Reactivity of Imines Towards 3-Trifloxypropeniminium and Propyniminium Triflates

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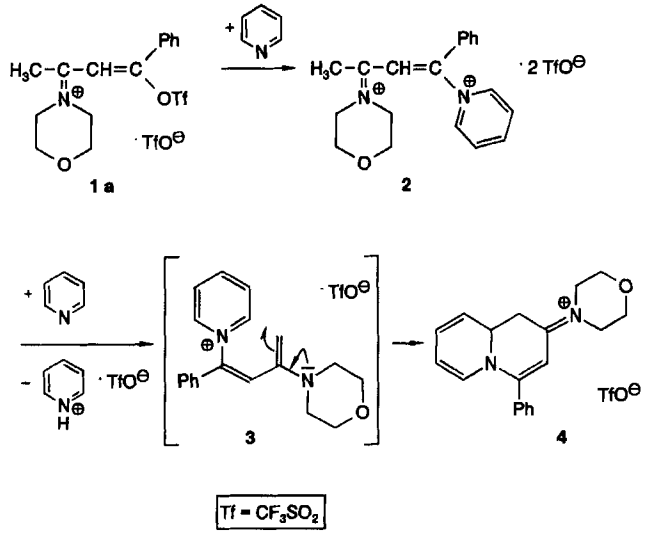
The imines **5** and **11** react with 3-trifloxypropeniminium triflates **1a–d** to afford the heterocyclic iminium salts **8**, **9**, **13**, **15**, and **17**, respectively, or the propeniminium salt **21**. Propyniminium triflates **22**, **24** react with imines by initial conjugated addition, followed by a reaction sequence analogous to the one observed for the reactions of **1a–d** with imines. Thus, salt **22** and aldimine **5b** yield the propeniminium salt **21**, while **24** reacts with tri-*tert*-butylazete **25** to afford the semicyclic vinamidinium salt **28**. A crystal structure analysis of **28** is performed.

In earlier papers we have reported[1,2] that the 3-trifloxypropeniminium triflate **1a** reacts with an equimolar amount of pyridine to give mainly the dicationic salt **2**, whereas only the dihydro-2*H*-quinolizine **4** is obtained when two equivalents of pyridine are used (Scheme 1). In the reaction sequence leading to **4**, pyridine acts first as a nucleophile (**1**→**2**), then as a base that generates the dienamine **3** from **2**. The latter intermediate undergoes a spontaneous cyclization to salt **4**. When pyridine is replaced by quinoline or isoquinoline, an analogous reaction sequence is observed.

Scheme 1



It is the imine functionality of pyridine and its benzo derivatives that is involved in these transformations, and therefore we anticipated that simple, "typical" imines would exhibit a similar reactivity towards 3-trifloxypropeniminium salts. In this paper, we present the results of our pertinent investigations. Furthermore, we report on similarities with and differences from analogous reactions of imines with propyniminium salts that are readily available from 3-trifloxypropeniminium salts by base-assisted[3] or thermal[3,4] β-elimination of triflic acid.

Results

The 1-methyl-substituted 3-trifloxypropeniminium salt **1a** reacts smoothly with two equivalents of aldimines **5a–f** to provide the (2,3-dihydropyridin-4(1*H*)ylidene)morpholinium triflates **8a–f** (Scheme 2). The separation of these semicyclic vinamidinium salts from the accompanying salts **5**·HOTf (HOTf = triflic acid) is easily achieved by extracting the latter from the reaction solution into an aqueous solution of $NaHCO_3$; this procedure leaves the salts **8** unaltered in the organic phase. By analogy with **1a**, the salt **1b**, bearing methyl groups at both ends of the propeniminium unit, reacts with imine **5a** to afford the pyrrolidinium triflate **9**.

The formation of **8** and **9** demonstrates that the aldimines **5** exhibit the same reactivity towards 3-trifloxypropeniminium salts **1** as pyridine and its benzo derivatives. In contrast to the 3-pyridinio-propeniminium bistriflate **2**[1], however, the dicationic salt **6** resulting from the S_N reaction between **1a** and **5** cannot be isolated, not even when the reactants are supplied in a 1:1 ratio. Obviously, **6** is readily deprotonated by still available imine **5** with formation of the intermediate **7**. The instantaneous 1,6-cyclization of the latter to the semicyclic vinamidinium salt **8** can be simply classified as an electrocyclic process, but it may also be considered as a Mannich cyclization reaction[5], here with an enamine function as the internal nucleophile. A completely analogous reaction sequence accounts for the formation of **9**.

The ^1H- and ^{13}C-NMR chemical shifts of the salts **8** and **9** (Table 1) generally agree well with the corresponding values of **4** and structurally related 1,9a-dihydro-2*H*-quinolizi-

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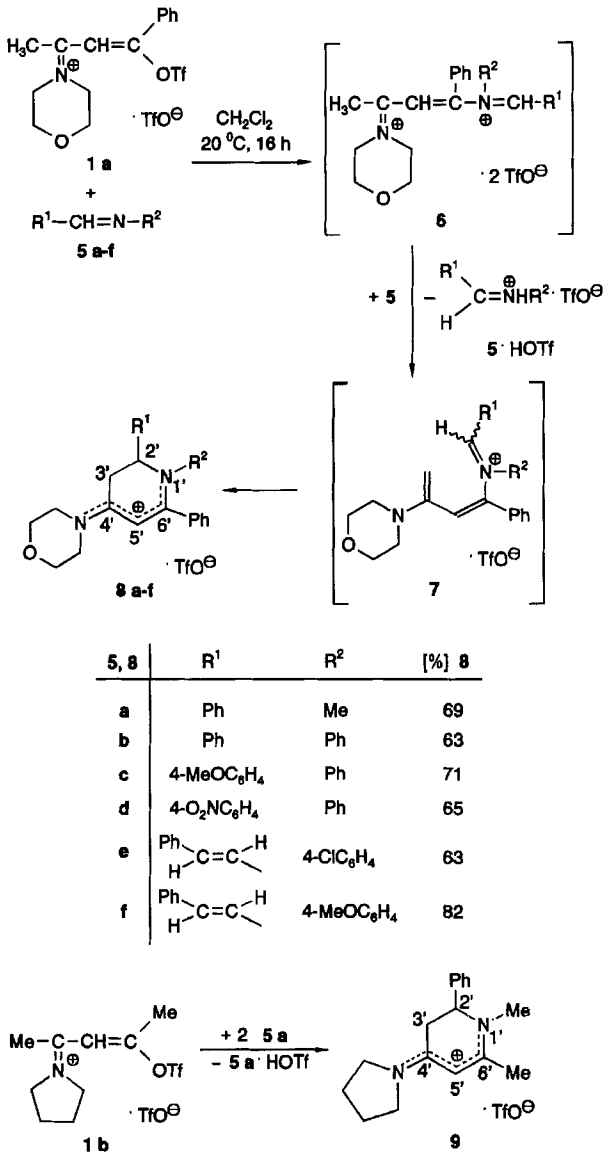
Scheme 2

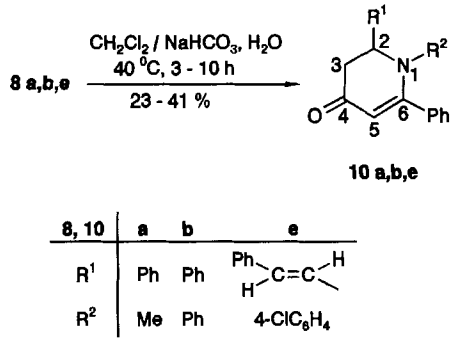


5, 8	R^1	R^2	[%] 8
a	Ph	Me	69
b	Ph	Ph	63
c	4-MeOC$_6$H$_4$	Ph	71
d	4-O$_2$NC$_6$H$_4$	Ph	65
e	Ph(H)C=C(H)	4-ClC$_6$H$_4$	63
f	Ph(H)C=C(H)	4-MeOC$_6$H$_4$	82

nium triflates[2]. Although some π-bond delocalization in the vinamidinium structural moiety of **4** has been found[2], the bond structure shown in the formula still prevails. This situation is attributed mainly to a better stabilization of the positive charge by the morpholine nitrogen than by the other nitrogen atom. Based on this observation, the assignments for C-4′ and C-6′ in the ^{13}C-NMR spectra of **8a** and **9** have been made in such a way that the resonance at lower field is attributed to C-4′. For **8b–f**, the chemical shift differences for these two carbon atoms appear not to be large enough, however, to allow a reliable assignment.

The conversion of salts **8** and **9** into 2,3-dihydro-4(1*H*)-pyridinones **10** by hydrolytic cleavage of the exocyclic iminium function proceeds only reluctantly (**8a,b,e**) or not at all (**8c,d,f,9**) (Scheme 3). Hydrolysis with aqueous $NaHCO_3$ in a two-phase system at reflux temperature has been found to give the best results. Spectral data of **10a,b,e** are given in Table 2.

Scheme 3



8, 10	a	b	e
R^1	Ph	Ph	Ph(H)C=C(H)
R^2	Me	Ph	4-ClC$_6$H$_4$

2,3-Dihydro-4(1*H*)-pyridinones can also be obtained in one or two steps from 1,3-diketones and Schiff bases in the presence of KNH_2 in liquid ammonia[6]. However, the yields are in general very low (e.g. 2.7% for **10b**), and the scope of this transformation appears to be rather limited. In this regard, our synthesis of **10a,b,e** represents a viable alternative that also starts from a 1,3-diketone (**1a** is prepared from benzoylacetone via the enamino ketone[7], Scheme 4). In this four-step synthesis, all steps but the last one proceed in good to high yield.

In contrast to the aldimines **5**, the reaction of the tautomerizable[8] ketimine **11** with the iminium salts **1a,c,d** affords the 5,6,7,8-tetrahydroquinolinium triflates **13** (Scheme 5). In these cases, the nucleophilic substitution of the trifloxy group in **1** is followed by a deprotonation that generates the salt **12**. When starting from **1c** and **11**, the product first isolated is the vinamidinium salt **12c**, obtained as a 1:1 mixture of two diastereomers. Upon heating for six hours in boiling acetonitrile, **12c** cyclizes to the quinolinium derivative **13c** with elimination of morpholine. When **1a** or **1d** are combined with **11**, the cyclization to **13a,d** occurs already at room temperature, and the vinamidinium salts **12a,d** cannot be isolated. The quinolinium derivative **13c** (perchlorate) has already been prepared from the corresponding 5,6,7,8-tetrahydrobenzopyrylium perchlorate and aniline[9].

The NMR spectra of the vinamidinium triflate **12c** have to be recorded at 0°C, since coalescence phenomena occur at 30°C. They cause broad, little structured signals in the ^{1}H-NMR spectrum for all but the morpholine protons and are obviously due to a rather easy *E/Z* isomerization around the C-1′–C-2′–C-3′, and C-3′–N′ bonds. A configurational assignment for the two diastereomers of **12c** has not been made; with regard to the dynamic processes mentioned, it is unimportant with respect to the subsequent reaction leading to **13** anyway. Some assignments of the ^{13}C-NMR signals of **13** (see Experimental) are based on comparisons with data for related pyridinium salts[10–12], since literature data and/or assignments for similar tetrahydroquinolinium salts[9,13] are not available.

The reaction of 3-trifloxypropeniminium salt **1b** with ketimine **11** represents a borderline case, since both the 5,6,7,8-tetrahydroquinolinium triflate **15** and the semicyclic vinamidinium salt **17** are obtained in a 3.1:1 ratio according to

Table 1. NMR data for the semicyclic vinamidinium salts **8** and **9**

	^{1}H NMR [a-c]	^{13}C NMR (δ [ppm], J [Hz]) [a,d,e]					
	δ [ppm], J [Hz]	C-2'	C-3'	C-4'	C-5'	C-6'	Other signals
8a	3.02 (s, NMe), 3.21-3.27 (m, 2 H,3'-H), 3.55-3.76 (m, NCH_2 and OCH_2), 5.13 (dd, ^3J = 7.7, 5.5, 2'-H), 5.32 (s, 5'-H), 7.33-7.54 (m, Ph)	61.1 (^1J = 145.1)	32.3 (^1J = 133.4)	168.9	92.1 (^1J = 133.4)	161.1	40.1 (NMe), 47.8 (NCH_2), 65.3/66.0 (OCH_2), 120.3 (TfO$^-$, $^1J_{C,F}$ = 320.5), 126.1-133.8 (Ph), 135.6/137.0 (*i*-C, 2-Ph and N-Ph)
8b	3.52-3.97 (m, 10 H, NCH_2, OCH_2 and 3'-H), 5.64 (pseudo-t, ^3J = 6.1, 2'-H)	64.2 (^1J = 147.9)	34.0 (^1J = 133.9)	164.7 or 167.9	96.1 (^1J = 168.8)	164.7 or 167.9	50.0 (NCH_2), 66.7/67.2 (OCH_2), 122.0 (TfO$^-$, $^1J_{C,F}$ = 318.7); 122.3, 124.3, 128.0-139.2 (Ph and NPh), 143.7 (*i*-C, NPh)
8c	3.46-3.91 (m, 10 H, NCH_2, OCH_2 and 3'-H), 3.79 (s, OMe), 5.36 (dd, ^3J = 4.1, 3.9, 2'-H), 5.64 (s, 5'-H), 6.88-7.47 (m, 10 H, Ph), 7.79/8.38 (AA'BB', 4-$MeOC_6H_4$)	62.8 (^1J = 145.9)	33.3 (^1J = 135.0)	163.2 or 166.7	94.8 (^1J = 168.7)	163.2 or 166.7	48.5/48.6 (NCH_2), 54.9 (OMe), 65.5/66.1 (OCH_2), 114.1 (d), 119.6 (s), 120.4 (TfO$^-$, $^1J_{C,F}$ = 320.2), 120.3-136.9 (Ph and C-2 of 4-$MeOC_6H_4$), 142.4 (*i*-C, NPh), 159.6 (C-OMe)
8d	3.53 (dd, ^2J = 17.5, ^3J = 4.6, 3'-H^A), 3.67-3.91 (m, 9 H, NCH_2, OCH_2 and 3'-H^B), 5.68 pseudo-t, ^3J = 4.6, 2'-H), 5.84 (s, 5'-H), 7.0-7.50 (m, 10 H, Ph), 7.77/8.24 (AA'BB', 4-$O_2NC_6H_4$)	63.5 (^1J = 146.6)	33.6 (^1J = 134.5)	164.3 or 167.8	96.5 (^1J = 169.7)	164.3 or 167.8	50.0/50.1 (NCH_2), 66.6/67.1 (OCH_2), 121.4 (TfO$^-$, $^1J_{C,F}$ = 327.6), 124.2-134.9 (Ph, C-2 and C-3 of 4-$O_2NC_6H_4$), 135.7 (*i*-C,Ph), 143.5 (s), 145.2 (s), 148.9 (s)
8e	3.22 (dd, ^2J = 17.4, ^3J = 4.2, 3'-H^A), 3.47 (dd, ^2J = 17.4, ^3J = 6.6, 3'-H^B), 3.73-3.90 (m, NCH_2 and OCH_2), 4.97 (ddd, 2'-H) [f], 5.78 (s, 5'-H), 6.54 [dd, ^3J = 16.0, ^3J(=CH, 2'-H) = 7.5, Ph-CH=C*H*], 6.75 (d, ^3J = 16.0, Ph-C*H*=CH-), 7.14/7.23 (AA'BB', 4-ClC_6H_4), 7.30-7.87 (m, Ph)	61.4 (^1J = 146.2)	30.8 (^1J = 134.2)	163.1 or 164.6	94.4 (^1J = 168.9)	163.1 or 164.6	48.0/48.1 (NCH_2), 64.8/65.3 (OCH_2), 120.4 (TfO$^-$, $^1J_{C,F}$ = 320.5), 118.3-135.0 (CH=CH, Ph; C-1, C-2, and C-3 of 4-ClC_6H_4), 140.6 (C-Cl)
8f	3.19 (dd, ^2J = 17.3, ^3J = 4.2, 3'-H^A), 3.45 (dd, ^2J = 17.3, ^3J = 6.7, 3'-H^B), 3.68 (s, OMe), 3.71-3.85 (m, NCH_2 and OCH_2),4.89-4.94 (m, 2'-H), 5.69(s, 5'-H), 6.54 [dd, ^3J = 16.0, ^3J(=CH, 2'-H) = 7.6, Ph-CH=C*H*-], 6.70 (d, ^3J = 16.0, Ph-C*H*=CH-), 6.76/7.10 (AA'BB', 4-$MeOC_6H_4$), 7.28-7.63 (m, Ph)	61.6 (^1J = 146.4)	30.5 (^1J = 133.8)	162.6 or 165.2	93.3 (^1J = 168.6)	162.6 or 165.2	47.7/47.8 (NCH_2), 64.7/65.3 (OCH_2), 113.1 (d), 114.5 (d), 120.5 (TfO$^-$, $^1J_{C,F}$ = 317.5), 122.7-134.8 (CH=CH and Ph), 157.7 (C-OMe)
9	1.94-2.08 (m, NCH_2CH_2), 2.36 (s, 6'-Me), 3.03 (dd, ^2J = 17.4, ^3J = 4.2, 3'-H^A), 3.15 (s, NMe), 3.40-3.51 (m, NCH_2), 3.61 (m_c, 3'-H^B), 4.97 (dd, ^3J = 8.0, 4.2, 2'-H), 5.16 (s, 5'-H), 7.24-7.40 (m, Ph)	61.1 (^1J = 144.9)	33.9 (^1J = 132.6)	166.9	91.4 (^1J = 168.9)	158.8	21.3 (6'-Me), 23.9/24.2 (NCH_2CH_2), 38.0 (NMe), 48.9/49.1 (NCH_2), 120.4 (TfO$^-$, $^1J_{C,F}$ = 321.1), 125.9/128.1/128.8 (Ph), 135.8 (*i*-C of Ph)

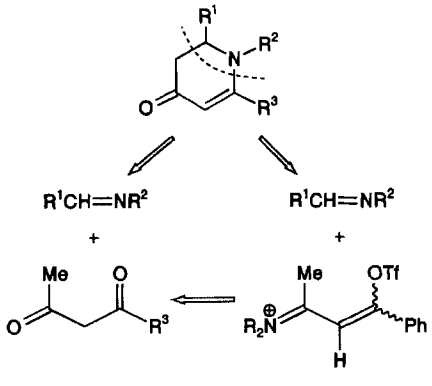
[a] In $CDCl_3$ (**8a, c, 9**), CD_3CN (**8b, d**) or $CDCl_3/CD_3CN \approx 1:1$ (**8e, f**). – [b] TMS as internal standard. – [c] 400.1 (**8a, b, e, f, 9**) or 200.1 MHz (**8c, d**). – [d] $CDCl_3$ (δ = 77.0; **8a, c, e, f, 9**) or CD_3CN (δ = 118.2; **8b, d**) as internal standard. – [e] 100.6 MHz. – [f] Coupling constants were not determined.

Table 2. NMR and selected IR data for the 2,3-dihydro-4(1*H*)-pyridinones **10a, b, e**

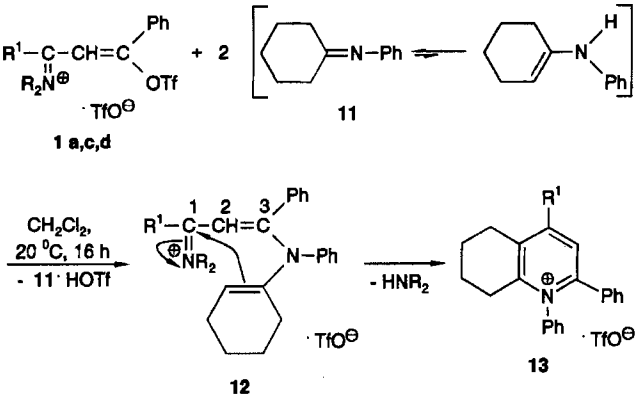
	IR [cm^{-1}] [a]	^{1}H NMR ($CDCl_3$/TMS) [b]
10	ν (C=O, C=C)	δ [ppm], J [Hz]
a	1625, 1575	2.70 (dd, ^2J = 16.2, ^3J = 6.9, 3-H^A), 2.72 (s, NMe), 3.01 (dd, ^2J = 16.2, ^3J = 6.9, 3-H^B), 4.57 (pseudo-t, ^3J = 6.9, 2-H), 5.03 (s, 5-H), 7.20-7.33 (m,Ph)
b	1640, 1575[e]	2.84 [ddd, ^2J = 16.7, ^3J = 2.1, ^4J(3-H^A, 5-H) = 1.1, 3-H^A], 3.40 (dd, ^2J = 16.7, ^3J = 6.5, 3-H^B), 5.28 (dd, ^3J = 6.5, 2.1, 2-H), 5.57(d,^4J = 1.1, 5-H), 6.88-7.53 (m, Ph)
e	1630, 1575	2.62 [ddd, ^2J = 16.7, ^3J = 2.3, ^4J(3-H^A, 5-H) = 0.8, 3-H^A], 3.26 (dd, ^2J = 16.7, ^3J = 6.3, 3-H^B), 4.83 (m_c, 2-H), 5.62 [d, ^4J = 0.8, 5-H), 6.62 [dd, ^3J = 15.9, ^3J(=CH,2-H) = 6.2, Ph-CH=C*H*-], 6.81 (d, ^3J = 15.9, Ph-C*H*=CH-), 6.94/7.14 (AA'BB', 4-ClC_6H_4), 7.24-7.29 (m, Ph)
	^{13}C NMR ($CDCl_3$) [c,d]	
10	δ [ppm], J [Hz]	
a	39.2 (NMe), 42.8 (C-3, ^1J = 131.8), 64.2 (C-2, ^1J = 138.9), 101.8 (C-5, ^1J = 166.0), 126.4/127.2/127.9/128.4/128.8/129.2 (Ph), 136.4/139.2 (*i*-C), 165.3 (C-6), 189.5 (C=O)	
b	41.7 (C-3, ^1J = 130.2), 65.5 (C-2, ^1J = 140.9), 107.9 (C-5, ^1J = 166.2), 124.5-129.7 (Ph), 136.2/139.4 (*i*-C), 160.1 (C-6), 191.1 (C=O)	
e	40.9 (C-3, ^1J = 133.0), 64.4 (C-2, ^1J = 141.3), 107.2 (C-5, ^1J = 166.3), 125.6-131.9 (CH=CH, Ph, C-2 and C-3 of 4-ClC_6H_4), 135.7/135.9 (*i*-C, Ph and C-Cl), 144.1 (C-1 of 4-ClC_6H_4), 159.0 (C-6), 191.4 (C=O)	

[a] KBr pellet. – [b] 400.1 (**10b, e**) or 200.1 MHz (**10a**). – [c] $CDCl_3$ (δ = 77.0) as internal standard. – [d] 100.6 MHz. – [e] Ref.[6a]: (C=O, C=C) = 1645, 1550 cm^{-1}.

Scheme 4



Scheme 5



12 a,d : spontan.
12 c : 82 °C, 6 h

1, 12, 13	R^1	NR_2	[%] **12**	[%] **13**
a	Me	morpholino	n. i.	41
c	Ph	morpholino	54	64[a]
d	H	NMe_2	n. i.	23

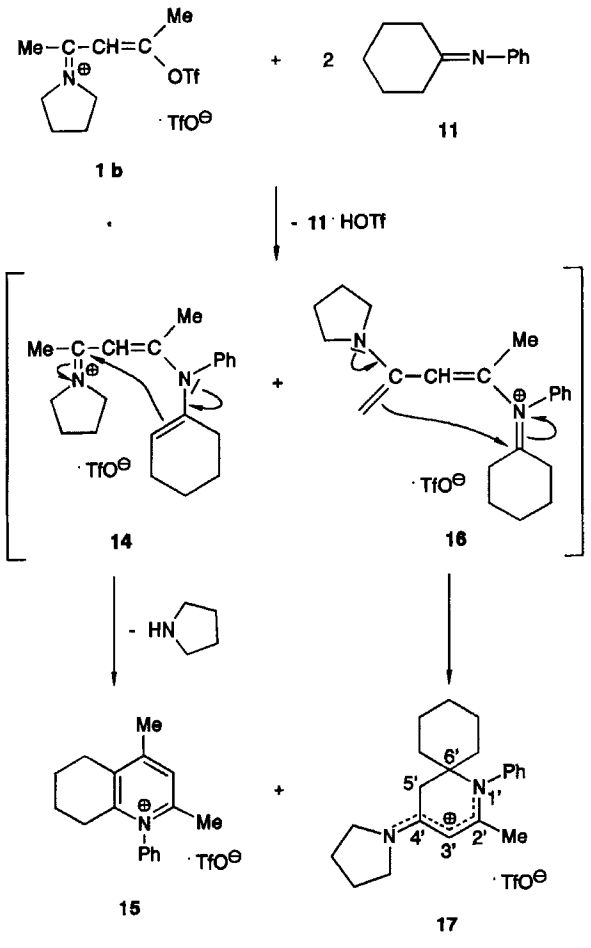
[a] Yield based on **12c**.

the ^{1}H-NMR spectrum. The mixture of the two salts cannot be separated by fractional crystallization. Consecutive S_N reaction, deprotonation, and cyclization account for the formation of both **15** and **17** (Scheme 6). The deprotonation step is likely to generate simultaneously the isomeric enamino-substituted propeniminium salts **14** and **16**, which are perhaps in a prototropic equilibrium and undergo 1,5-cyclization to **15** and **17**. Remarkably enough, salt **12c**, in contrast to **14**, is not subject to such a prototropy. It may be concluded that the mere replacement of the morpholinium by the pyrrolidinium substituent gives rise to the additional reaction pathway leading to **17** via **16**.

All the preceding combinations of 3-trifloxypropeniminium salts **1a–d** with imines **5** or **11** have been designed in such a way that after the nucleophilic replacement of the trifloxy group by the imine, a tandem deprotonation/(Mannich)cyclization reaction can take place. When **1c** and **5b** are allowed to react, the structural prerequisites for the analogous deprotonation step are not given. From **1c** and two equivalents of **5b**, the intensely yellow, diastereomerically pure propeniminium salt **21** is formed in a slow reaction at room temperature (Scheme 7). Again, it is to be assumed that the initial step is a S_N reaction leading to **18**, but this time followed by an imine-induced deprotonation at C-3 of the propeniminium moiety. The allenyliminium ion **19** thus formed undergoes a 1,4-cyclization to give **20**, which finally affords **21** by an electrocyclic ring-opening reaction. Surprisingly, no reaction is observed when **1c** and **5b** are exposed to each other in a 1:1 ratio at 40°C. One could have expected either the formation of the substitution product **18** (compare the formation of **2**, Scheme 1) or the elimination of HOTf from **1c** under the influence of **5b**, which has already been observed with stronger bases[3]. It appears that **1c** and **5b** on one hand and **18** on the other

are in an equilibrium which is far on the side of the components and is only rendered productive when **18** is consumed by an excess of imine **5b**.

Scheme 6

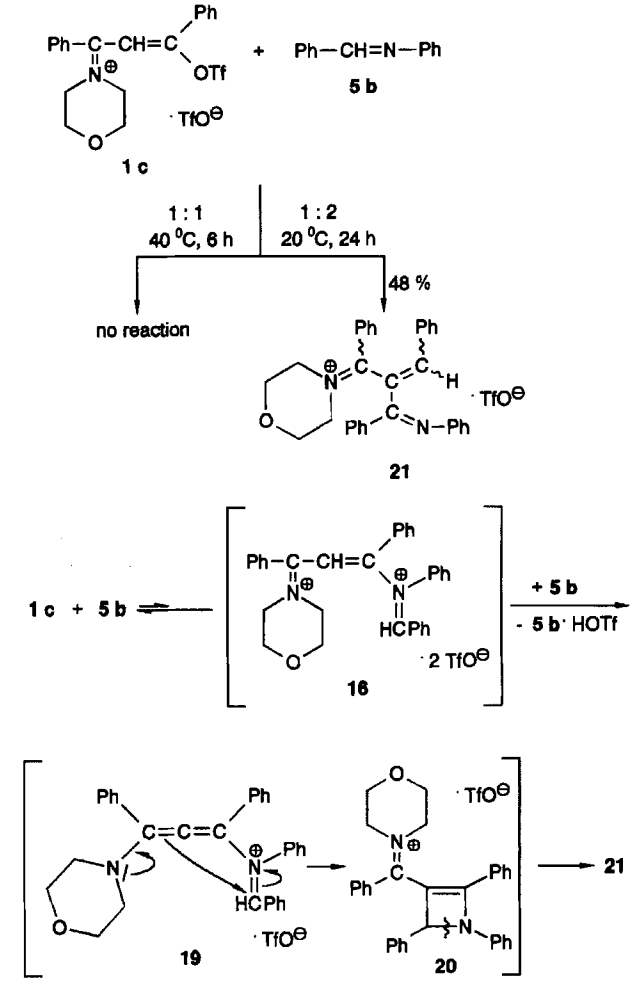


An independent and, with regard to the yield, superior access to **21** is provided by the reaction of the propyniminium salt **22**, obtained from **1c** by base-mediated[3] or thermal[4] HOTf elimination in high yield, with imine **5b** (Scheme 8). Without doubt, the reaction begins with the formation of the allenyliminium salt **19** and thus merges with the reaction sequence given in Scheme 7. Enamino ketones undergo a comparable metathetical addition to propyniminium salts[3].

Iminium salt **21** can be transformed into the 1-aza-1,3-diene **23** by mild hydrolysis in a two-phase system. As for **21**, the NMR spectra of **23** indicate the presence of only one diastereomer of unknown stereochemistry.

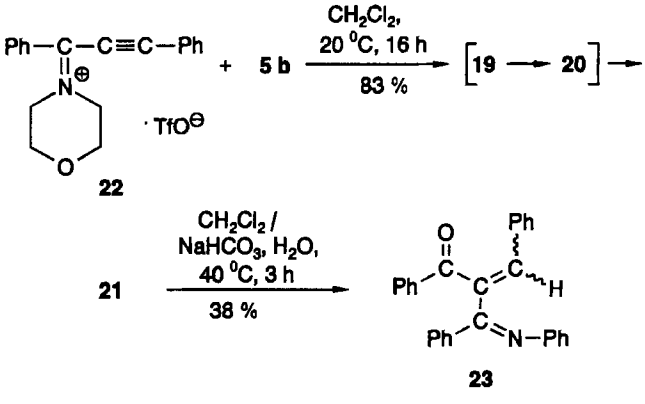
In contrast to **22**, the propyniminium salt **24** does not react cleanly with imine **5b**. In various differently conducted reaction runs, only complex, unseparable reaction mixtures are obtained in which no products can be identified. Presumably, complications arise by deprotonation **24** leading to an enamine which then reacts further with excess **24** in an uncontrolled manner.

Scheme 7



With a special imine, namely the kinetically stabilized, but highly reactive azete **25**[14,15], **24** reacts regiospecifically and in good yield to form the bicyclic vinamidinium salt **28** (Scheme 9). The also feasible cycloaddition product **29** cannot be detected. By analogy with the preceding mechanistic interpretations, **26** and **27** are postulated as intermediates on the way to **28**.

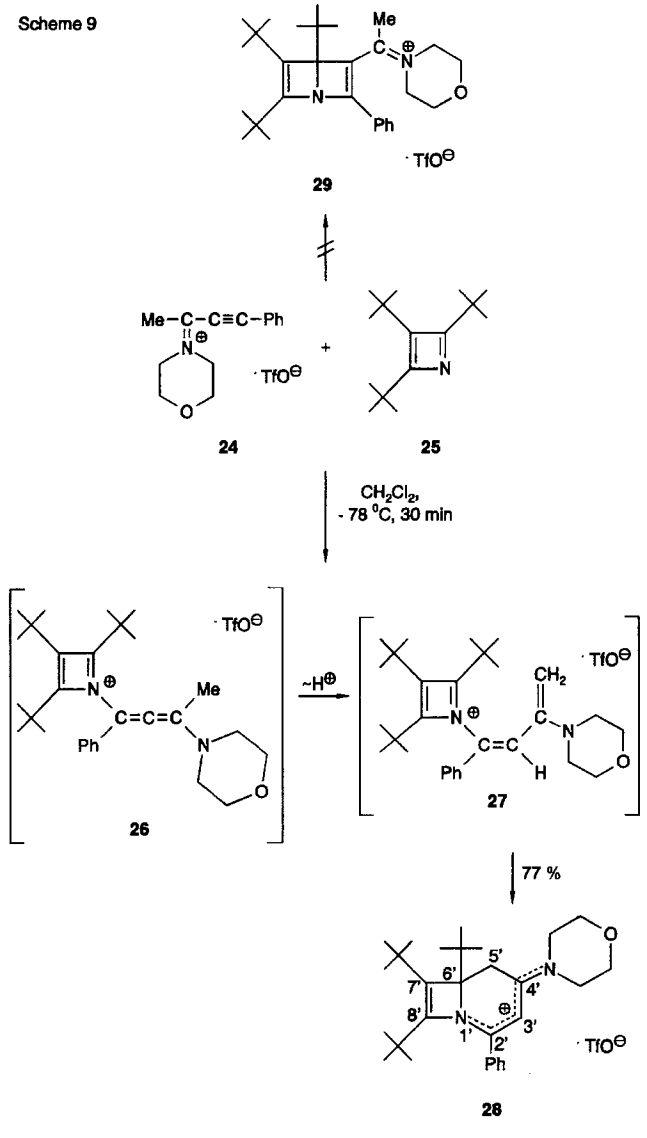
Scheme 8



The constitution of **28** is firmly established by an X-ray crystal structure analysis (Figure 1, the numbering scheme

does not agree with IUPAC rules). Partial π-bond delocalization in the vinamidinium structural moiety is indicated by the bond lengths, even though the character of an α,β-unsaturated morpholinium system prevails strongly. This conclusion is based on the shortening of the N2–C3 and C1–C2 bonds with regard to the N1–C1 and C2–C3 bonds by 0.043 and 0.042 Å, respectively. The bridgehead nitrogen atom has a pyramidal coordination (sum of valence angles at N1 343.4°) and therefore cannot enter into optimal conjugation with the neighboring π system. In contrast, N2 has a perfect trigonal-planar coordination. The bond lengths in the four-membered ring are in good agreement with those found in a 6,7,8-tri-*tert*-butyl-5-oxa-1-azabicyclo[4.2.0]octa-3,7-diene[16a], whereas in another, tricyclic molecule containing the tri-*tert*-butylazetine unit, the bond corresponding to N1–C5 is enlarged by 0.23 Å[16b].

Scheme 9



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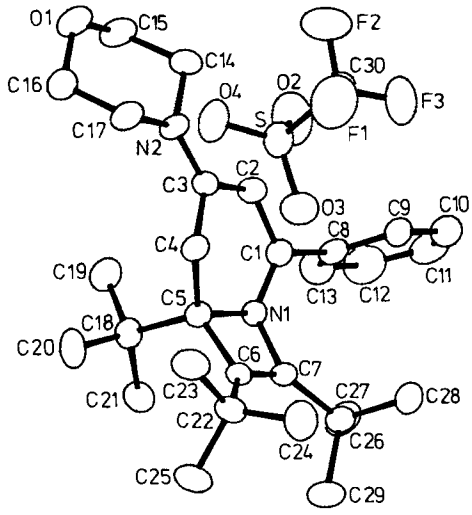

Figure 1. Molecular structure of **28** (ORTEP plot). Selected bond lengths [Å] and bond angles [deg]: N1–C1 1.340(4), N1–C5 1.500(4), N1–C7 1.467(4), N2–C3 1.297(4), C1–C2 1.367(4), C2–C3 1.409(5); C1–N1–C5 120.4(3), C1–N1–C7 134.8(3), C5–N1–C7 88.2(3), N1–C1–C2 122.8(3), C1–C2–C3 122.1(3), N2–C3–C2 124.0(3), N2–C3–C4 120.6(3), C2–C3–C4 115.4(3)

Experimental

IR: Perkin-Elmer 1310. – ^{1}H NMR: Varian EM 390 (90 MHz), Bruker AC 200 (200.1 MHz), Bruker AM 400 (400.1 MHz), TMS as internal standard. – ^{13}C NMR: Bruker AM 400 (100.6 MHz); solvent signal as internal standard [δ($CDCl_3$) = 77.0, δ(CD_3CN) = 118.2, δ($CDCl_3$/CD_3CN mixtures) = 77.0]. – X-ray diffraction: Enraf-Nonius CAD4. – Melting points: Copper block, temperatures given are not calibrated. – Elemental analyses: Perkin-Elmer EA 2400. – Silica gel: Particle size 0.063–0.2 mm.

N-(4-Methoxybenzylidene)aniline (**5c**): Preparation by analogy with ref.[17] from aniline and 4-methoxybenzaldehyde; yield: 83%; yellow crystals, m.p. 61°C. – IR (nujol): $\tilde{\nu}$ = 1590 cm^{-1} (C=N). – ^{1}H NMR (90 MHz): δ = 3.70 (s, OMe), 6.85 and 7.76 (AA'BB' system, C_6H_4), 7.00–7.43 (m, Ph), 8.29 (s, CH=N). – $C_{14}H_{13}NO$ (211.3): calcd. C 79.60, H 6.20, N 6.63; found C 79.5, H 6.3, N 6.5.

N-(4-Nitrobenzylidene)aniline (**5d**): Preparation by analogy with ref.[17] from aniline and 4-nitrobenzaldehyde; yield: 71%; yellow-greenish crystals, m.p. 87°C. – IR (nujol): $\tilde{\nu}$ = 1585 cm^{-1} (C=N). – ^{1}H NMR (90 MHz): δ = 7.05–7.50 (m, Ph), 7.96 and 8.24 (AA'BB' system, C_6H_4), 8.49 (s, CH=N). – $C_{13}H_{10}N_2O_2$ (226.2): calcd. C 69.02, H 4.46, N 12.38; found C 68.9, H 4.6, N 12.4.

4-Chloro-N-cinnamylideneaniline (**5e**): Preparation by analogy with ref.[18] from 4-chloroaniline and cinnamaldehyde; yield: 72%; yellow powder, m.p. 107–108°C. – IR (nujol): $\tilde{\nu}$ = 1585, 1565 cm^{-1} (C=C, C=N). – ^{1}H NMR (90 MHz): δ = 6.85–7.53 (m, 11 H; Ph, C_6H_4, and PhC*H*=C*H*), 8.11 (dd, ^3J = 6.0, $|\,^4J\,|$ = 4.2 Hz, CH=N). – $C_{15}H_{12}ClN$ (241.7): calcd. C 74.53, H 5.00, N 5.79; found C 74.1, H 5.0, N 5.7.

4-(2,3-Dihydro-1-methyl-2,6-diphenyl-pyridin-4(1 H)-ylidene)-morpholinium Trifluoromethanesulfonate (**8a**); *Typical Procedure:* *N*-Benzylidenemethylamine (**5a**)[19] (0.86 g, 7.21 mmol) is added to a solution of the 3-trifloxypropeniminium triflate **1a**[7] (1.85 g, 3.60 mmol) in CH_2Cl_2 (25 ml). After stirring at room temp. for 16 h, the dark red solution is extracted with a saturated aqueous solution of $NaHCO_3$ (30 ml), and the aqueous phase is then extracted with CH_2Cl_2 (20 ml). The combined organic layers are dried ($MgSO_4$) and concentrated to a volume of ca. 10 ml. Upon addition of ether

(50 ml) a red oil separates which after reprecipitation from CH_3CN/ether yields a solid. After drying at 0.005 mbar, 1.20 g (69%) of light red **8a** is obtained, m.p. 58–61°C. – IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} (C=C), 1570 (C=N), 1270/1260/1145/1025 (TfO^-). – ^1H- and ^{13}C-NMR data: Table 1. – $C_{23}H_{25}F_3N_2O_4S$ (482.5): calcd. C 57.25, H 5.22, N 5.81; found C 57.5, H 5.2, N 5.8.

4-(2,3-Dihydro-1,2,6-triphenylpyridin-4(1H)-ylidene)morpholinium Trifluoromethanesulfonate (**8b**): Prepared from **1a** (1.92 g, 3.73 mmol) and *N*-benzylidenaniline (**5b**)[17] (1.35 g, 7.47 mmol) in CH_2Cl_2 (25 ml) according to the synthesis of **8a**; 1.27 g (63%) of **8b**, yellow powder, m.p. 92–94°C. – IR (KBr): $\tilde{\nu}$ = 1585 cm^{-1} (C=C), 1565 (C=N), 1255/1225/1145/1025 (TfO^-). – $C_{28}H_{27}F_3N_2O_4S$ (544.6): calcd. C 61.75, H 5.00, N 5.14; found C 61.8, H 4.9, N 5.1.

4-[2,3-Dihydro-2-(4-methoxyphenyl)-1,6-diphenylpyridin-4(1H)-ylidene]morpholinium Trifluoromethanesulfonate (**8c**): Prepared from **1a** (4.54 g, 8.84 mmol) and **5c** (3.74 g, 17.69 mmol) in CH_2Cl_2 (70 ml) according to the synthesis of **8a**; 3.61 g (71%) of **8c**, intensely yellow powder, m.p. 98–101°C. The elemental analysis (see below) could not be improved. – IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1} (C=C), 1560 (C=N), 1250/1140/1020 (TfO^-). – $C_{29}H_{29}F_3N_2O_5S$ (574.6): calcd. C 60.62, H 5.09, N 4.88; found C 61.9, H 5.2, N 4.9.

4-[2,3-Dihydro-2-(4-nitrophenyl)-1,6-diphenylpyridin-4(1H)-ylidene]morpholinium Trifluoromethanesulfonate (**8d**): Prepared from **1a** (6.46 g, 12.58 mmol) and **5d** (5.69 g, 25.17 mmol) in CH_2Cl_2 (100 ml) according to the synthesis of **8a**. The crude oily product obtained after workup is dissolved in CH_3CN (10 ml). At −36°C, **8d**, crystallizes as an intensely yellow powder (4.79 g, 65%), m.p. 180–182°C. – IR (KBr): $\tilde{\nu}$ = 1585 cm^{-1} (C=C), 1560 (C=N), 1260–1240/1220/1210/1140/1025 (TfO^-). – $C_{28}H_{26}F_3N_3O_6S$ (589.6): calcd. C 57.04, H 4.45, N 7.13; found C 57.2, H 4.7, N 7.2.

4-{1-(4-Chlorophenyl)-2,3-dihydro-6-phenyl-2-[(E)-styryl]pyridin-4(1H)-ylidene}morpholinium Trifluoromethanesulfonate (**8e**): A solution of **1a** (4.25 g, 8.28 mmol) and **5e** (3.40 g, 16.54 mmol) in CH_2Cl_2 (70 ml) is stirred for 16 h. A fraction of the salt **5e** · HOTf crystallizes and is removed by filtration. Workup of the remaining reaction solution as described above for **8a** affords **8e** as an orange-red powder (3.15 g, 63%), m.p. 111–114°C. The salt could not be obtained analytically pure. – IR (nujol): $\tilde{\nu}$ = 1650/1610 cm^{-1} (C=C), 1565 (C=N), 1290–1210/1155–1130/1025 (TfO^-). – $C_{30}H_{28}ClF_3N_2O_4S$ (605.1): calcd. C 59.55, H 4.66, N 4.63; found C 61.3, H 5.0, N 4.6.

4-{2,3-Dihydro-1-(4-methoxyphenyl)-6-phenyl-2-[(E)-styryl]-pyridin-4(1H)-ylidene}morpholinium Trifluoromethanesulfonate (**8f**): The synthesis from **1a** (7.10 g, 13.83 mmol) and **5f**[18] (6.56 g, 27.66 mmol) in CH_2Cl_2 (100 ml) as described above for **8e** affords **8f** as an orange-red powder (6.79 g, 82%), m.p. 98–100°C. The salt could not be obtained analytically pure. – IR (nujol): $\tilde{\nu}$ = 1645/1595 cm^{-1} (C=C), 1560 (C=N), 1270–1210/1160–1130/1020 (TfO^-). – $C_{31}H_{31}F_3N_2O_5S$ (600.7): calcd. C 61.99, H 5.20, N 4.66; found C 60.9, H 5.0, N 4.4.

1-(2,3-Dihydro-1,6-dimethyl-2-phenylpyridin-4(1H)-ylidene)pyrrolidinium Trifluoromethanesulfonate (**9**): From **1b**[7] (7.04 g, 16.17 mmol) and **5a** (3.85 g, 32.34 mmol) in CH_2Cl_2 (100 ml) as described above for **8a**. The crude product is precipitated twice from CH_2Cl_2/ether and once from CH_3CN/ether. In this way, **9** is obtained as a red-brown powder (5.62 g, 86%), m.p. 98°C. – IR (KBr): $\tilde{\nu}$ = 1595 cm^{-1} (C=C), 1575 (C=N), 1285–1235/1210/1140/1020 (TfO^-). – $C_{18}H_{23}F_3N_2O_3S$ (404.4): calcd. C 53.45, H 5.73, N 6.93; found C 53.7, H 5.7, N 6.9.

2,3-Dihydro-1-methyl-2,6-diphenyl-4(1H)-pyridinone (**10a**): A saturated aqueous solution of $NaHCO_3$ (20 ml) is added to the solution of **8a** (2.69 g, 5.57 mmol) in CH_2Cl_2 (20 ml), and the mixture is refluxed for 3 h with vigorous stirring. The organic layer is separated and the aqueous layer extracted with CH_2Cl_2 (2 × 10 ml). The combined organic layers are dried ($MgSO_4$) and filtered over silica gel (20 g). After evaporation of the solvent, a yellow oil is left that yields colorless crystals (0.66 g, 45%) on trituration with low-boiling petroleum ether, m.p. 89°C. Spectral data: Table 2. – $C_{18}H_{17}NO$ (263.3): calcd. C 82.10, H 6.51, N 5.32; found C 81.8, H 6.6, N 5.2.

2,3-Dihydro-1,2,6-triphenyl-4(1H)-pyridinone (**10b**): Prepared from **8b** (3.63 g, 6.66 mmol) according to the preceding protocol. After crystallization from ether/petroleum ether at 2°C, yellow crystals of **10b** are obtained (0.89 g 41%), m.p. 162°C (ref.[6a] 149–151°C). Spectral data: Table 2. – $C_{23}H_{19}NO$ (325.4): calcd. C 84.89, H 5.89, N 4.30; found C 84.7, H 6.0, N 4.3.

1-(4-Chlorophenyl)-2,3-dihydro-6-phenyl-2-[(E)-styryl]-4(1H)-pyridinone (**10e**)

a) Prepared from **8e** (3.77 g, 6.23 mmol) by hydrolysis with aqueous $NaHCO_3$ (20 ml) as described above for **10a**. The solution of the crude product in ether (50 ml) is chromatographed over a column filled with silica gel (30 g), the eluated ether solution is discarded, and the product is eluated with CH_2Cl_2 (30 ml). After evaporation of the solvent, the residue is dissolved in ether and allowed to crystallize at −36°C. Yield of **10e**: 0.55 g (23%), yellow powder, m.p. 72–73°C. Spectral data: Table 2.

b) To a solution of **8e** (3.47 g, 5.73 mmol) in CH_2Cl_2 (20 ml) is added 1 N HCl (10 ml), and the mixture is refluxed for 4 h. The organic layer is separated, the aqueous layer is extracted with CH_2Cl_2 (10 ml), and the conmbined organic layers are washed with a 10% aqueous $NaHCO_3$ solution (20 ml). Further workup as described under a) yields 0.24 g (11%) of **10e**. – $C_{25}H_{20}ClNO$ (385.9): calcd. C 77.81, H 5.22, N 3.63; found C 77.2, H 5.5, N 3.6.

5,6,7,8-Tetrahydro-4-methyl-1,2-diphenylquinolinium Trifluoromethanesulfonate (**13a**): A solution of **1a** (4.82 g, 9.39 mmol) and *N*-cyclohexylideneaniline (**11**)[20,21] (3.25 g, 18.78 mmol) in CH_2Cl_2 (50 ml) is stirred at room temp. for 16 h. The dark-red reaction solution is extracted with an aqueous saturated solution of $NaHCO_3$ (20 ml), the organic layer is separated, dried ($MgSO_4$), and concentrated to a volume of 20 ml. Upon addition of ether (50 ml) a red oil separates which is dissolved in CH_3CN. By addition of ether, a colorless powder is obtained (1.72 g, 41%), m.p. 150°C (after recrystallization from CH_3CN/ether). – IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1}, 1590, 1280/1270/1260/1150/1025 (TfO^-). – ^1H NMR ($CDCl_3$, 400.1 MHz): δ = 1.85–1.94 (m, CH_2-6,7), 2.58 (s, CH_3), 2.61 (s, broad, CH_2-5), 2.92 (t, CH_2-8), 7.17–7.40 (m, Ph), 7.55 (s, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 19.9/20.8 (C-6,7), 20.2 (CH_3), 25.8/30.1 (C-5,8), 120.4 [J(C,F) = 321.7 Hz, TfO^-], 127.0–130.0 (Ph and C-3), 132.4 (*i*-C of 2-Ph), 136.7, 138.1 (C-4a, *i*-C of NPh), 152.5/153.3 (C-4,8a), 157.1 (C-2). – $C_{23}H_{22}F_3NO_3S$ (449.5): calcd. C 61.46, H 4.93, N 3.12; found C 61.1, H 4.9, N 3.1.

4-{3-[N-(1-Cyclohexen-1-yl)anilino]-1,3-diphenyl-2-propenylidene}morpholinium Trifluoromethanesulfonate (**12c**): Prepared from **1c**[7] (4.04 g, 7.01 mmol) and **11** (2.43 g, 14.02 mmol) in CH_2Cl_2 (50 ml) as described for **13a**. An intensely yellow powder of **12c** is obtained upon addition of ether to the solution of the crude oily product in CH_2Cl_2. Reprecipitation from CH_2Cl_2/ether yields 2.28 g (54%) of **12c** as a mixture of two diastereomers (ca. 1:1 according to ^1H NMR). – IR (KBr): $\tilde{\nu}$ = 1570 cm^{-1}, 1260/1230/1210/1145/1020 (TfO^-). – ^1H NMR (CD_3CN, 0°C, 400.1 MHz): δ = 1.15 (s, broad, 1H), 1.31 (t, 1H), 1.69–1.86 (m, 4H),

2.12–2.48 (m, 2H) (cyclohexenyl-CH_2); 3.23–3.34 (m, 2H), 3.70 (m_c, 4H), 3.98 (s, broad, 2H) (NCH_2 and OCH_2); 5.40/5.44 (two s, 2-H, cyclohexenyl), 5.97/6.00 (two s, 2′-H), 6.82–7.77 (m, Ph). – ^{13}C NMR (CD_3CN, 0°C): δ = 21.3, 21.8, 22.5, 23.1, 24.9, 25.2, 26.8, 28.7 (cyclohexenyl-CH_2, two diastereomers); 51.8/52.0/52.1 (NCH_2), 66.0/66.2/67.0 (OCH_2); 104.2 [J(C,H) = 159.2 Hz]/104.4 [J(C,H) = 159.4 Hz] (C-2′), 121.7 [J(C,F) = 321.1 Hz, TfO^-]: 127.3–133.8, 141.0, 142.8, 143.1, 144.5 (Ph, 1- and 2-cyclohexenyl]; 170.9/173.4, 175.4 (C-1′,3′). – $C_{32}H_{33}F_3N_2O_4S$ (598.7): calcd. C 64.20, H 5.56, N 4.68; found C 64.3, H 5.6, N 4.7.

5,6,7,8-Tetrahydro-1,2,4-triphenylquinolinium Trifluoromethanesulfonate (**13c**): A solution of **12c** (1.07 g, 1.79 mmol) in CH_3CN (10 ml) is refluxed for 6 h. Concentration to a volume of 5 ml and addition of ether (30 ml) yield a red oil. Trituration of this oil with ether affords 0.59 (64%) of **13c** as a colorless powder, m.p. 204°C. – IR (KBr): $\tilde{\nu}$ = 1610 cm^{-1}, 1585, 1260/1145/1020 (TfO^-). – ^{1}H NMR (CD_3CN, 200.1 MHz): δ = 1.60–1.90 (m, CH_2-6,7), 2.64 (t, CH_2-5), 2.87 (t, CH_2-8), 7.21–7.65 (m, 3-H and Ph). – ^{13}C NMR (CD_3CN): δ = 21.5, 22.1 (C-6,7), 28.8, 31.6 (C-5,8), 122.2 [J(C,F) = 321.5 Hz, TfO^-], 128.2–131.5 (Ph and C-3), 134.0, 137.3, 139.8 (*i*-C of 2-Ph, C-4a, *i*-C of NPh), 154.5, 156.8 (C-4,8a), 159.7 (C-2). – $C_{28}H_{24}F_3NO_3S$ (511.6): calcd. C 65.74, H 4.73, N 2.74; found C 65.3, H 4.7, N 2.8.

5,6,7,8-Tetrahydro-1,2-diphenylquinolinium Trifluoromethanesulfonate (**13d**): From **1d**[3] (4.92 g, 10.75 mmol) and **11** (3.73 g, 21.50 mmol) in CH_2Cl_2 (50 ml) as described for **13a**. After two recrystallizations from CH_2Cl_2/ether, 1.80 g (23%) of colorless **13d** are obtained, m.p. 171°C. – IR (KBr): $\tilde{\nu}$ = 1605 cm^{-1}, 1580, 1270/1255/1250/1020 (TfO^-). – ^{1}H NMR (CD_3CN, 400.1 MHz); δ = 1.71–1.87 (m, CH_2-6,7), 2.70 (t, CH_2-5), 2.84 (t, CH_2-8), 7.50–7.74 (m, 3-H and Ph), 8.50 (d, ^3J = 6.4 Hz, 4-H). – ^{13}C NMR (CD_3CN): δ = 21.6/21.8 (C-6,7), 28.7/30.5 (C-5,8), 122.1 [J(C,F) = 321.2 Hz, TfO^-], 126.0–132.2 (Ph and C-3), 137.2, 138.5 (*i*-C of 2-Ph, C-4a), 141.9 (*i*-C, NPh), 143.5 [J(C,H) = 193.3 Hz, C-4], 156.5 (C-8a), 160.1 (C-2). – $C_{22}H_{20}F_3NO_3S$ (435.5): calcd. C 60.68, H 4.63, N 3.22; found C 60.7, H 4.7, N 3.3.

5,6,7,8-Tetrahydro-2,4-dimethyl-1-phenylquinolinium Trifluoromethanesulfonate (**15**) *and 1-(2-Methyl-1-phenyl-1-azaspiro[5.5]-undec-2-en-4-ylidene)pyrrolidinium Trifluoromethanesulfonate* (**17**): From **1b** (3.00 g, 6.89 mmol) and **11** (2.47 g, 13.78 mmol) in CH_2Cl_2 (50 ml) as described for **13a**. An unseparable mixture (1.89 g) of the two solid salts **15** and **17** in a 3.1:1 ratio (^{1}H NMR) is obtained. – ^{1}H NMR (CD_3CN, 400.1 MHz): **15**: δ = 1.72–1.84 (m, CH_2-6,7), 2.26 (s, Me), 2.47 (t, CH_2-5), 2.52 (s, Me), 2.83 (t, CH_2-8). – **17**: δ = 0.94–1.04 (m, 2H), 1.25–1.32 (m, 2H), 1.39–1.50 (m, 2H), 1.59–1.62 (m, 4H), (all cyclohexane-CH_2); 1.80 (s, Me), 2.03–2.10 (m, NCH_2CH_2), 3.11 (s, CH_2-5′), 3.56/3.74 (both t, NCH_2), 5.37 (s, 3-H). – The resonances for C_6H_5 (**15** and **17**) and 3-H (**15**) appear at δ = 7.28–7.74. – ^{13}C NMR: **15**: δ = 20.3 (Me), 21.1, 21.9 (C-6,7), 26.4 (Me), 33.3, 34.8 (C-5,8), 136.3, 139.3 (C-4a; *i*-C of NPh), 153.1, 154.3 (C-4,8a), 159.4 (C-2). – **17**: δ = 23.0 (Me), 25.1, 25.4, 25.6 (cyclohexane-CH_2, NCH_2CH_2), 34.8 [J(C,H) = 148.6 Hz, C-5′], 50.7/50.8 (NCH_2), 62.9 (C-6′), 92.3 [J(C,H) = 170.1 Hz, C-3′], 139.0 (*i*-C of Ph), 162.2, 166.7 (C-2′,4′). Further signals of both compounds: δ = 122.0 [J(C,F) = 321.5 Hz, TfO^-], 126.8, 127.9, 130.2, 130.6, 131.7, 131.9 (Ph and C-3 of **15**).

4-{1,3-Diphenyl-2-[α-(phenyliminobenzyl)-2-propenylidene}morpholinium Trifluoromethanesulfonate (**21**)

a) A solution of **1c** (3.33 g, 5.79 mmol) and **5b** (2.10 g, 11.58 mmol) in CH_2Cl_2 (20 ml) is stirred for 24 h. Workup as described for **8a** and twofold recrystallization from CH_2Cl_2/ether afford 1.69 g (48%) of **21** as an intensely yellow powder, m.p. 162°C.

b) A solution of **22**[3,4] (1.84 g, 4.32 mmol) and **5b** (0.86 g, 4.75 mmol) in CH_2Cl_2 (20 ml) is stirred for 16 h. After concentration to a volume of ca. 10 ml and chilling to −78°C, **21** is precipitated as a yellow powder by addition of ether. Reprecipitation from CH_3CN/ether at room temp. gives 2.18 g (83%) of **21d**. – IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1}, 1585/1570 (C=N), 1275–1250/1220/1030 (TfO^-). – ^{1}H NMR (CD_3CN, 400.1 MHz): δ = 3.1–4.5 (m, NCH_2 and OCH_2), 6.53 (d, ^3J = 6.7 Hz, 2H), 6.73–7.92 (19H, C*H*Ph and Ph). – ^{13}C NMR (CD_3CN): δ = 56.9/57.1 (NCH_2), 66.6/66.9 (OCH_2), 121.3 (d), 123.7 [J(C,F) = 325.5 Hz, TfO^-], 126.3 (d), 129.4–137.0 (C-2′ and Ph), 146.5 [J(C,H) = 159.8 Hz, =*C*HPh], 150.2 (*i*-C of NPh), 169.0 (*C*=NPh), 182.9 (C-1′). – $C_{33}H_{29}F_3N_2O_4S$ (606.7): calcd. C 65.34, H 4.82, N 4.62; found C 64.9, H 4.9, N 4.5.

1,3-Diphenyl-2-[α-(phenylimino)benzyl]-1-propanone (**23**): An aqueous saturated solution of $NaHCO_3$ is added to a solution of **21** (0.42 g, 0.68 mmol) in CH_2Cl_2 (10 ml), and the mixture is refluxed for 3 h with vigorous stirring. The organic layer is separated, the aqueous phase is extracted with CH_2Cl_2 (2 × 5 ml), and the combined organic layers are dried ($MgSO_4$) and filtered over silica gel (4 g). The solvent is evaporated, and the residue is recrystallized from CH_2Cl_2/ether. Yield of **23**: 0.099 g (38%); light yellow powder, m.p. 108°C. – IR (KBr): $\tilde{\nu}$ = 1630 cm^{-1} (C=O), 1590 (C=N). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 6.68 (d, ^2J = 8.4 Hz, 2H), 6.94–7.57 (m, 17H, C*H*Ph and Ph), 8.03 (d, ^3J = 8.4 Hz, 2H). – ^{13}C NMR ($CDCl_3$); δ = 118.6 (d), 123.7 (d), 128.1–131.9 (Ph), 133.6, 136.4, 137.1, 137.5 (*i*-C of Ph, *C*=CHPh), 144.5 [J(C,H) = 154.9 Hz, =*C*HPh], 151.7 (*i*-C of NPh), 166.5 (*C*=NPh), 196.0 (C=O). – $C_{28}H_{21}NO$ (387.5): calcd. C 86.79, H 5.46, N 3.61; found C 86.2, H 5.6, H 3.6.

4-(6,7,8-Tri-tert-butyl-2-phenyl-1-azabicyclo[4.2.0]octa-2,7-dien-4-ylidene)morpholinium Trifluoromethanesulfonate (**28**): A solution of **24**[3,4] (1.49 g, 4.11 mmol) in CH_2Cl_2 (15 ml) is gradually added at −78°C to a solution of tri-*tert*-butylazete (**25**[14]) (0.930 g, 4.20 mmol) in the same solvent. After further 30 min at −78°C, the mixture is allowed to warm up to room temp. Upon addition of ether (50 ml) a red oil separates, which is dissolved in CH_3CN. Salt **28** (1.85 g, 77%) is precipitated as an intensely yellow powder by addition of ether, m.p. 165°C. – IR (KBr): $\tilde{\nu}$ = 1580 cm^{-1} (C=N), 1265/1155/1035 (TfO^-). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 0.97, 1.18, 1.37 (all s, *t*Bu), 3.41 (s, CH_2-5′), 3.59–4.14 (m, NCH_2 and OCH_2), 5.26 (s, 3′-H), 7.33–7.56 (m, Ph). – ^{13}C NMR ($CDCl_3$): δ = 27.7, 29.8, 31.5 (CMe_3), 30.3 [J(C,H) = 132.5 Hz, C-5′], 32.3, 32.8, 39.2 (*C*Me$_3$), 48.6/49.7 (NCH_2), 65.4/66.4 (OCH_2), 76.8 (C-6′), 98.2 [J(C,H) = 167.6 Hz, C-3′], 120.7 [J(C,F) = 321.3 Hz, TfO^-]; 127.9/128.1 (2 d), 128.5/128.9 (2 d), 130.7 (d) (all aromatic CH), 136.3 (*i*-C of Ph), 146.0 (C-7′), 157.1 (s), 160.5 (s), 165.1 (C-4′). – $C_{30}H_{43}N_2O_4S$ (584.7): calcd. C 61.62, H 7.41, N 4.79; found C 61.4, H 7.5, N 4.6.

X-Ray Crystal Structure Analysis of **28**[22]: *Crystal data:* $C_{30}H_{43}F_3N_2O_4S$, molecular mass 584.7, orthorhombic, space group *Pbca*, a = 13.188(3), b = 17.688(3), c = 26.327(4) Å, α = β = γ = 90°, Z = 8, d_{calc} = 1.26 g cm^{-3}. – *Data collection:* Crystal size 0.8 × 0.4 × 0.3 mm, monochromatized Mo-K_α radiation, 3625 reflections measured (2.0 ≤ Θ ≤ 22.0°, one octant), 3625 unique, 2331 observed [$I > 2\sigma(I)$], ω/2Θ scan, scan width (1.00 + 0.35 tanΘ)°; no absorption correction (μ = 1.52 cm^{-1}). – *Structure solution and refinement*[23]: Structure solution by direct methods (MULTAN), refinement by a full-matrix least-squares method, refinement on *F*. Hydrogen atoms were located in a difference electron map and included into refinement with fixed *B* values. Refinement converged at R = 0.0528, R_w = 0.0508 (unit weights, 533

parameters); final shift/error ratio ≤ 1.20, residual electron density ≤0.20 e Å^{-3}.

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[22] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57987, the names of the authors, and the journal citation.
[23] The program system *MolEN, An Interactive Structure Solution Procedure* (Enraf-Nonius, Delft, The Netherlands, **1990**) was used.

[22/94]