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Structures and Reactivities of 2-Trityl- and 2-(Triphenylsilyl)pyrrolidine-Derived Enamines: Evidence for Negative Hyperconjugation with the Trityl Group

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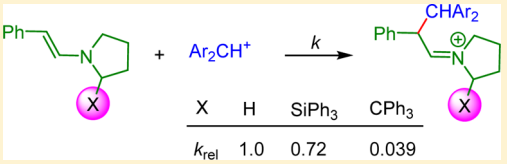
Supporting Information

ABSTRACT: X-ray structures of enamines and iminium ions derived from 2-tritylpyrrolidine (Maruoka catalyst) and 2-(triphenylsilyl)pyrrolidine (Bolm–Christmann–Strohmann catalyst) have been determined. Kinetic investigations showed that enamines derived from phenylacetaldehyde and pyrrolidine (R = H) or 2-(triphenylsilyl)pyrrolidine (R = $SiPh_3$) have similar reactivities toward benzhydryl cations Ar_2CH^+ (reference electrophiles), while the corresponding enamine derived from 2-tritylpyrrolidine (R = CPh_3) is 26 times less reactive. The rationalization of this phenomenon by negative hyperconjugative interaction of the trityl group with the lone pair of the enamine nitrogen is supported by the finding that the trityl group in the 2-position of the pyrrolidine increases the electrophilic reactivity of iminium ions derived from cinnamaldehyde by a factor of 14. The consequences of these observations for the rationalization of the reactivity of the Jørgensen–Hayashi catalyst (diphenylprolinol trimethylsilyl ether) are discussed.

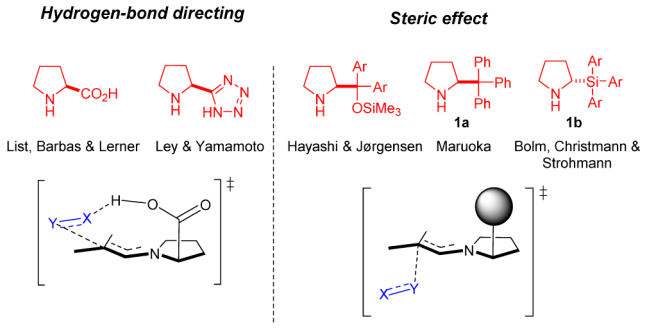


INTRODUCTION

Enamine formation has emerged as a powerful mode of activation in organocatalysis. This methodology is based on the use of chiral secondary amines as catalysts to transform achiral carbonyl derivatives into chiral enamines, which subsequently react with electrophiles to yield enantioenriched α-functionalized carbonyl compounds.[1] The design of effective catalysts for enamine activation has commonly been based on two factors: hydrogen bonding and steric shielding.[1,2]

The first factor, i.e., hydrogen bonding, was probed by List, Barbas, and Lerner for proline-catalyzed enantioselective intermolecular aldol reactions.[3] In this process, as well as in many other proline-catalyzed reactions, the carboxylic proton activates the electrophile through hydrogen bonding and directs the electrophile to the *Re* face of the enamine (Scheme 1).

Scheme 1. Hydrogen Bonding and Steric Control in Enamine Activated Reactions



The corresponding transition state was proposed by List and Houk to rationalize the enantioselectivity in proline-catalyzed reactions.[4] Inspired by this work, researchers have developed a large number of bifunctional catalysts, which were expected to operate by a mechanism similar to that for proline.[5]

The second factor, which has been employed for the development of other generations of organocatalysts, is the steric effect, and various pyrrolidines bearing a bulky substituent at the 2-position were used for enamine-activated reactions. Diphenylprolinol trimethylsilyl ether, for instance, also known as the Jørgensen–Hayashi catalyst, has been shown to be a powerful catalyst in enamine-activated reactions as well as in many other modes of activation (Scheme 1).[1b,g−i,6]

Substitution of the trimethylsiloxy group in the Jørgensen–Hayashi catalyst by a phenyl ring yields Maruoka's catalyst **1a**, which showed high efficiency in enamine-activated asymmetric benzoyloxylations and hydroxyaminations of aldehydes[7] but gave only moderate yields and diastereoselectivities in Michael additions of aldehydes to nitroolefins (Scheme 2).[8a]

Better yields and diastereoselectivities have been reported simultaneously by Bolm et al. as well as by Christmann, Strohmann, et al., when 2-silyl-substituted pyrrolidines were used.[8] In particular, 2-(triphenylsilyl)pyrrolidine (**1b**) and 2-(*tert*-butyldiphenylsilyl)pyrrolidine provided high diastereo- and enantioselectivities.[8a,c]

Christmann et al. have attributed the higher efficiency of **1b** compared with **1a** to the larger steric effect (C–Si longer than

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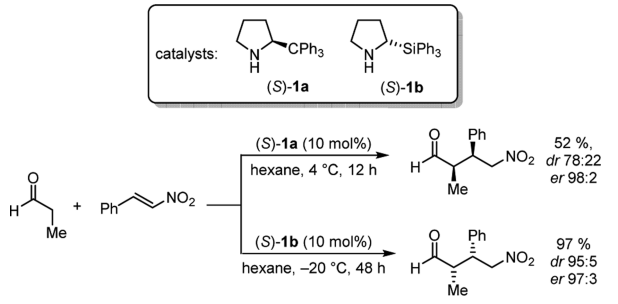
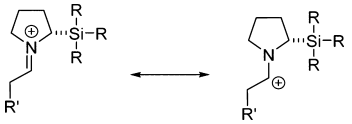
Scheme 2. Michael Addition of Propionaldehyde to Nitrostyrene Catalyzed by the Pyrrolidines 1a,b[8a]



C–C) and higher polarization of the C–Si bond in comparison to the C–C bond.[8a] MP2 calculations by Mersmann, Raabe, and Bolm showed that β-trimethylsilyl-substituted iminium ions, analogues to those formed from **1b** and aldehydes (Scheme 3), are stabilized by the interaction of the Si–C σ bond with the π^* orbital of the C=N double bond.[9]

Scheme 3. Resonance Structures of β-Silyl-Substituted Iminium Ion



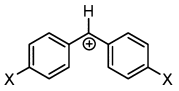
We now report on structural and kinetic investigations of the role of trityl and triphenylsilyl substituents on the catalytic activities of the corresponding pyrrolidine derivatives.

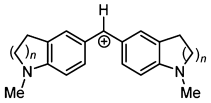
In previous work, we have shown that the reactivities of benzhydrylium ions (Table 1), quinone methides, Michael acceptors, and iminium ions with n, σ, and π nucleophiles can be described by the linear free energy relationship (1), where s_N and N are solvent-dependent nucleophile-specific parameters and E is an electrophilicity parameter.[10]

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

By studying the rates of various electrophile–nucleophile combinations, we have been able to establish comprehensive reactivity scales for electrophiles and nucleophiles covering more than 35 orders of magnitude.[11] This methodology has now been employed to characterize the nucleophilicities of the enamines **3** derived from phenylacetaldehyde (**2**) and the pyrrolidines **1a,b** and to compare them with that of the corresponding enamine derived from the Jørgensen–Hayashi catalyst.

Table 1. Benzhydrylium Ions 4a–g Employed in This Work and Their Electrophilicity Parameters E



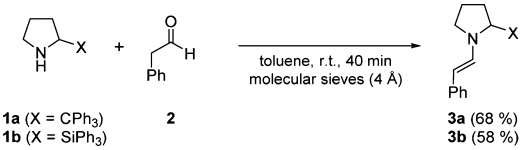
Benzhydrylium Ion		E[a]
4a	X = NPh_2	–4.72
4b	X = $N(CH_2CH_2)_2O$	–5.53
4c	X = N(Ph)(Me)	–5.89
4d	X = NMe_2	–7.02
4e	X = $N(CH_2)_4$	–7.69
4f (n = 2)		–8.22
4g (n = 1)		–8.76

[a]Electrophilicities E were taken from ref 10b.

RESULTS AND DISCUSSION

Synthesis of the Enamines 3a–c. The enamines **3a,b** were obtained as colorless crystals by condensation of the racemic amines **1a,b** and phenylacetaldehyde **2** in dry toluene in the presence of molecular sieves (4 Å), as shown in Scheme 4.[12]

Scheme 4. Synthesis of the Enamines 3a,b



1a (X = CPh_3) **1b** (X = $SiPh_3$) **2** **3a** (68 %) **3b** (58 %)

Single crystals suitable for X-ray diffraction were grown by vapor diffusion of *n*-pentane into dichloromethane solutions of **3a,b**.[13] Enamines **3a,b** both have *E*-configured double bonds and adopt the *s-trans* conformation, as shown in Figure 1.

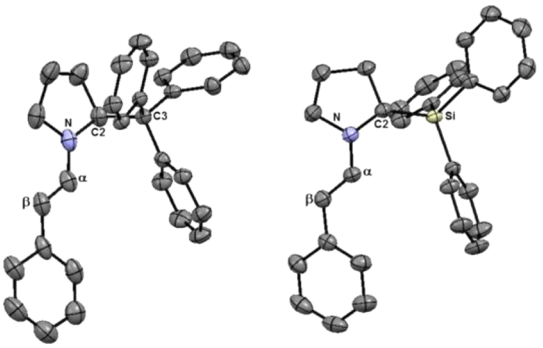


Figure 1. X-ray structures of the enamines **3a** (left) and **3b** (right).

The olefinic bonds (C^α=C^β) of both enamines **3a,b** have comparable bond lengths, 1.347 and 1.339 Å, respectively, showing that the substituents at the 2-position of the pyrrolidine ring do not significantly affect the structures of the enamines. Accordingly, the Dunitz parameters[14] for the enamine nitrogen, which is defined as the distance between the nitrogen and the center of the plane defined by the three nitrogen ligands, were measured to be 0.04 and 0.09 Å, respectively, indicating that both enamines **3a,b** are almost planar.

The NOESY spectra of **3a,b** (in $CDCl_3$) reveal strong interactions between α-H and the 2-H as well as between β-H and 5-H (see numbering in Table 2) and thus confirm that the *s-trans* conformations observed in the crystals also dominate in solution.

Though correlations between ^{13}C NMR chemical shifts and charge densities have to be interpreted with caution, the distance between the substituents X in the 2-position and C^β is so large that the increased shielding of C^β in the order **3a** < **3c** < **3b** might be assigned to the relative electron densities on C^β.

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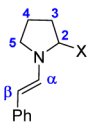
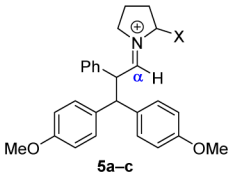
Table 2. NMR Chemical Shifts for the Enamines 3a–c (in $CDCl_3$) and the Corresponding Iminium Ions 5a–c (in CD_3CN)



3a–c



5a–c

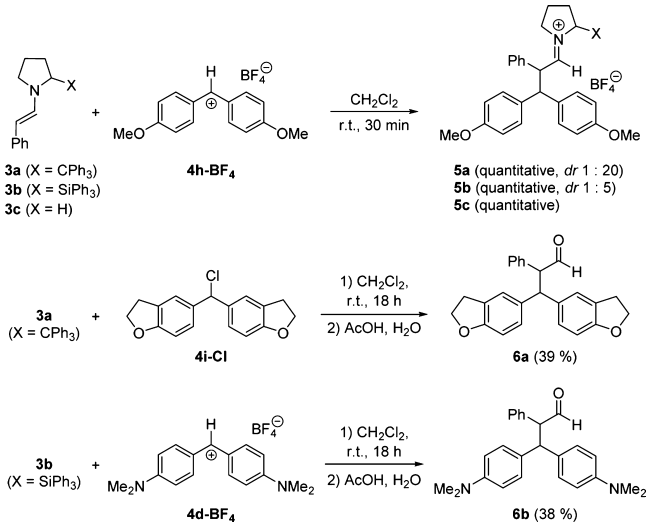
compd	X	$\delta(C^{\alpha},\mathbf{3})$	$\delta(C^{\beta},\mathbf{3})$	$\delta(C^{\alpha},\mathbf{5})$
3a or **5a**	CPh_3	136.9	98.0	178.0
3b or **5b**	$SiPh_3$	136.9	97.1	174.0
3c or **5c**	H	135.8[a]	97.4[a]	176.6

[a]From ref 12.

The differences are so small, however, that ground state effects in enamines **3a–c** cannot explain the different catalytic activities of the corresponding pyrrolidines.

Products of the Reactions of the Enamines 3a,b with Benzhydrylium Ions. Combination of the enamines **3a–c** with the dimethoxybenzhydrylium tetrafluoroborate **4h-BF_4** in dichloromethane at 20 °C resulted in quantitative formation of iminium salts (**5a–c**)-**BF_4** (Scheme 5), which crystallized from a mixture of dichloromethane and *n*-pentane or acetone, yielding crystals suitable for X-ray diffraction analyses (Figure 2).[15]

Scheme 5. Reactions of the Enamines 3a–c with the Electrophiles 4d,h,i



The iminium ions formed analogously from **3a** and the benzhydryl chloride **4i-Cl** and from the combination of **3b** and the benzhydrylium tetrafluoroborate **4d-BF_4** were not isolated but hydrolyzed with aqueous acetic acid to give the corresponding aldehydes **6a,b** (Scheme 5).

The X-ray structures depicted in Figure 2 show that the major diastereoisomers of the iminium ions **5a,b** have a *syn* configuration and an *E* configuration about the C=N bond. While lengthening of the C–Si bond from 1.889 Å in enamine **3b** to 1.924 Å in iminium **5b** can be explained by the interaction of the C–Si σ bond with π^* of the C=N bond in **5b** (see above), the expected complementary lengthening of the C=N bond in **5b** due to electron donation into the π^*_{CN} orbital is not observed, as the C=N bond lengths are almost the same in **5a** (1.273 Å), **5b** (1.278 and 1.272 Å), and **5c** (1.271 Å).

Further evidence for the interaction of σ_{C-Si} with π^*_{CN} can be derived from the ^{13}C NMR chemical shifts of C^{α} of the iminium ions **5** (Table 2). While $\delta(C^{\alpha})$ is exactly the same in enamines **3a,b**, C^{α} is shifted to high field by 4 ppm in the silyl-substituted iminium ion **5b** in comparison to the trityl-substituted analogue **5a**. As the nitrogen atoms are coordinated in a trigonal-planar fashion in enamines **3** (Figure 1) and in the iminium ions **5** (Figure 2), geometrical differences cannot account for the differences in chemical shifts. The observation that $\delta(C^{\alpha})$ is more shielded in **5b** than in **5a,c** can thus be assigned to the electron-donating effect of the σ_{C-Si} bond.[9]

Kinetics. All kinetic investigations were carried out in dichloromethane at 20 °C by following the disappearance of the colored benzhydrylium ions **4a–g** in the presence of more than 10 equiv of the enamines **3a–c** (first-order conditions). The first-order rate constants k_{obs} were obtained by least-squares fitting of the single exponential $A_t = A_0 \exp(-k_{obs}\, t)$ to the decays of the UV–vis absorbances of the electrophiles.

Plots of k_{obs} (s^{-1}) against the concentrations of the nucleophiles **3a–c** were linear, as exemplified for the reaction of **3a** with **4c** in Figure 3. Negligible intercepts for these plots were found for the reactions which proceeded quantitatively, while positive intercepts were found for the reactions which led to an equilibrium (for details see the Supporting Information). In both cases, the second-order rate constants k_2 were extracted from the slopes of the plots of k_{obs} against $[\mathbf{3}]_0$ (Table 3).

Figure 4 shows linear correlations between the logarithms of the second-order rate constants (log k_2) and the previously published electrophilicity parameters *E* of the benzhydrylium ions, as required by eq 1. The slopes of the correlation lines yield the nucleophile-specific sensitivity parameters s_N, and the intercepts on the abscissa give the nucleophilicity parameters *N*, which are given in Table 3.

The similar values of the slopes ($0.93 < s_N < 1.06$) of the correlation lines imply that the relative nucleophilicities of the enamines **3a–c** are only slightly affected by the reactivities of the electrophilic reaction partner.

Lewis Basicities of the Enamines 3a–c. As the reactions of the enamines **3a–c** with some benzhydrylium ions proceeded incompletely, we have also studied the corresponding equilibrium constants by UV–vis spectroscopy.

Assuming proportionality between the absorbances and the concentrations of the benzhydrylium ions, the equilibrium constants for the reactions (eq 2) can be determined from the initial absorbances (A_0) of the benzhydrylium ions and the absorbances at equilibrium (A) according to eq 3 and are given in Table 4.

$$Ar_2CH^+ + Nu \underset{CH_2Cl_2}{\overset{K}{\rightleftharpoons}} Ar_2CH\text{-}Nu^+ \qquad (2)$$

$$K = \frac{[Ar_2CH\text{-}Nu^+]}{[Ar_2CH^+][Nu]} = \frac{A_0 - A}{A[Nu]} \qquad (3)$$

Equilibrium constants for the reactions of **3b** with the benzhydrylium ions **4e–g** could be determined in this way, and the ratio of the equilibrium constants for the reactions of **3b** with **4e** and **4g** (K_{4e}/K_{4g} = 3.70; $\log(K_{4e}/K_{4g})$ = 0.57) was in good agreement with that derived from a statistical treatment of the equilibrium constants for the reactions of these two

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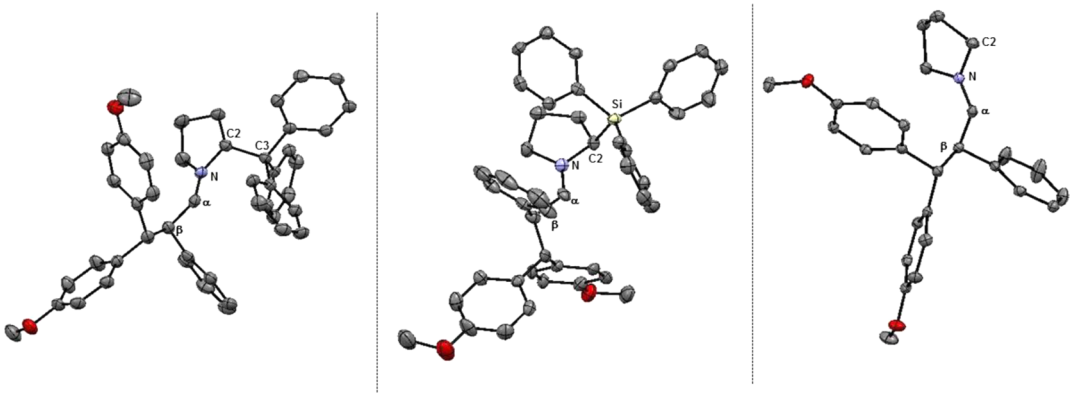

Figure 2. X-ray structures for the iminium ions **5a** (left), **5b** (center), and **5c** (right). Hydrogens and the counterion BF_4^- are omitted for clarity.

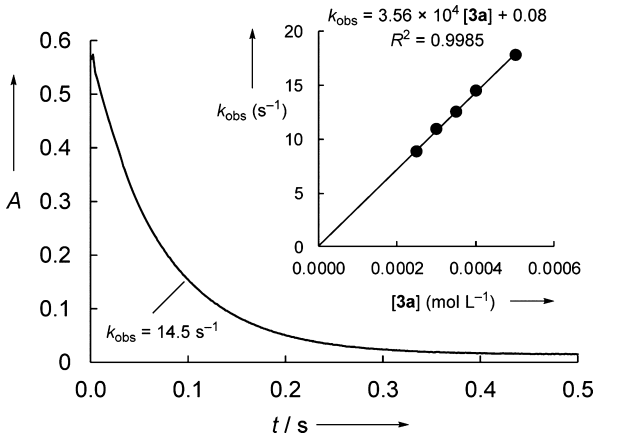

Figure 3. Exponential decay of the absorbance A at 613 nm during the reaction of **4c** (1.12×10^{-5} M) with **3a** (4.01×10^{-4} M). Inset: plot of the rate constant k_{obs} versus [**3a**] (20 °C in CH_2Cl_2).

Table 3. Second-Order Rate Constants k_2 for the Reactions of the Benzhydrylium Salts 4a–g with the Enamines 3a–c in CH_2Cl_2 at 20 °C

enamine	electrophile	k_2/M^{-1} s^{-1}	N, s_N
3a (X = CPh_3)	**4a**	7.66×10^5	10.19, 1.06
	4b	6.40×10^4	
	4c	3.56×10^4	
	4d	2.56×10^3	
3b (X = $SiPh_3$)	**4d**	4.71×10^4	11.77, 0.98
	4e	8.97×10^3	
	4f	3.25×10^3	
	4g	8.77×10^2	
3c (X = H)	**4c**	8.48×10^5 [a]	12.26, 0.93
	4d	6.60×10^4	
	4e	1.86×10^4	

[a]This value was determined under second-order conditions (small excess of **3c**).

benzhydrylium with a large number of Lewis bases (ΔLA = 0.70; see Table 4). For that reason, the difference of the Lewis acidities of **4e** and **4d** (ΔLA = 1.16) could also be used to calculate the equilibrium constant for the reaction of **3b** with **4d** (8.02×10^4 M^{-1}), which is too large to be directly measured.

From the ratio of the equilibrium constants for the reactions of **3a**,**b** with **4d**, we can now derive that the triphenylsilyl-substituted enamine **3b** is a 76 times stronger Lewis base than

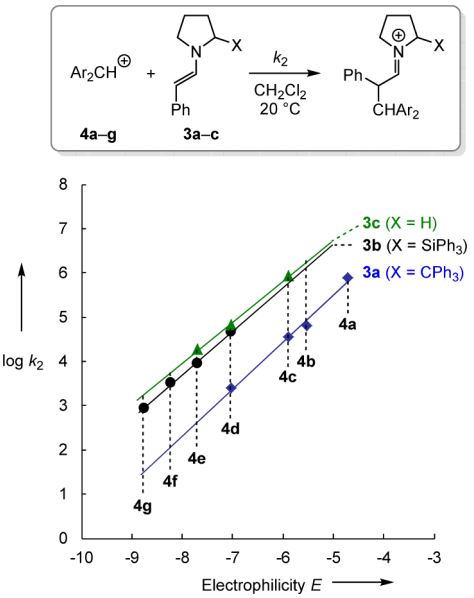

Figure 4. Plots of log k_2 for the reactions of the enamines **3a–c** with the benzhydrylium ions **4a–g** versus their electrophilicity parameters E in CH_2Cl_2 at 20 °C.

Table 4. Equilibrium Constants K (M^{-1}) and Reaction Free Energies $\Delta G°$ (kJ mol^{-1}) for the Reactions of the Enamines 3a–c with the Benzhydrylium Ions 4 in CH_2Cl_2 at 20 °C

enamine	Ar_2CH^+	LA[a]	K	$\Delta G°$
3a (X = CPh_3)	**4d**	−9.30	1.05×10^3	−17.0
3b (X = $SiPh_3$)	**4d**	−9.30	(8.02×10^4)[b]	(−27.5)
	4e	−10.46	5.55×10^3	−21.0
	4f	−10.92	1.63×10^3	−18.0
	4g	−11.16	1.50×10^3	−17.8
3c (X = H)	**4e**	−10.46	1.87×10^3	−18.4

[a]LA = Lewis acidity derived from equilibrium constants for the reactions of *p*- and *m*-substituted benzhydrylium ions with a variety of Lewis bases (pyridines, phosphines, etc.). ΔLA values equal Δ(log K) in dichloromethane at 20 °C.[16] [b]Calculated as described in the text.

the trityl-substituted enamine **3a**. The thermodynamic effect of the triphenylsilyl stabilization is thus 4 times larger than the kinetic effect derived from the relative rates of the reactions with **4d** (k_{3b}/k_{3a} = 18, Table 3).

While the reaction of **4e** with the triphenylsilyl-substituted enamine **3b** is 2 times slower than the corresponding reaction

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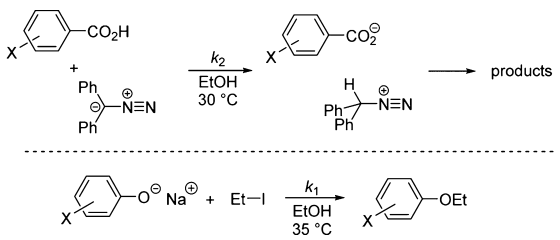
with the parent **3c** (Table 3), the equilibrium constants for these reactions showed that the triphenylsilyl-substituted enamine **3b** is an about 3 times stronger Lewis base than the parent enamine **3c** (Table 4), indicating that the hyperconjugative stabilization of the triphenylsilyl-substituted iminium ion is not yet effective in the transition state of the electrophilic additions to **3b**.

Origin of the Trityl Effect. Why is the trityl-substituted enamine **3a** approximately 26 times less reactive than the parent enamine **3c**? Since the planar arrangement of the nitrogen substituents in **3a** was shown by X-ray analysis (Figure 1), we can exclude perturbation of the enamine resonance as the origin of the low reactivity of **3a**. Shielding will block one face of the enamine **3a** and can account for a reduction of the nucleophilic reactivity by a factor of 2.

In order to rationalize the remaining effect, we must conclude that the trityl group acts as an electron acceptor in **3a**. However, when standard reactions to determine Hammett constants had been employed, i.e., reactions of substituted benzoic acids with diphenyldiazomethane or alkylation of phenolates with iodoethane, Hammett σ constants close to 0 were found (Table 5).[17] Consequently, the trityl group was considered to be an electronically neutral substituent, comparable to H.

Table 5. Determination of the Hammett σ Constant for the Trityl Group[a]



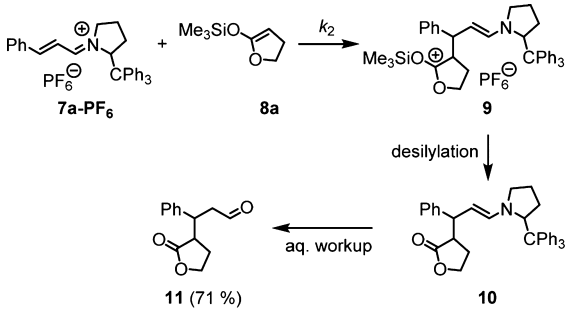
X	$k_2/M^{-1}\ s^{-1}$	k_1/s^{-1}
m-CH_3	1.54×10^{-2}	7.70×10^{-4}
H	1.83×10^{-2}	6.48×10^{-4}
m-Ph_3C	1.85×10^{-2}	7.65×10^{-4}
p-Ph_3C	2.01×10^{-2}	7.43×10^{-4}
p-Cl	3.12×10^{-2}	
p-Br	3.21×10^{-2}	3.63×10^{-4}
m-Cl		2.90×10^{-4}
p-NO_2	8.80×10^{-2}	5.08×10^{-5}

[a]Data from ref 17.

If, on the other hand, the trityl group really acted as an electron acceptor in enamine **3a**, and thus would be the major reason for the reduced nucleophilicity of **3a**, the opposite effect should be operating in iminium ions: i.e., iminium ions derived from 2-tritylpyrrolidine would be expected to be more electrophilic than the corresponding iminium ions derived from the parent pyrrolidine.

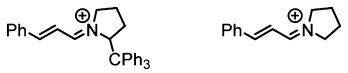
Unfortunately, we have not been able to synthesize a persistent iminium ion from **1b** and phenylacetaldehyde. It was possible, however, to prepare the cinnamaldehyde-derived iminium ion **7a** in analogy to a procedure described by Gilmour and co-workers.[18] The reaction of **7a-PF$_6$** with the cyclic ketene acetal **8a** gave 71% of the conjugate addition product **11** after aqueous workup (Scheme 6), in analogy to our earlier studies with other cinnamaldehyde-derived iminium ions.[19]

Scheme 6. Reaction of the Trityl-Substituted Iminium Ion 7a with the Silyl Ketene Acetal 8a in Dichloromethane at 20 °C



Kinetic investigations of the reactions of **7a** with the ketene acetals **8a,b**, following the previously described procedure,[19a] showed that **7a** is indeed about 10 times more reactive than the iminium ion **7c** (Table 6).

Table 6. Comparison of the Electrophilic Reactivities of the Iminium Ions 7a,c ($k_2/M^{-1}\ s^{-1}$, in CH_2Cl_2 at 20 °C)

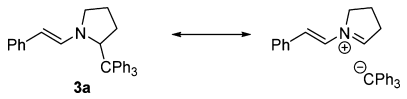


Iminium Ions	Nucleophiles	
	Me$_3$SiO, O **8a**	Me$_3$SiO, O **8b**
7a	1.00×10^3	4.81×10^1
7c	$1.30 \times 10^{2\,a}$	3.49[a]

[a]From ref 19a.

These observations prompted us to rationalize the low nucleophilic reactivity of the trityl-substituted enamine **3a** by a negative hyperconjugative effect, as depicted in Scheme 7.[20]

Scheme 7. Negative Hyperconjugation in the Trityl-Substituted Enamine 3a



This interaction, which reduces the nucleophilic reactivity of **3a**, is on the other hand a product-stabilizing factor in the formation of the enamine **9** by nucleophilic attack at the iminium ion **7a** (Scheme 6) and thus explains the increase of iminium reactivity by trityl substitution in the pyrrolidine.

Our postulate of a negative hyperconjugative effect of the trityl group is not supported by geometrical parameters, as the distance of the trityl group from the pyrrolidine ring (C3−C2 in Figures 1 and 2) is almost the same in the enamine **3a** (1.574 Å) as in the iminium ion **5a** (1.577 Å). Probably, the negative hyperconjugative effect, which may explain the approximately 5 kJ mol^{-1} difference in activation energies, is too small to be visible in geometrical changes.

These observations have an important consequence for the interpretation of the reactivities of iminium ions and enamines derived from the Jørgensen−Hayashi catalyst.[12,19] As shown in Table 7, the $CPh_2(OSiMe_3)$ substituent of the Jørgensen−

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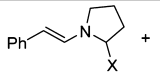
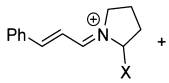
Table 7. Comparison of the Effects of the $CPh_2(OSiMe_3)$ Substituent (Jørgensen–Hayashi Catalyst) and CPh_3 (Maruoka Catalyst) on the Nucleophilicities of Enamines and Electrophilicities of Iminium Ions (k_{rel} in CH_2Cl_2 at 20 °C)

Reaction	X = H	CPh_3	$CPh_2(OSiMe_3)$
 + **4d**	1.0	1/26	1/28 [a]
 + **8b**	1.0	12	19 [b]

[a]Calculated from $k = 2.33 \times 10^3$ M^{-1} s^{-1} for the reaction of the 2-($CPh_2(OSiMe_3)$)-substituted enamine with **4d** in MeCN.[12] [b]Calculated from $k = 67.0$ M^{-1} s^{-1} for the reaction of the 2-($CPh_2(OSiMe_3)$)-substituted iminium ion with **8b**.[19a]

Hayashi catalyst deactivates the enamine only slightly more than the CPh_3 substituent in the Maruoka catalyst. Vice versa, the $CPh_2(OSiMe_3)$ group has only a slightly larger activating effect on the iminium ion than the trityl group.

For these reasons our earlier explanation of the $CPh_2(OSiMe_3)$ effect by the electronegativity of oxygen[12] can only account for a minor fraction of the effect and we now suggest that negative hyperconjugation of the $CPh_2(OSiMe_3)$ group also accounts for the reactivities of the intermediates of "Jørgensen–Hayashi catalyzed" reactions.

CONCLUSION

The X-ray structures of the enamines **3a,b** derived from the reactions of phenylacetaldehyde with 2-tritylpyrrolidine (**1a**) and 2-(triphenylsilyl)pyrrolidine (**1b**), respectively, indicate almost perfect planarity of the enamine nitrogen and closely resemble that previously reported[21] for the analogous enamine derived from the Jørgensen–Hayashi catalyst.

Equilibrium measurements showed that the hyperconjugative interaction of σ_{C-Si} with π^*_{CN} increases the Lewis basicity of enamine **3b** by a factor of 3 relative to that of the parent compound **3c**, corresponding to a factor of 6 if the reduced symmetry (two faces accessible in **3c**) is taken into account. This interaction is not yet effective in the transition states of the electrophilic additions, as the silylated enamine **3b** reacts with the same rate as one face of the enamine **3c** (Figure 5).

Though the trityl group had previously been reported to be an electronically neutral substituent with a Hammett substituent constant of $\sigma \approx 0$,[17] the trityl group behaves as an electron-withdrawing substituent at the 2-position of pyrrolidine, which we explain by negative hyperconjugation. This effect rationalizes why the trityl-substituted enamine **3a** is 26 times less nucleophilic than the parent analogue **3c** and the trityl substituted iminium ion **7a** is 8–14 times more electrophilic than the parent analogue **7c**.

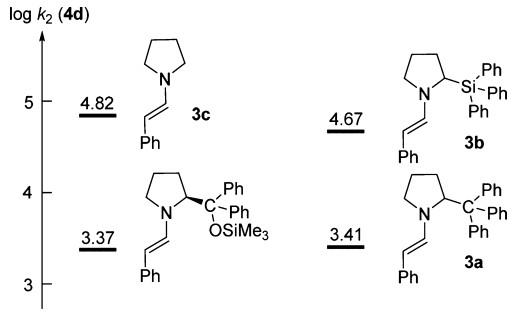


Figure 5. Reactivities of the enamines **3a–c** toward **4d** (data from Table 3 and ref 12).

Comparison of the reactivities of the 2-tritylpyrrolidine-derived enamine **3a** and the 2-tritylpyrrolidine-derived iminium ion **7a** with the corresponding Jørgensen–Hayashi pyrrolidine-derived analogues (Table 7) indicates that the CPh_3 group and the CPh_2OSiMe_3 group exert similar electronic effects on the enamine and iminium intermediates of organocatalytic reactions. This similarity rules out specific interactions between the $OSiMe_3$ group and the π system of the intermediate enamines or iminium ions.

For that reason, the high stereoselectivity observed in reactions catalyzed by the Jørgensen–Hayashi pyrrolidine can be entirely assigned to a steric effect. Seebach and co-workers have demonstrated that the enamines and iminium ions derived from 2-(CPh_2OSiR_3)-substituted pyrrolidines preferred synclinal-exo conformations, in which the silyloxy substituent shields one face of the trigonal reaction center.[21a,b] Thus, steric effects can also explain why even higher stereoselectivities have been observed when the $OSiMe_3$ substituent was replaced by the $OSiPh_2Me$ group.[21b,e,22] While 2-tritylpyrrolidine (**1a**) catalyzed stereoselective additions of aldehydes to nitrostyrenes less efficiently than the Jørgensen–Hayashi catalyst,[8c] high enantioselectivities for **1a**-catalyzed reactions have so far only been reported for α-benzoyloxylations and hydroxyaminations of aldehydes.[7] It is not clear whether the small number of reports using **1a** as an organocatalyst[7,8a,c,23] is due to its less convenient accessibility[7a,24] or its poorer performance in comparison to the Jørgensen–Hayashi catalyst in other enamine activated reactions.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving experimental procedures, product characterization, kinetic experiments, all NMR spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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