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Generation of α,β-Unsaturated Iminium Ions by Laser Flash Photolysis**

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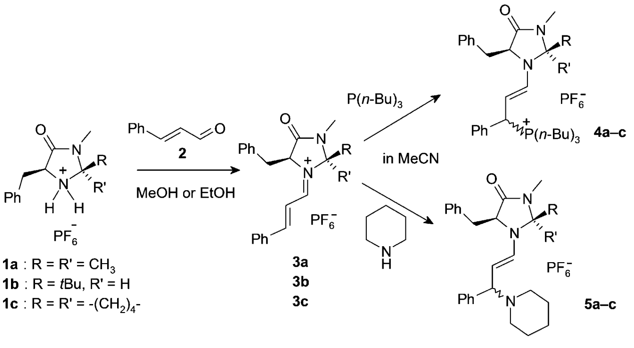
Dedicated to Professor Gerhard Bringmann on the occasion of his 60th birthday

Iminium activation has become one of the most important methods in enantioselective synthesis.[1] For the optimization and the rational design of organocatalytic cycles, knowledge of the mechanism of these reactions is crucial.[2] In previous work, we have shown that the rate constants for the reactions of unsaturated iminium ions with ketene acetals,[2d] sulfur ylides,[3] and pyrroles[4] can be determined by UV/Vis spectroscopy employing conventional spectrometers or stopped-flow equipment. Both methods require the mixing of the reactants, and therefore are not applicable to reactions that proceed on the sub-millisecond time scale.

We now report on the in situ laser-flash-photolytic generation of iminium ions derived from cinnamaldehyde and imidazolidinones, which allowed us to measure rate constants for the reactions of iminium ions with strong nucleophiles. This method along with previously reported kinetic procedures have been employed to directly compare the electrophilic reactivities of iminium ions derived from different imidazolidinones.

Treatment of the imidazolidinonium salts **1a**–**c** with cinnamaldehyde (**2**) in methanol or ethanol following literature procedures[5,6] gave precipitates of the iminium salts **3a**–**c** (Scheme 1), which were previously analyzed by X-ray crystallography.[5a,6c] When these crystals were dissolved in acetonitrile, only the *E* isomers of **3a**–**c** were observed by NMR spectroscopy.[7]

Combination of the iminium salts **3a**–**c** with one equivalent of tributylphosphine gave the (*E*)-enaminophosphonium salts **4a**–**c** as mixtures of two diastereoisomers (2:1 for **4a** and **4c** and 1:1 for **4b**; Scheme 1). Selective formation of the (*E*)-enamines **5a**–**c** (1:1 ratio of two diastereoisomers) was observed when solutions of **3a**–**c** in acetonitrile were treated with excess piperidine (Scheme 1).[8]



Scheme 1.

As organocatalytic processes involving **3a**–**c** are often highly enantioselective,[9] we have to conclude that the low stereoselectivities of the stoichiometric reactions with PBu_3 and piperidine in Scheme 1 are due to reversible reactions under the conditions employed.

Tri-*n*-butylphosphine has previously been reported to be an effective photo-leaving group for the laser-flash-photolytic generation of stabilized carbocations.[10] Irradiation of acetonitrile solutions of the phosphonium salts **4a**–**c** with 7 ns laser pulses from the fourth harmonic of a Nd/YAG laser (266 nm, 30–60 mJ pulse^{-1}) yielded the iminium ions **3a**–**c** which showed the same UV/Vis absorption maxima λ_{max} as solutions of the isolated iminium salts in acetonitrile (Figure 1 a).

When salts **3a**–**c** were generated in the presence of a large excess of the nucleophiles **6j** or **6l**–**o**, we observed monoexponentional decays of their absorbances, from which the rate constants k_{obs} (s^{-1}) were obtained (Figure 1 b). Plots of k_{obs} versus the nucleophile concentrations were linear (Figure 1 c) and provided the second-order rate constants k_2 ($\text{M}^{-1}\,\text{s}^{-1}$) which are listed in Table 1.

In order to provide a broader experimental basis for the comparison of the electrophilicities of iminium ions derived from different imidazolidinones we have also determined rate constants of the reactions of **3a**, **3b**, and **3c** with weaker nucleophiles using convential UV spectrometers and stopped-flow techniques. The rate of the reaction of **3a** with DBU (**6l**) has been determined in two ways, with laser-flash-photolytically generated iminium ions as well as with solutions of isolated iminium salts, and the values differed by less than 6 %. This agreement is remarkable in view of Seebach's hypothesis that (*E*)-iminium ions are more reactive than their *Z* isomers.[6e] As we do not know the configuration of the photolytically generated iminium ions, the monoexpo-

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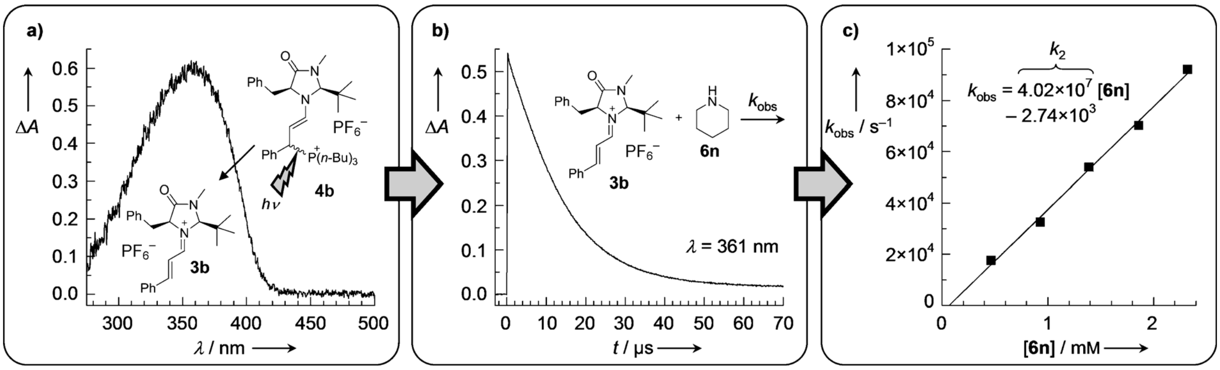

Figure 1. a) UV/Vis spectrum of **3b** immediately after the laser pulse in CH_3CN. b) Decay of the absorbance of **3b** obtained after irradiation of a 1.51×10^{-4} M solution of **4b** in CH_3CN in the presence of piperidine (**6n**; 1.86×10^{-3} M). c) Plot of the pseudo-first-order rate constants k_{obs} (s^{-1}) versus the concentration of piperidine.

Table 1: Second-order rate constants (k_2) for the reactions of the iminium ions **3a–c** with the nucleophiles **6a–o** (20 °C, MeCN).

Nucleophile		N[a]	s_N[a]	k_2 (**3a**) [$M^{-1}s^{-1}$]	k_2 (**3b**) [$M^{-1}s^{-1}$]	k_2 (**3c**) [$M^{-1}s^{-1}$]
pyrrole	**6a**	4.63	1.00	6.8×10^{-4}[b]	–	–
N-methylpyrrole	**6b**	5.85	1.03	7.2×10^{-3}[b]	–	–
1-(trimethylsiloxy)-pentene	**6c**	6.57	0.93	–	5.18×10^{-1}	4.28×10^{-2}
2,5-dimethylpyrrole	**6d**	8.01	0.96	3.6[b]	1.34×10^{3}[c]	–
1,2,5-trimethylpyrrole	**6e**	8.69	1.07	5.3[b]	–	–
2-(trimethylsiloxy)-5,6-dihydro-4*H*-pyran	**6f**	10.61	0.86	5.23×10^{2}[d]	–	–
2,4-dimethylpyrrole	**6g**	10.67	0.91	3.5×10^{3}[b]	6.87×10^{4}[c]	–
kryptopyrrole	**6h**	11.63	0.95	1.3×10^{4}[b]	1.33×10^{5}[c]	5.20×10^{3}[c]
2-(trimethylsiloxy)-4,5-dihydrofuran	**6i**	12.56	0.70	1.14×10^{4}[b,e]	1.12×10^{5}	–
$H_2NCH_2CH_2OH$	**6j**	14.11	0.71	7.56×10^{5}	5.27×10^{7}	–
$P(Ph)_3$	**6k**	14.33	0.65	2.40×10^{5}	9.91×10^{5}	1.53×10^{4}
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	**6l**	15.29	0.70	6.81×10^{5}	7.54×10^{7}	–
$P(nBu)_3$	**6m**	15.49	0.69	3.69×10^{5}	1.96×10^{7}	2.86×10^{5}
piperidine	**6n**	17.35	0.68	1.86×10^{7}	4.02×10^{7}	1.51×10^{7}
1,4-diazabicyclo[2.2.2]octane (DABCO)	**6o**	18.80	0.70	4.95×10^{8}	5.88×10^{8}	4.86×10^{8}

[a] See reference [11] for the origin of the nucleophilicity parameters N and s_N determined in MeCN or CH_2Cl_2. [b] From reference [4]. [c] These rate constants were derived in the presence of potassium trifluoroacetate (as base) from plots of $1/k_{obs}$ versus 1/[base] as described in reference [4] because the initial C–C bond-forming step is reversible. [d] Second-order rate constant k_2 for the reaction of **3a**-OTf with **6f** in CH_2Cl_2, from reference [2d]. [e] In CH_2Cl_2.

nential decays of the photolytically generated iminium ions and the identical reactivities of the iminium ions generated in different ways either imply that only the *E* isomers are formed by the photolytic process or that the *E* and *Z* isomers have the same reactivities.

In previous work, we have shown that the reactions of carbocations and Michael acceptors with σ, *n*, and π nucleophiles follow Equation (1), in which electrophiles are described by *E* (electrophilicity parameter) and nucleophiles are described by *N* (nucleophilicity parameter) and s_N (nucleophile-specific sensitivity parameter).[12]

$$\lg k_2\ (20\,^{\circ}\mathrm{C}) = s_N(E+N) \tag{1}$$

In this way, we were able to set up comprehensive electrophilicity and nucleophilicity scales, covering more than 30 orders of magnitude.[13] These scales have found wide application for the design of polar organic reactions, in particular in organocatalysis.[14]

Figure 2, in which $(\lg k_2)/s_N$ is plotted versus the nucleophilicity parameter *N*, demonstrates not only that the rate constants obtained with different kinetic methods are consistent, but also that the *N* and s_N parameters of nucleophiles,[11,12] which were derived from their reactions with benzhydrylium ions such as **7**, are suitable for predicting the rates of the reactions of these nucleophiles with the iminium ions **3**. Therefore, the electrophilicity parameters *E* of **3a–c** were determined by a least-squares fit, that is, by minimization of $\Delta^2 = \Sigma[\lg k_2 - s_N(N+E)]^2$, using k_2, *N*, and s_N from Table 1.

Apart from the rate constants for DABCO (**6o**) which are close to the diffusion limit, only the second-order rate constants for the reactions of ethanolamine (**6j**) were excluded from these correlations. For unknown reasons, the observed rate constants for the reactions of **6j** with **3a** and **3b** are 11 and 44 times larger, respectively, than the values calculated by Equation (1). As these deviations are still within the confidence interval of Equation (1), we will not speculate about their origin.

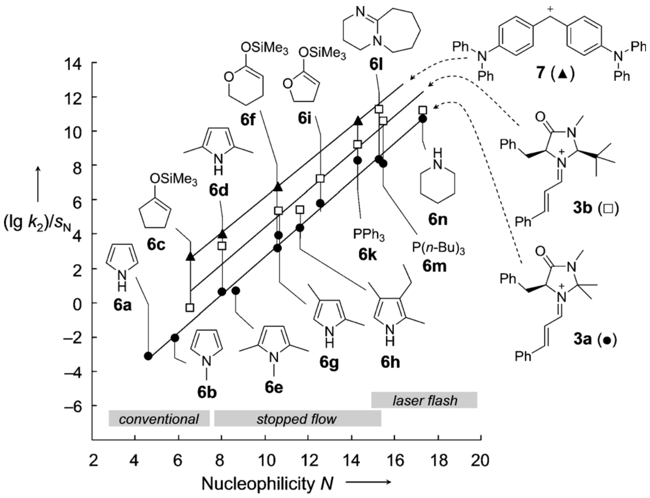

Figure 2. Correlation of $(\lg k_2)/s_N$ against the nucleophilicity parameters N of the nucleophiles **6a–n** for their reactions with the iminium ions **3a** and **3b** and the benzhydrylium ion **7** (correlation for **3c** is omitted for the sake of clarity; it is shown on page S25 of the Supporting Information).

Table 2: Electrophilicity parameters E of **3a–c**.

Electrophile	**3a**	**3b**	**3c**
E[a]	−7.37	−5.52	−7.67

[a] Determined from data in Table 1 by minimization of the term $\Delta^2 = \Sigma[\lg k_2 - s_N(N+E)]^2$.

The electrophilicity parameters of the α,β-unsaturated iminium ions **3a–c** in Table 2 show that **3b** is about 10^2 times more reactive than **3a** and **3c**, which have quite similar electrophilicities. This finding is in line with Larsen's observation that **1b**-$CF_3CO_2^-$ is a more active catalyst in Diels–Alder reactions of cinnamaldehyde than **1a**-$CF_3CO_2^-$, despite the fact that the equilibrium concentration of the iminium salt **3b**-$CF_3CO_2^-$ is only half of that of **3a**-$CF_3CO_2^-$.[15,16] The greater scope of reactions accessible with MacMillan's second-generation catalyst **1b**[17] can now be unambiguously attributed to the significantly higher electrophilicity of the iminium ion **3b**.

What is the origin of the high electrophilicity of **3b**? Seebach's structural studies of iminium ions by X-ray analysis, NMR spectroscopy, and DFT calculations have shown that the benzylic phenyl group of **3a** resides preferentially over the heterocyclic ring, while in the case of **3b** benzyl is sitting above the iminium π system and blocking the approach of nucleophiles from the *Re* face. An X-ray crystal structure of **3c** (page S5 in the Supporting Information) shows that its conformation resembles that of **3a**. While the preferred *Si* approach to **3a** and **3c** is slowed down by the steric shielding of a methyl group and the cyclopentane ring, respectively, the reactive *Si* face of **3b** is free from any steric hindrance and, therefore, exhibits higher electrophilicity.

In conclusion, we have shown that the laser-flash-photolytic generation of iminium ions has allowed us to extend our kinetic investigations over the whole conceivable reactivity range, from the slowest to diffusion-controlled bimolecular reactions. We have also determined the first quantitative data on the extraordinarily high electrophilicities of iminium ions derived from MacMillan's second-generation catalyst **1b** and finally demonstrated the applicability of the benzhydrylium-derived nucleophilicity parameters N and s_N for analyzing scope and limitations of iminium-activated reactions.

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