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Organocatalysis

Structures and Ambident Reactivities of Azolium Enolates**

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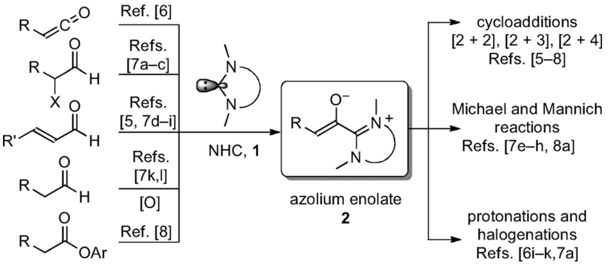
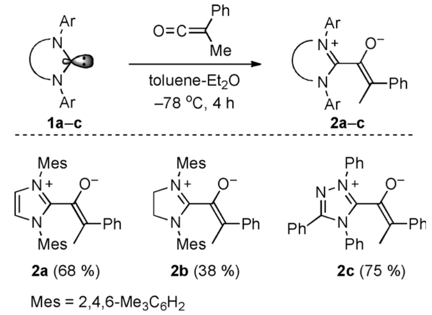
Dedicated to Professor Reinhard W. Hoffmann on the occasion of his 80th birthday

Since their first isolation as stable species in 1991,[1] N-heterocyclic carbenes (NHCs, **1**) have been used extensively as catalysts for C–C bond-forming reactions.[2,3] In organocatalytic applications[3] they mostly serve as "umpolung" reagents.[4,3f] As shown in Scheme 1, their reactions with ketenes,[6] aldehydes,[5,7] and esters[8] give rise to the formation of azolium enolates **2**,[3h,5–8] equivalents of ester enolates, which have recently gained great attention. Enolates **2** are usually generated in situ and serve as reactive and synthetically useful nucleophiles in [2+2],[6a–e] [2+3],[6f] and [2+4][6g,h,7,8b] cycloadditions,[5–8] Michael additions,[7e–h] and Mannich reactions[8a] as well as in enantioselective protonations[6i,j,7a] and halogenations (Scheme 1).[6k]



Scheme 1. Generation and reactions of azolium enolates **2**.

Despite numerous theoretical and experimental studies on the intermediates of NHC-catalyzed reactions,[9] the ambident reactivities[10] of azolium enolates, which may react at either oxygen or carbon, have not been investigated. As part of our ongoing research on structures and reactivities of intermediates of NHC-catalyzed reactions,[11] we now report on the synthesis and reactivities of the azolium enolates **2a–c** (Scheme 2).[12] After acceptance of this Communication a profound, simultaneously submitted investigation characterizing intermediates of NHC-catalyzed reactions, including an azolium enolate of type **2b**, was brought to our attention.[12d]



Scheme 2. Synthesis of the azolium enolates **2a–c**.

Dropwise addition of a diethyl ether solution of methyl phenyl ketene into a solution of 1,3-dimesitylimidazol-2-ylidene **1a** in toluene at 20 °C led to the formation of a yellow precipitate, which was identified by ^{1}H NMR analysis as a 4:1 mixture of two stereoisomers of **2a**.[6] When the reaction was conducted at −78 °C the major stereoisomer of **2a** was obtained (purity >97 %, ^{1}H NMR analysis) in 68 % yield (Scheme 2); compound **2a** has a characteristic ^{1}H NMR resonance at $\delta = 1.47$ for C*Me* showing a gHMBC correlation to the ^{13}C NMR resonances at $\delta = 94.9$ and 150.1 for the two enolate carbons Me*C*=*C*(O$^-$). The *Z* configuration of the enolate, which is formed by attack of **1a** on the less hindered side of the ketene, was confirmed by a NOESY experiment. A single-crystal X-ray analysis of (*Z*)-**2a** (Figure 1)[13] shows that the phenyl ring is in the plane of the enolate (C4-C5-C6-C11 dihedral angle = 2.92°), while the imidazolium moiety is

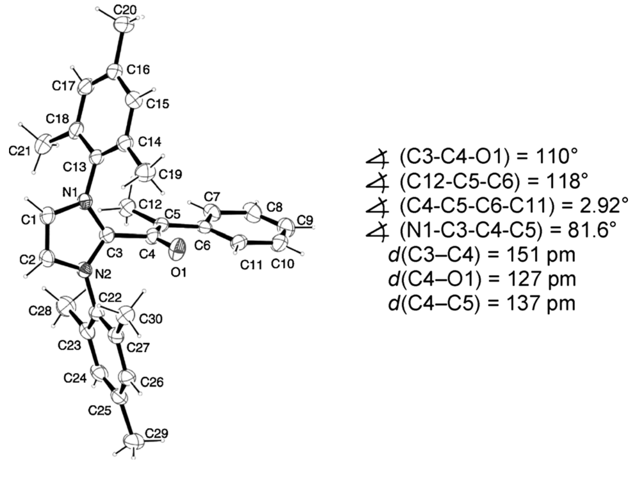


Figure 1. Crystal structure of **2a** (50 % probability ellipsoids). One of the two asymmetric units shown.[13]

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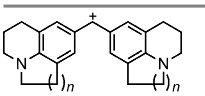
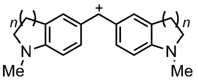
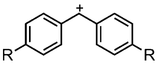
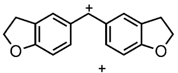
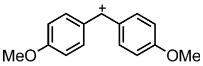
almost perpendicular (N1-C3-C4-C5 dihedral angle = 81.6°). A perpendicular orientation of the azolium ring to the enolate plane was also found by quantum chemical calculations of triazolium enolates.[5,9] Enolates **2b** and **2c** were synthesized analogously from 1,3-dimesitylimidazolidin-2-ylidene **1b** and Enders' carbene **1c**, respectively (Scheme 2).

In order to elucidate the relationship between structures and reactivities of **2a–c** we studied the kinetics of their reactions with the benzhydrylium ions **3** (Table 1), which had been used as reference electrophiles for the construction of comprehensive nucleophilicity scales on the basis of Equation (1). In Equation (1) nucleophiles are characterized by two solvent-dependent parameters (nucleophilicity N and sensitivity s_N) and electrophiles by one solvent-independent parameter (electrophilicity E).[14]

Table 1: Benzhydrylium ions Ar$_2$CH$^+$ employed as reference electrophiles in this work.

Ar$_2$CH$^+$			E[a]
	$n = 1$	**3a**	−10.04
	$n = 2$	**3b**	−9.45
	$n = 1$	**3c**	−8.76
	$n = 2$	**3d**	−8.22
	R = N(CH$_2$)$_4$	**3e**	−7.69
	R = NMe$_2$	**3f**	−7.02
		**3g**	−1.36
		**3h**	0

[a] Electrophilicity parameters E for **3a–h** from Ref. [14a].

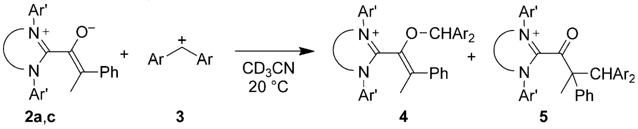
$$\lg k(20\,°\mathrm{C}) = s_N(N + E) \qquad (1)$$

Addition of **2a** to the blue solution of **3f**-BF$_4$ in CD$_3$CN led to a fading of the blue color due to the exclusive formation of the acyl azolium tetrafluoroborate **5af** as revealed by the ^{1}H NMR chemical shift of the benzhydryl proton at $\delta = 4.64$ and the NMR signals of two diastereotopic phenyl rings of the benzhydryl group as well as the ^{13}C NMR chemical shift for the carbonyl carbon at $\delta = 193.4$ (Table 2, entry 1). Analogously the reaction of **2c** with **3f**-BF$_4$ exclusively yields the acyl azolium tetrafluoroborate **5cf** (Table 2, entry 5).

Different observations were made for the reactions of **2a** and **2c** with the more strongly Lewis acidic benzhydrylium ions **3h** and **3g** (Table 2, entries 2–4 and 6–11), as illustrated for the reaction of **2c** and **3h** (Figure 2). When **2c** was mixed with **3h**-Cl in CD$_3$CN at 20 °C, the ^{1}H NMR spectra showed the formation of the O-addition product **4ch** and the C-addition product **5ch** in a 74:26 ratio. When the same mixture was analyzed after 24 h, the ratio **4ch**/**5ch** changed to 29:71 and after 48 h only the thermodynamically more stable acyl triazolium chloride **5ch** was observed.

Under the same conditions, the combination of **2c** with the slightly less Lewis acidic benzhydrylium ion **3g** initially gave a 63:37 mixture of O- and C-addition products which rearranged somewhat faster into the thermodynamically more stable **5cg** (Table 2, entries 6–8, Figure S1 in the Supporting Information). Similar observations were made for the reaction of **2a** with **3h** (Table 2, entries 2–4, Figure S2).

Table 2: Reactions of the azolium enolates **2a,c** with the benzhydrylium ions **3f–h** in CD$_3$CN at 20 °C.



2a,c **3** **4** **5**

Entry	2	3	t	Product ratio[a]
1	**2a**	**3f**	5 min	[**4af**]/[**5af**] < 4:96
2	**2a**	**3h**	5 min[b]	[**4ah**]/[**5ah**] = 76:24
3			2 h[b]	[**4ah**]/[**5ah**] = 22:78
4			24 h[b]	[**4ah**]/[**5ah**] < 4:96
5	**2c**	**3f**	5 min	[**4cf**]/[**5cf**] < 4:96
6	**2c**	**3g**	5 min	[**4cg**]/[**5cg**] = 63:37
7			1.5 h	[**4cg**]/[**5cg**] = 12:88
8			3 h	[**4cg**]/[**5cg**] < 4:96
9	**2c**	**3h**	5 min	[**4ch**]/[**5ch**] = 74:26
10			24 h	[**4ch**]/[**5ch**] = 29:71
11			48 h	[**4ch**]/[**5ch**] < 4:96

[a] From the ^{1}H NMR spectrum. [b] The reaction was performed in [D$_6$]DMSO.

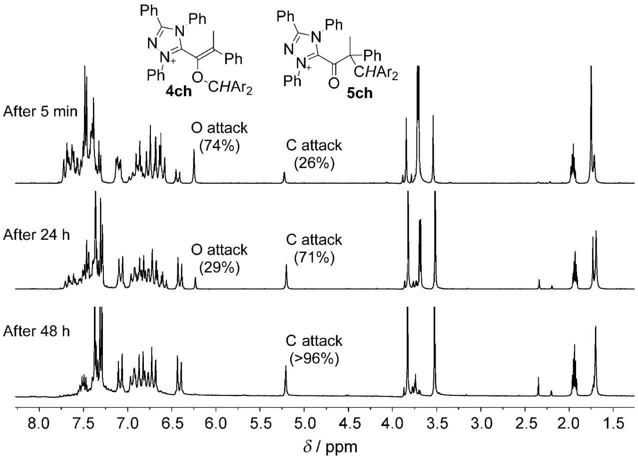


Figure 2. Time-dependent ^{1}H NMR spectra for the reaction of **2c** with **3h**-Cl in CD$_3$CN at 20 °C (Ar = 4-MeOC$_6$H$_4$).

Following previously described methods,[14] we measured the rates of the reactions of the carbocations **3** (Table 1) with the enolates **2a–c** photometrically by monitoring the disappearance of the absorbances of the diarylcarbenium ions **3**, using stopped-flow UV/Vis spectrometers. All kinetic experiments were performed at 20 °C in THF or DMSO with a large excess of the nucleophiles **2** in order to achieve conditions corresponding to first-order kinetics.

For the reactions of **2a,b** with carbocations **3a–d**, monoexponential decays were observed (for an example see, Figure S3), which correspond to the attack of the electrophiles **3a**–**d** at the β-carbons of the enolates **2a**,**b** to form the acyl azoliums **5**. The first-order rate constants, k_{obs}, were obtained by least-squares fitting of the function $A_t = A_0 e^{-k_{obs}t} + C$ to the time-dependent absorbances of the electrophiles. Plots of k_{obs} versus the concentrations of the nucleophiles [**2a**,**b**] were linear, as exemplified in the inset in Figure S3. The slopes of these plots gave the second-order rate constants k (in $M^{-1}s^{-1}$), which are summarized in Table 3.

Table 3: Second-order rate constants k (C attack) and k' (O attack) for the reactions of azolium enolates **2** with the reference electrophiles **3** at 20 °C in THF.

3	k [$M^{-1}s^{-1}$]				k' [$M^{-1}s^{-1}$]
	2a	**2a**[a]	**2b**	**2c**	**2c**
3a	1.57×10^4		1.70×10^4		
3b	4.69×10^4				
3c	1.37×10^5	3.88×10^3	1.27×10^5	5.58×10^3	
3d	4.66×10^5	1.10×10^4	3.58×10^5	1.23×10^4	
3e		2.08×10^4		2.86×10^4	5.4×10^5
3f		5.42×10^4			1.43×10^6

[a] In DMSO.

In contrast, the kinetic behavior of enolate **2c** depended on the nature of the benzhydrylium ions. The less electrophilic benzhydrylium ions **3c**,**d** react with **2c** in a similar way as with **2a**,**b** (monoexponential decay, Figure S4) to give the second-order rate constants k for C attack, which are listed in Table 3. However, the reaction of **2c** with the more reactive carbenium ion **3e** showed bisexponential decay of the absorbance of **3e**. At low concentration, as shown in Figure 3a for a 0.11 mM solution of **2c**, about 20% of the absorbance of **3e** disappeared within 50 ms, whereas reaching a constant concentration of **3e** required 1000 ms. At higher concentrations of **2c** (0.40 mM, Figure 3b) about 50% of the absorbance of **3e** disappeared within 10 ms and it was almost completely extinguished after 500 ms. With the more reactive benzhydrylium ion **3f**, the first part of the bisexponential decay dominated, and about 75% of **3f** was consumed within 15 ms in the reaction with a 0.23 mM solution of **2c** (Figure 3c). In all cases, k_{obs} was obtained by least-squares fitting of the function $A_t = A_0 e^{-k_{obs}t} + C$ to the time-dependent absorbances of the electrophiles in the particular range, and the second-order rate constants were obtained from the slopes of the k_{obs} versus [**2c**] plots (insets in Figure 3).

This behavior can be rationalized by the mechanism depicted in Scheme 3. The fast and incompletely proceeding reactions correspond to the attack of the electrophiles at the oxygen center of the enolate **2c**, while the slower reactions correspond to the attack at the β-carbon atom of **2c**. With the less Lewis acidic carbenium ions **3c**,**d** the equilibrium for the fast reaction, which yields the benzhydryl enol ethers **4**, is completely on the side of the reactants and attack at the oxygen of **2c** does not affect the slow process (C attack), which is then observed exclusively. The more Lewis acidic carbenium ion **3f**, on the other hand, is converted into the benzhydryl enol ether **4** to a large extent, before its quantitative conversion into **5**, the thermodynamically more stable product of C attack (Figure 3c).

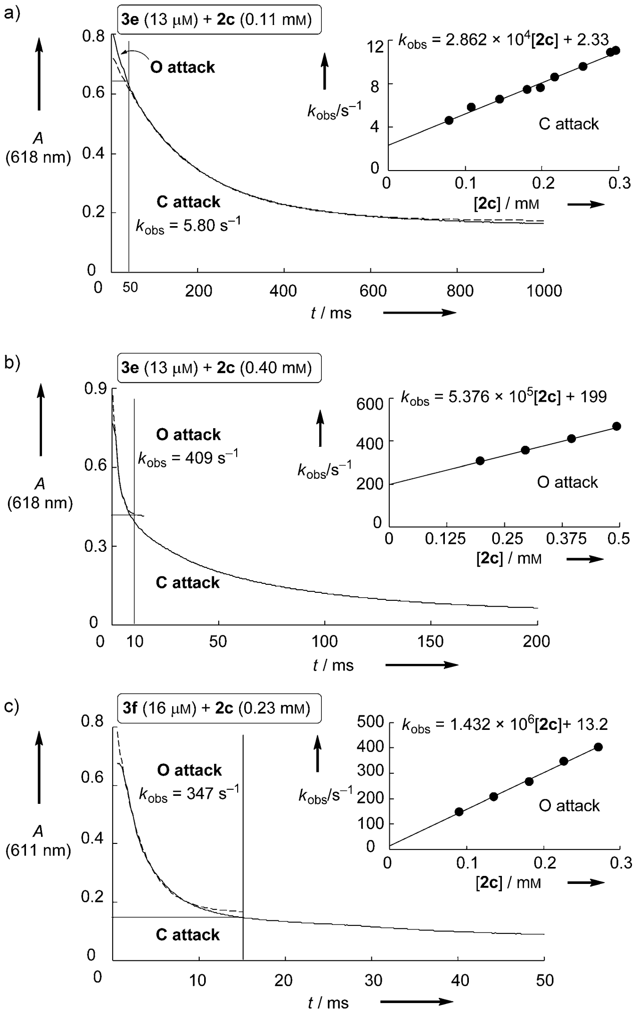
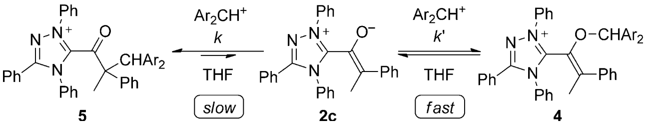


Figure 3. Decrease in the absorbances during the reactions of **3e**,**f** with **2c** in THF at 20 °C (solid lines) and determination of k_{obs} from the monoexponential fit of the absorbance (dashed lines). Insets: Plots of k_{obs} versus [**2c**] yield the second-order rate constants k and k' in Table 3.



Scheme 3. Ambident reactivity of the azolium enolate **2c**.

As shown by entry 5 in Table 2, the conversion of **4cf** to **5cf** is complete within 5 min. With **3e**, a borderline situation is encountered: At low concentrations of **2c** the equilibrium for O attack is on the side of reactants and one can observe the slow C attack (Figure 3a), whereas at higher concentrations of **3e** the faster O attack becomes observable (Figure 3b).

Figure 4 shows that the logarithms of the rate constants (lg$k$) for the reactions of **2a**,**b** with the carbenium ions **3a**–**d** (in THF) correlate linearly with the empirical electrophilicity parameters E (● and ◆ in Figure 4), indicating that Equation (1) is applicable and can be used to determine N and s_N

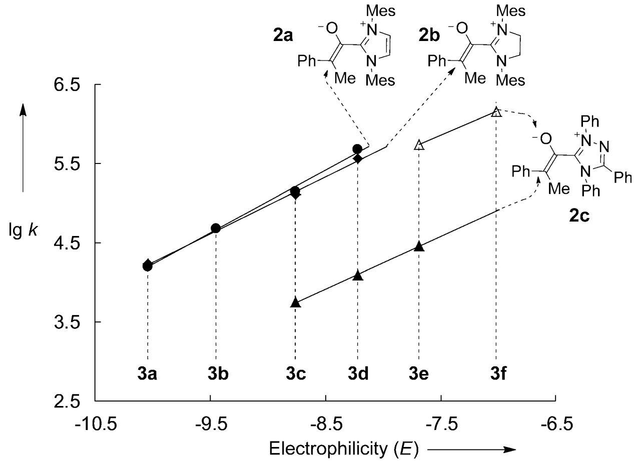
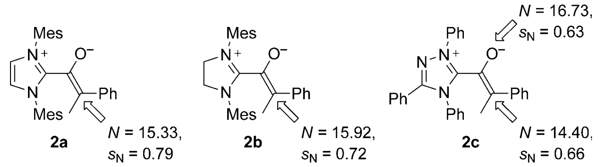


Figure 4. Plot of lg*k* (solid symbols, C attack) and lg*k*′ (open triangles, O attack) for the reaction of azolium enolates **2a–c** with the benzhydrylium ions **3** in THF at 20 °C.

parameters for the C-reactivity of the enolates **2a**,**b** which are listed in Scheme 4. Two correlation lines are found for **2c**, which correspond to the two sites of attack. Table 3 and Figure 4 show that the enolate oxygen in **2c** is approximately 20-times more reactive than carbon.

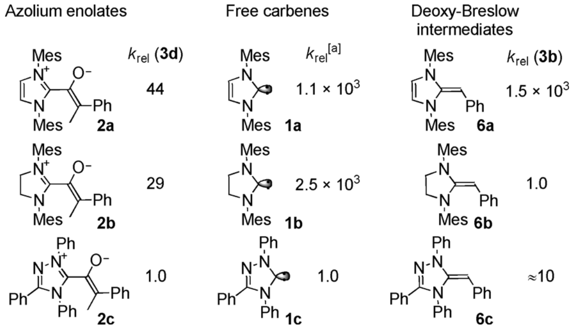


Scheme 4. *N* and s_N parameters as defined by Equation (1) for the azolium enolates **2a–c** in THF (for **2a** in DMSO: $N=14.40$, $s_N=0.64$).

Table 3 shows that the reactions of **2a** with the electrophiles **3** are about one order of magnitude slower in DMSO than in THF. Table 3, Figure 4, and Scheme 4 furthermore show that the azolium enolates **2a** and **2b** derived from imidazol-2-ylidene **1a** and imidazolidin-2-ylidene **1b**, respectively, have similar reactivities and are 50 times more nucleophilic than the triazole-derived enolate **2c** (C-nucleophilicity).

The different ranking of the nucleophilic reactivities of the carbenes ($\mathbf{1a} \approx \mathbf{1b} \gg \mathbf{1c}$, Scheme 5, middle)[11a] and the corresponding deoxy Breslow intermediates ($\mathbf{6a} \gg \mathbf{6c} > \mathbf{6b}$, Scheme 5, right)[11b] has been explained by inductive effects (reduced reactivities of **1c** and **6c**) and the fact that electrophilic attack at **6a** and **6c** is associated with the gain of aromaticity. Since the corresponding carbenes **1a** and **1c** are already aromatic, electrophilic attack at these carbenes is not associated with a gain of aromaticity.

As the azolium ring is perpendicular to the plane of the enolate double bond (Figure 1) the reactivity order $\mathbf{2a} \approx \mathbf{2b} > \mathbf{2c}$ (Scheme 5, left) is not related to the different aromaticities of the azolium rings and can be explained by the stronger inductive electron-withdrawing effect of the triazole ring.[11b]



Scheme 5. Relative reactivities of the free carbenes **1** (Ref. [11a]) and comparison with the corresponding azolium enolates **2** and deoxy Breslow intermediates **6** (Ref. [11b]) (THF, 20 °C).[a] k_{rel} towards 5′-(4-(dimethylamino)benzylidene)-[1,1′:3′,1″-terphenyl]-2′(5′*H*)-one.

In conclusion, we have synthesized and elucidated the structures of the azolium enolates **2a–c** and investigated the kinetics of their reactions with benzhydrylium ions. By using the rule of thumb that electrophile–nucleophile combinations may take place at room temperature when $E+N>-5$[14] and when the *N* values for the enolate carbon of the azolium enolates **2a–c** are between 14.4 and 15.9, we can explain their reactions with *N*-activated imines ($-11.5>E>-15.1$),[15a] azodicarboxylates ($-8.9>E>-12.2$),[15b] enones ($E\approx -18.8$),[15a] and 2,3,4,5,6,6-hexachlorocyclohexa-2,4-dienone ($E=-6.8$)[15c] as electrophilic partners.

From the kinetic data, one can derive that benzhydrylium ions attack the enolate oxygen of **2c** 20 times faster than the enolate carbon to give the benzhydryl ethers **4** as the initial products, which subsequently rearrange to the thermodynamically stable products of C attack (**5**). The higher nucleophilicity of the enolate oxygen, which is a consequence of the lower intrinsic barrier for O attack,[10] may also be the origin of the oxyanion steering effect (interaction of the enolate oxygen with the carbonyl carbon of acrolein), derived by Bode, Kozlowski et al. from quantum chemical calculations for the Diels–Alder reaction of a triazolium enolate with acrolein.[9g]

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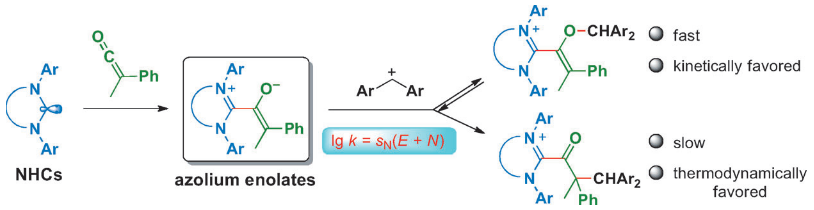
Communications

Organocatalysis



Oxygen versus carbon: Azolium enolates were generated by the reactions of N-heterocyclic carbenes (NHCs) with methyl phenyl ketene and characterized by X-ray crystallography. Kinetic studies show that the enolate oxygen is 20 times more nucleophilic than the carbon but under thermodynamic control exclusive C-addition products were formed.