadiene	–0.74	1.03	$1.05\cdot10^{-4}$	–3.12
1,3-Diethoxy-1,3-bis(p-tolyl)-2-aza-allylium tetrafluoroborate (**2a**$^+$·BF_4^-)				
Tributylphosphite	10.81	0.70	no reaction	<–15.81
Pyridine[a]	13.76	0.67	$5.37\cdot10^{-5}$	–20.13
Dimethyl(p-methylbenzylidene)ammonium triflate (**3**$^+$·$CF_3SO_3^-$)				
H_2O	5.80	0.80	$1.97\cdot10^{-4}$	–10.43

[a] Only small linear range (12000 s).

The E parameter calculated for **2a**$^+$·BF_4^- (ca. –20) from the reaction with pyridine ($N = 13.76$, $s = 0.67$) seems to be unrealistically low and should be interpreted as a lower limit; from preparative reactions with aniline ($N = 12.50$, $s = 0.77$; spontaneous reaction) and with tributylphosphite ($N = 10.81$, $s = 0.70$, no reaction) an E parameter of ca. –16 to –17 seems to be more appropriate. The kinetic data for pyridine, as well as the preparative experiments,[5] indic-

ate the rather low reactivity of the system $\mathbf{2a^+}\cdot\mathbf{BF_4^-}$ which is, of course, mainly due to the $+M$ effects of the two ethoxy groups present. The different molecular structure of the C–N–C moiety compared to $\mathbf{1b^+}$ is an indication of a different electronic structure which contributes to the low reactivity (see below).

The *E* parameter obtained for the aromatic iminium salt $\mathbf{3^+}\cdot\mathbf{CF_3SO_3^-}$ has an estimated value of -10.43, which is 2 to 3 units lower than the value for methylene ammonium ions.[8] The ion $\mathbf{3^+}$ should thus be about 6 powers of ten less reactive than the 2-azaallenium system $\mathbf{1b^+}$. However, as stated above, water might not be a very representative nucleophile within the framework of this LFER.[7,12]

Quantum Chemical Calculations of Electrophilicities

Mayr et al.[14] have recently shown that their electrophilicity parameters *E* correlate surprisingly well with AM1[15] calculations of the methyl anion affinity of the electrophiles, although the chloromethylenedimethyl ammonium ion deviates somewhat from the correlation line. We have calculated the AM1 methyl anion affinities of our systems $\mathbf{1b^+}$, $\mathbf{2a^+}$, and $\mathbf{3^+}$ and compared them with the data published by Mayr et al.[14] Ab initio and *DFT* calculations[16] of these systems and a few other carbocations fit even better with the experimental *E* parameters than the AM1 data (Table 3).[17] The best correlation between experimental *E* values and calculated methyl anion affinities (correlation coefficient = 0.944) is found for the MP2/6–31G*//RHF/6–31G* method (Figure 1). Interestingly, the chloromethylenedimethyl ammonium ion mentioned above deviates, for still-unknown reasons, from all correlation lines. These calculations again underline the suitability of quantum chemistry to estimate rate constants for the reactions of carbocations with nucleophiles in agreement with this LFER. Hence, we have taken these theoretical results as an indication of the quality of our kinetic data and for the experimental reactivity sequence of the ions $\mathbf{1b^+} > \mathbf{3^+} > \mathbf{2a^+}$.

Table 3. Calculated methyl anion affinities $\Delta_r H°$ for the ions $\mathbf{1b^+}$, $\mathbf{2a^+}$ and $\mathbf{3^+}$ [kcal/mol]

No	AM1[a]	RHF/6–31G*// RHF/6–31G*	MP2/6–31G*// RHF/6–31G*	B3LYP/6–31G*// B3LYP/6–31G*
$\mathbf{1b^+}$	–202.43	–226.23	–240.71	–222.17
$\mathbf{2a^+}$	–187.47	–193.74	–214.71	–193.83
$\mathbf{3^+}$	–197.67	–211.92	–225.00	–211.61

[a] With $\Delta_f H°(CH_3^-)$ = 33.4 kcal/mol (ref.[14]).

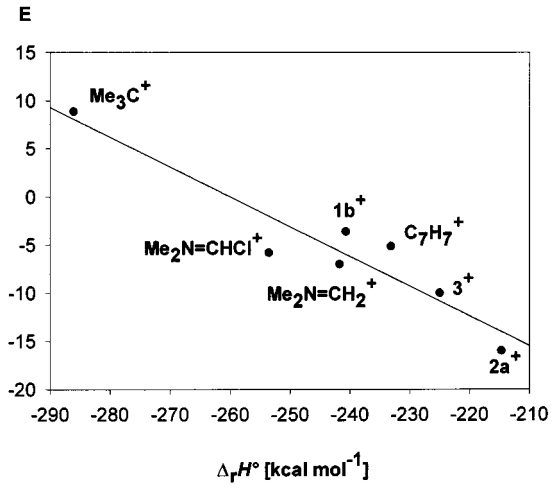


Figure 1. Correlation of the electrophilicity parameters *E* for nitrogen-containing carbocations, the tropylium ion and the trimethylmethyl cation with their calculated methyl anion affinities [kcal/mol] (MP2/6–31G*//RHF/6–31G*)

X-ray Structure of $\mathbf{3^+}\cdot\mathbf{CF_3SO_3^-}$

In the course of this work we were able to grow crystals of $\mathbf{3^+}\cdot\mathbf{CF_3SO_3^-}$ which were suitable for X-ray crystallography (Figure 2). This X-ray crystal structure determination is a welcome addition to those of simple iminium salts,[18] since arylaldehyde-derived iminium salt structures are rare. As expected, the nitrogen atom and the iminium carbon atom are sp^2 hybridized (sum of angles: 360.0°); the *p*-tolyl group is not fully coplanar with the iminium moiety, but twisted by ca. 29° out of the plane of the C=N bond. The cation and anion do not show strong interactions, although it is noteworthy that the oxygen atom O2 of the anion points to the empty p-orbital of the iminium carbon atom C1 (distance: 2.99 Å).[19] The bond lengths and bond angles are close to standard values (see Figure 1).[20]

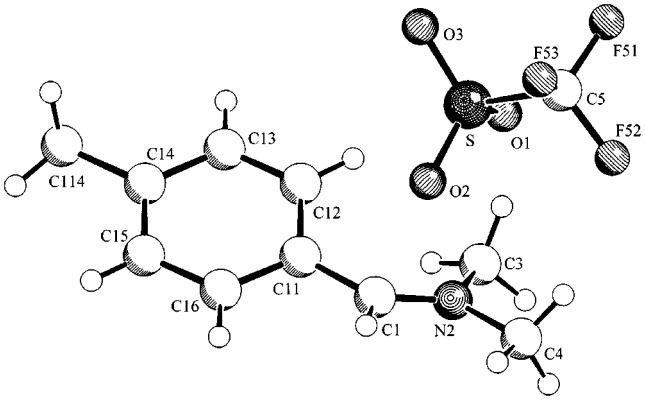


Figure 2. Molecular structure of dimethyl(*p*-methylbenzylidene)-ammonium triflate $\mathbf{3^+}\cdot\mathbf{CF_3SO_3^-}$. Crystallographic numbering; selected bond lengths [Å]: C1–N2 1.290(4), N2–C3 1.467(4), N2–C4 1.465(4), C1–C11 1.443(4); selected bond angles [°]: N2–C1–C11 129.2(3), C16–C11–C1 116.2(3), C12–C11–C1 125.6(3), C1–N2–C3 124.8(3), C1–N2–C4 120.0(3), C4–N2–C3 115.2(3); selected dihedral angles [°]: N2–C1–C11–C16 155.6(0.4), N2–C1–C11–C12 –29.0(0.6), C11–C1–N2–C4 174.2(0.3), C11–C1–N2–C3 –3.1(0.5).

Discussion

The structural properties and the observed order of reactivity of the three systems studied with the enormous difference in reactivity ($\approx 10^{12}$:10^6:1 for $\mathbf{1b^+}$: $\mathbf{3^+}$:$\mathbf{2a^+}$) seem to be in some way dependent on the hybridization of the central nitrogen atom and on the C–N bond length in the cations. As previously noted, substituent effects, especially of donor groups, have a strong influence on the structural properties of these cations.[3] Thus, the X-ray structure of the 2-azaallenium ion $\mathbf{1b^+}\cdot\mathbf{CF_3SO_3^-}$ with its two aromatic substituents

and the sp-hybridized nitrogen atom shows a C=N=C bond angle of 172.2(2)° and a C=N bond length of 1.258 Å,[9] which is well in line with RHF/6–31G* (1.252 Å) and B3LYP/6–31G* calculations (1.270 Å). This value is quite short for a C=N bond[18,20] and reflects the influence of the central sp-hybridized nitrogen atom on the bond length. Correspondingly, the group charges on carbon and nitrogen of $\mathbf{1b}^+$ are significantly higher than those in $\mathbf{3}^+$ (ab initio and *DFT* calculations, Mulliken population analysis[1]). The iminium ion $\mathbf{3}^+$ exhibits a longer "normal" bond length (X-ray: 1.29Å; RHF/6–31G*: 1.281 Å; B3LYP/6–31G*: 1.308 Å), which is close to the standard data for C=N bonds[18,20] involving an sp^2-hybridized nitrogen atom. An analogue of the third system $\mathbf{2a}^+$ [diphenyl instead of bis(*p*-tolyl)] with its two electron-donating ethoxy groups was subjected to an X-ray diffraction study some time ago;[11] the C=N bond length obtained was 1.30 Å, (RHF/6–31G* 1.294 Å; B3LYP/6–31G* 1.308 Å), slightly longer than in $\mathbf{3}^+$. The C–N–C bond angle was found to be 132.3(3)°, indicating a nitrogen hybridization close to sp^2. Thus, introduction of donor substituents, such as alkoxy groups, simultaneously leads to bent structures and reduced reactivity.

However, for a hypothetical 1,3-bis(*p*-tolyl)-2-azaallylium ion without these donor substituents, a CN bond length of 1.314 Å (RHF/6–31G*//RHF/6–31G*) resp. 1.329Å (B3LYP/6–31G*//B3LYP/6–31G*) was calculated.[9] The relative energy of this species, which corresponds to the transition state for the automerization (enantiomerization) of $\mathbf{1b}^+$, was calculated to be higher than $\mathbf{1b}^+$ by 4.5 kcal/mol (MP2/6–31G*//RHF/6–31G*) and 2.85 kcal/mol (B3LYP/6–31G*//B3LYP/6–31G*). Therefore, a higher reactivity for such a hypothetical species without alkoxy groups has to be expected, quite in contrast to $\mathbf{2a}^+$.

Conclusion

We conclude from these kinetic and structural data that, for nitrogen-containing systems, a dependence of reactivity and structural parameters on hybridization exists similar to the well-known dependence for the corresponding series of carbon compounds. Due to the greater electronegativity of nitrogen than carbon, the electrophilicity range at the respective carbon centers is surprisingly large.

Experimental Section

General Methods: All solvents are rigorously dried by standard methods. – All experiments were carried out with rigorous exclusion of moisture (argon; septum – syringe technique) in glassware which was thoroughly dried by repeatedly heating under argon and subsequent evacuation. – Melting points: uncorrected. – NMR spectroscopy: Bruker WM 300 and WM 360, internal standard tetramethylsilane (TMS, δ = 0.00 ppm). – Laser Desorption-TOF-MS (LDI-MS): Construction Dr. H. Luftmann, University of Münster; N_2-Laser 337 nm, 3 ns pulses.

1,3-Bis(*p*-tolyl)-2-azaallenium Trifluoromethylsulfonate ($\mathbf{1b}^+\cdot\mathbf{CF_3SO_3^-}$) was prepared according to ref.[9]

1,3-Diethoxy-1,3-bis(*p*-tolyl)-2-azaallylium Tetrafluoroborate ($\mathbf{2a}^+\cdot\mathbf{BF_4^-}$): Triethyloxonium tetrafluoroborate (1.94 g, 10.2 mmol) was dissolved in dichloromethane (20 mL). Ethyl *N*-(*p*-tolyl)-*p*-tolylimidacetate[21] (2.87 g, 10.2 mmol) in dichloromethane was then added dropwise at room temp. The reaction mixture was stirred for 18 h at room temp. Diethyl ether was then added dropwise until the solution became slightly cloudy. To complete the precipitation, the mixture was stored at –20 °C for 18 h. The solid was filtered off, washed with diethyl ether and dried in vacuo. Yield 3.70 g (91%). mp 154 °C (dec.). – ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.65 (t, ^3J = 7.0 Hz, 3 H), 2.37 (s, 3 H), 4.83 [q, br., 2 H], 7.30 (d, ^3J = 8.6 Hz, 2 H), 7.66 (d, ^3J = 8.3 Hz, 2 H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.8 (q), 21.8 (q), 43.9 (q), 71.1(t), 122.3 (q), 125.0 (s), 130.6 (d), 133.8 (d), 148.7 (s), 169.6 (s). – LDI-MS: *m*/*z* (%) = 310 (100) [M^+].

Dimethyl(*p*-methylbenzylidene)ammonium Triflate ($\mathbf{3}^+\cdot\mathbf{CF_3SO_3^-}$): [α-Dimethylamino(*p*-methylbenzyl)]dimethylamine[22] (1.95 g, 10.2 mmol) was dissolved in acetonitrile (20 mL) and cooled to 0 °C with stirring. This solution was treated dropwise with trifluoromethanesulfonic anhydride (2.85 g, 1.7 mL, 10.2 mmol). The reaction mixture was then stirred for 1 h at 0 °C, and for 18 h at room temp. The solution was treated dropwise with 15 mL of diethyl ether and stored at –20 °C for 5 h. The colorless microcrystalline precipitate was then filtered off, washed with diethyl ether and dried in vacuo: Yield 2.14 g (71%). mp 157 °C (dec.). – ^{1}H NMR (300.13 MHz, CD_3NO_2): δ = 2.47 (s, 3 H), 3.86 (s, 3 H), 3.90 (s, 3 H), 7.53 (d, ^3J = 8.3 Hz, 2 H), 7.83 (d, ^3J = 8.6 Hz, 2 H), 8.82 (s, 1 H). – ^{13}C NMR (75.47 MHz, CD_3NO_2): δ = 21.5 (q), 43.9 (q), 51.5(q), 121.1 [q, ^1J(C,F) = 320.4 Hz], 125.0 (s), 130.8 (d), 133.4 (d), 148.6 (d), 172.0 (s). – LDI-MS: *m*/*z* (%) = 148 (100) [M^+].

X-ray Diffraction Analysis of $\mathbf{3}^+\cdot\mathbf{CF_3SO_3^-}$ ($\mathbf{C_{11}H_{14}F_3NO_3S}$):[23] The colorless single crystals were analyzed using a CAD4 diffractometer (Enraf–Nonius) with Cu-K_α radiation (λ = 1.54178 Å) using a graphite monochromator at 222 K. Crystal system: orthorhombic, space group $Pca2_1$ with cell parameters a = 15.932(1), b = 10.313(1), c = 8.323(1) Å, V = 1367.5(2) Å^3, ρ_{calc} = 1.444 g cm^{-3}, Z = 4. Crystal size: 0.30 × 0.20 × 0.05 mm. 1496 Reflections were collected, which were all independent; 1350 Observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 25.00 cm^{-1}, no absorption correction. 176 Refined parameters. Non-hydrogen atoms were refined anisotropically. H-atoms were geometrically positioned (riding model). R = 0.037, wR^2 = 0.100. Residual electron density: 0.32/–0.35 e Å^{-3}. Flack parameter –0.01(3). The structure was solved and refined using SHELXS-86 and SHELXL-93.[24]

Acknowledgments

The authors are very grateful to Prof. Dr. H. Mayr and Dr. A. R. Ofial (TU Darmstadt, now University of München) for numerous helpful discussions and experimental advice. This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Hochreaktive Mehrfachbindungssysteme" and Sonderforschungsbereich 424) and by the Fonds der Chemischen Industrie (Frankfurt).

[1] G. M. Böttger, taken in part from the Ph. D. Thesis, University of Münster, **1998**.
[2] X-ray diffraction structure determination.
[3] E.-U. Würthwein, *J. Org. Chem.* **1984**, *49*, 2971–2978; M. Al-Talib, I. Jibril, E.-U. Würthwein, J. C. Jochims, G. Huttner, *Chem. Ber.* **1984**, *117*, 3365–3373; R. Kupfer, S. Meier, E.-U. Würthwein, *Chem. Ber.* **1992**, *125*, 2487–2492.
[4] A. Geisler, E.-U. Würthwein, *Tetrahedron Lett.* **1994**, *35*, 77–80.

[5] R. Schleimer, K. Hornig, M. H. Möller, E.-U. Würthwein, *Chem. Ber.* **1993,** *126*, 133–141.
[6] E. Albrecht, J. Mattay, S. Steenken, *J. Am. Chem. Soc.* **1997**, *119*, 11605–11610.
[7] H. Mayr, M. Patz, *Angew. Chem.* **1994**, *106*, 990–1010; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 938–957.
[8] H. Mayr, A. R. Ofial, *Tetrahedron Lett.* **1997**, *38*, 3503–3506.
[9] G. Böttger, A. Geisler , R. Fröhlich, E.-U. Würthwein, *J. Org. Chem.* **1997**, *62*, 6407–6411.
[10] E.-U. Würthwein, *Angew. Chem.* **1981**, *93*, 110–111; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 99–100.
[11] E.-U. Würthwein, R. Kupfer, R. Allmann, M. Nagel, *Chem.Ber.* **1985**, *118*, 3632–3642.
[12] [12a] S. Eldin, W. P. Jencks, *J. Am. Chem. Soc.* **1995**, *117*, 4851–4857. – [12b] S. Eldin, J. A. Digits, S.-T. Huang, W. P. Jencks, *J. Am. Chem. Soc.* **1995**, *117*, 6631–6632.
[13] A. Geisler, Ph. D. Thesis, University of Münster, **1996**.
[14] H. Mayr, M. Patz, M. F. Gotta, A. R. Ofial, *Pure Appl. Chem.* **1998**, *70*, 1993–2000.
[15] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
[16] Gaussian 98, Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.
[17] Details of the quantum mechanical calculations (MOPAC93 and GAUSSIAN 98 archive entries) are available from E.-U.W. upon request.
[18] L. M. Trefonas, R. L. Flurry, Jr., R. Majeste, E. A. Meyers, R. F. Copeland, *J. Am. Chem. Soc.* **1966**, *88*, 2145–2149; S. Hollenstein, T. Laube, *Angew. Chem.* **1990**, *102*, 194–195, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 188–189; H. Bock, I. Göbel, C. Nöther, B. Solouki, A. John, *Chem. Ber.* **1994**, *127*, 2197–2208; P. Klinzing, A. El-Kholi, U. Müller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1989**, *569*, 83–90; O. Knop, T. S. Cameron, P. K. Bakshi, W. Kwiatkowski, S. C. Choi, D. Adhikesavalu, *Can. J. Chem.* **1993**, *71*, 1495–1523.
[19] H. Mayr, A. R. Ofial, E.-U. Würthwein, N. C. Aust, *J. Am. Chem. Soc.* **1997**, *119*, 12727–12733.
[20] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, in *International Tables of Crystallography,* Vol. C (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, **1995**, p. 685–706. R. Allmann in S. Patai *The Chemistry of Functional groups. The Chemistry of Hydrazo, Azo and Azoxy groups.* (Ed.: S. Patai), Wiley, London, **1975**, § 2, p. 23–52.
[21] H. Böhme, M. Haake, G. Auterhoff, *Arch. Pharmaz.* **1972**, *305*, 10–17.
[22] R. Kupfer, M. Nagel, E.-U. Würthwein, R. Allmann, *Chem. Ber.* **1985**, *118*, 3089–3104.
[23] Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-124677 ($\mathbf{3^+ \cdot CF_3SO_3^-}$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
[24] G. M. Sheldrick, *SHELXS-86, Program for crystal structure solution,* Universität Göttingen, Germany, **1986**; G. M. Sheldrick, *SHELXL-93, Program for the refinement of crystal structures*, Universität Göttingen, Germany, **1993**.

Received September 6, 1999
[O99509]