JOC The Journal of Organic Chemistry

Article

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Stereoselectivity of Additions to *N*-Methyl Acetonitrilium Fluorosulfonate

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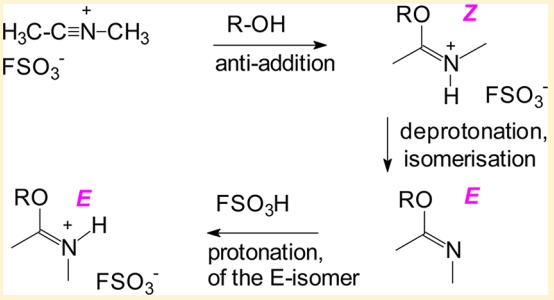
Supporting Information

ABSTRACT: Alkoxy-*N*-methyl-acetiminium salts were prepared by addition of CH_3OH and C_2H_5OH to *N*-methyl acetonitrilium fluorosulfonate at low temperature. Analysis of the $^5J_{HH}$ and $^3J_{^{13}C-H}$ coupling constants in the NMR spectra showed an anti addition with a diastereoselectivity of >95%. Deprotonation of these salts with (*Z*)-configuration gave the corresponding *N*-methyl-alkoxyacetimines with very high (*E*)-configuration. Upon protonation at −78 °C, these iminoesters gave the corresponding alkoxy-*N*-methyl-acetiminium salts with (*E*)-configuration. Computational analyses of the iminoesters and the corresponding iminium cations including the conformations give insight into the relative stability. Nitrilium salts can be used as reagents, exemplified by some esterifications between simple acids and alcohols.



INTRODUCTION

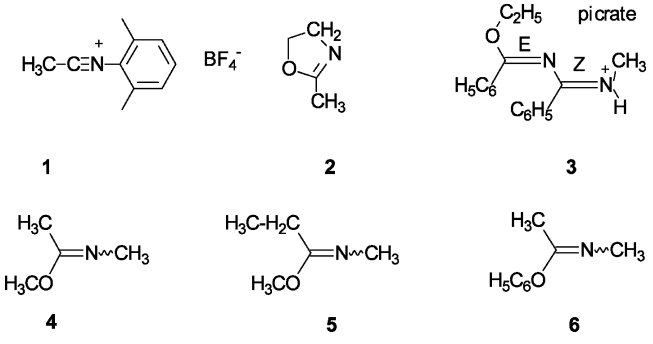
Nitrilium salts were first prepared by Meerwein by reaction of trialkyloxonium salts and aryl diazonium fluoroborates with nitriles or by reaction of N-substituted chloroimines with strong Lewis acids.[1] Methylation with FSO_3CH_3 is a very convenient method for methylation of alkyl- and aryl-nitriles because the FSO_3^- salts are less hygroscopic than the BF_4^- salts.[2−4] The N-methylation of nitriles by treatment with FSO_3CH_3 occurs at lower temperature and provides higher yields of these hygroscopic salts.

Also, N-alkylation is readily achieved by reaction of nitriles with Lewis acids and alkylhalides.[5,6] Furthermore, nitrilium cations are intermediates in Beckmann rearrangements,[7,8] in the Schmidt-[9] and the Ritter-reaction,[10] as well as in the Ugi reaction.[11] Nitrilium salts are highly reactive and can undergo a variety of reactions. Addition of nucleophiles leads to reactive intermediates which can undergo a wide variety of further reactions.[5,6] According to the X-ray structure analysis of *N*-(2,6-dimethyl)phenyl acetonitrilium BF_4^- (**1**), the nitrilium moiety is linear with a C≡N bond length of 1.13 Å, slightly shorter than that in nitriles (1.16 Å; Scheme 1).[12,13] A detailed analysis by advanced ab initio calculations has appeared.[14]

We report here our results about the stereoselectivity of additions of simple alcohols to *N*-methyl-acetonitrilium fluorosulfonate **7**. Reaction of CH_3OH and C_2H_5OH to **7** at −20° gave the alkoxy-*N*-methyl-acetiminium salts (*Z*)-**8** and (*Z*)-**9**, respectively, from which the corresponding *N*-methyl-alkoxy-acetimines (*E*)-**10** and (*E*)-**11** were obtained by deprotonation (Scheme 2).[15]

Treatment of the alkoxyacetimines (*E*)-**10** and (*E*)-**11** with FSO_3H at −70° gave stereoselectively the *N*-methyl-alkoxyacetiminium salts (*E*)-**8** and (*E*)-**9**, respectively (Scheme 2).[16,17]

Scheme 1



RESULTS AND DISCUSSION

The assignment of the E-configuration to (*E*)-**10** and (*E*)-**11** is based on $^5J_{HH}$ coupling constants. Protonation under controlled conditions led to the acetiminium salts (*E*)-**8** and (*E*)-**9**. The $^5J_{HH}$ coupling constants measured were compared with those obtained for the acetiminium cations prepared by addition of alcohols to the nitrilium salt **7**.

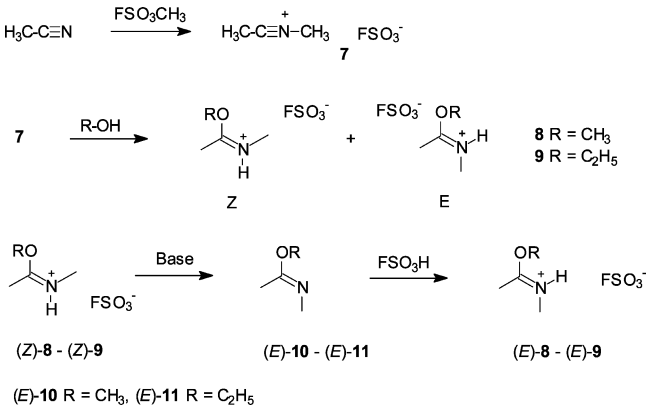
The key information for the assignment of the configuration in *N*-methyl alkoxyacetimines is due to Weinberger, who reported that the ^{1}H NMR spectrum of 2-methyloxazolin (**2**), where the CH_3 and the CH_2 group are *trans* to each other, showed a $^5J_{HH}$ coupling constant of 1.38 Hz.[18]

Kandel used this information to assign the $^5J_{HH}$ coupling constant of 1.25 Hz in phenoxy-*N*-methyl-acetimine to the (*Z*)

Special Issue: Howard Zimmerman Memorial Issue

Received: September 12, 2012
Published: October 31, 2012

Scheme 2



isomer and the smaller one of 0.25 Hz to the (*E*)-isomer, where the two CH_3 groups are *cis* to each other.[19] Walter analyzed several open chain alkoxyimines, such as **4**–**6**, and associated the $^5J_{HH}$ coupling constants of 1.25 Hz and 0.3–0.5 Hz with the (*Z*)- and (*E*)-isomers, respectively (Table 1).[20] Measurement

Table 1. Coupling Constants $^5J_{HH}$ (Hz) of the *N*-Methyl-alkoxyimines 4–6 with Their *E*:*Z* Ratios[20]

iminoester	solvent	$^5J_{HH}$ (*Z*)	$^5J_{HH}$ (*E*)	ratio *E*:*Z*
4	CCl_4		0.4 q	100:0
	CD_3OD	1.2	0.4 q	95:5
5	CCl_4		0.3 t	100:0
	CD_3OD	1.0 t	0.3 t	95:5
6	CCl_4	1.3 q	0.5 q	69:31
	CD_3OD	1.3 q	0.5 q	56:44

of dipole moments of 2-substituted oxazolines with (*Z*)-configuration, being smaller, and cyclic 2 methoxyimines ((*E*)-configuration), being larger, are compatible with the configuration determined by NMR measurements.[21]

Thus, it is evident that N–CH_3-alkoxyacetimines such as **4**–**6** have preferentially, if not exclusively, (*E*) configuration, with the 2 alkylgroups of the C=N double bond being *cis* to each other. The X-ray structure of **3** with the ethoxyimine-substructure shows this stereochemistry.[22] It should be noticed that the adjacent *N*-methyl-iminium substructure has (*Z*) configuration (cf. Scheme 5 for computational results). In our case, the *N*-methyl-alkoxyacetimines (*E*)-**10** and (*E*)-**11** were prepared by deprotonation of the adducts obtained by addition of alcohols to the nitrilium salt **7**.

The $^5J_{HH}$ coupling constant for (*E*)-**10** closely corresponds to that of (*E*)-**4**, whereas we measured a slightly larger coupling constant for (*E*)-**11** than that reported for (*E*)-**5** (cf. Table 2); **4** and **5** are identical with **10** and **11**, respectively). Upon protonation under conditions where an isomerization can be

Table 2. ^{1}H-NMR Results (ppm; *J*(Hz)) for the *N*-CH_3-Alkoxyacetimines (*E*)-10 and (*E*)-11 Prepared by Deprotonation of the *N*-CH_3-Alkoxyacetiminium Salts 8 and 9 in CD_2Cl_2 (Scheme 2)

	R	R—O	=N—CH_3	H_3C—C=N	$^5J_{HH}$
(*E*)-**10**	H_3C	3.62 s	3.00 q	1.88 q	0.51
(*E*)-**11**	H_3C–CH_2	4.03 q	2.98 q	1.87 q	0.49

excluded, the *N*-CH_3-alkoxyacetiminium cations of (*E*)-**8** and (*E*)-**9** should have preserved the (*E*)-configuration (Table 3).

When (*E*)-*N*-CH_3-methoxyacetimine (*E*)-**10** was slowly added to FSO_3H in CD_2Cl_2 at −78 °C, the ^{1}H NMR spectrum showed the expected signals for (*E*)-**8** with $^5J_{HH}$ = 0.46 Hz. In addition, signals of minor intensity were observed at 2.58, 3.07, and 4.28 ppm including the coupling constant $^5J_{HH}$ = 1.0 Hz. These signals correspond to those observed in the product (*Z*)-**8**, formed by addition of CH_3OH to the nitrilium salt **7**. Addition in the inverse sequence, i.e. treatment of *N*-CH_3-methoxyacetimine (*E*)-**8** with FSO_3H at rt, gave the two sets of signals for the (*E*)- and (*Z*)-isomers of *N*-CH_3-methoxyacetiminium cations **8** in the ratio *Z*:*E* = 5:2. The mechanistic pathways for the formation of this diastereomeric mixture have not been determined.[20]

These results are to be compared with the appropriate *N*-CH_3-alkoxyacetiminium cations (*Z*)-**8** and (*Z*)-**9** obtained by addition of alcohols to *N*-CH_3-nitrilium salts (Scheme 2) (Table 4). It is apparent that the addition of alcohols to *N*-CH_3-acetonitrilium cation proceeds preferentially, if not exclusively, in an anti fashion to give the (*Z*)-isomers (*Z*)-**8** and (*Z*)-**9**.

Olefins with one vinylic H show $^3J_{^{13}C-C-C-H}$ coupling constants of ca. 7 Hz in the case where the C atom of the allylic substituent is *trans* to the vinylic H and a $J_{^{13}C-C=C-H}$ coupling constant of 11 Hz for a *cis* relationship.[23,24] A similar result has been reported for acetamide where the $^3J_{^{13}C-H}$ in $(H_3CCO)H_3\underline{C}C-N\underline{H}_2$ is 7.1 Hz for the *trans*- and <1 Hz for the *cis* relationship.[25,26] In view of these results it was of interest to analyze the $^3J_{^{13}C-C=N\underline{H}^+}$ in the $(R)_3\underline{C}$—C=N$\underline{H}^+$(CH_3) substructure for the stereoisomers of the *N*-methyl-methoxy-acetiminium cations. As shown in Tables 2 and 3, the (*E*) isomer with a *trans* H_3C—C=N^+H arrangement shows a larger coupling constant than the (*Z*) isomers prepared from the nitrilium salts directly. Although we have only a few examples in hand, it was tempting to use these observations for analyzing the configuration in *N*-methyl-alkoxy-iminium cations, where a $^5J_{HH}$ is absent.

In a first example, the *N*-methyl-methoxy-2,4,6-trisisopropylbenzonitrilium FSO_3^- salt **13**, prepared from **12c**, was submitted to the same reaction sequence as described above for the acetiminium salts (Scheme 3).

Addition of CH_3OH at low temperature gave the *N*-methyl-iminium cation (*Z*)-**14** with (*Z*)-configuration, from which the imine (*E*)-**15** was obtained by base treatment (Scheme 3). Reaction of this imine with FSO_3H gave the (*E*)-*N*-methyl-iminium cation (*E*)-**14**. On the basis of the (*E*)-configuration, shown for the *N*-methyl-alkoxy-acetimines (*E*)-**10** and (*E*)-**11**, it is reasonable to assume that the imine **15** also has the (*E*)-configuration. Protonation under mild conditions should preserve this configuration: Consequently, the $^3J^{13}_{Cipso-C=N^+-H}$ of ∼5.4 Hz is assigned to the (*E*)-isomer (*E*)-**15**. The $^3J_{^{13}Cipso-C=N^+-H}$ coupling constant of 1.5 Hz found for the iminium salt (*Z*)-**14**, prepared by addition of CH_3OH to the nitrilium salt **13** is compatible with an anti addition and formation of the (*Z*)-isomer (Z)-**14**. The ^3J coupling constants were extracted from selective decoupling experiments (cf. the Experimental Part).

The mechanism of the highly stereoselective additions of alcohols to the nitrilium salts **7** and **13** leading to the (*Z*)-isomers via an anti addition may be discussed in terms of a reaction at a stereoelectronically optimal angle.[27] The concomitant addition of H^+ terminates the reaction.

dx.doi.org/10.1021/jo301983s | J. Org. Chem. 2013, 78, 1965–1970

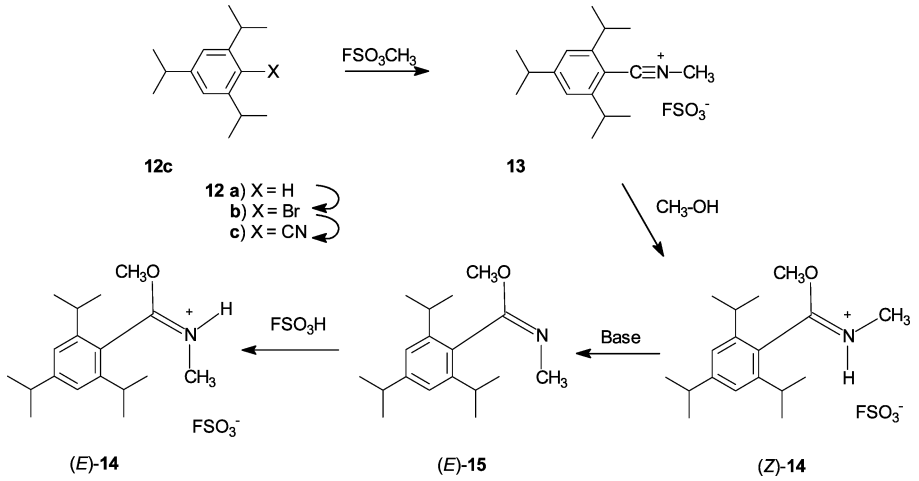
Table 3. ^{1}H-NMR Results (ppm; J(Hz)) for the N-CH_3-Alkoxyiminium Salts Prepared by Protonation of the (E)-N-CH_3-Alkoxyimines (E)-8 and (E)-9 in CD_2Cl_2 at −78 °C (Scheme 2)

	R	R—O	=NH$^+$—C$\underline{H}_3$	$\underline{H}_3$C—C=NH$^+$	$^5J_{HH}$	$^3J_{^{13}C-H}$
(E)-**8**	$\underline{H}_3$C	4.19 s	3.29 dxq	2.44 m	0.46	5.0
(E)-**9**	H$_3$C—C$\underline{H}_2$	4.48 q	3.27 d	2.41 m	0.3	4.72

Table 4. ^{1}H-NMR Results (ppm; J(Hz)) for the N-CH_3-Alkoxyiminium Salts Prepared by Addition of Alcohols to N-CH_3-Acetonitrilium FSO_3^- 7 at −20 °C in CD_3CN (Scheme 2)

	R	R—O	=NH$^+$—C$\underline{H}_3$	$\underline{H}_3$C—C=NH$^+$	$^5J_{HH}$	$^3J_{^{13}C-H}$
(Z)-**8**	$\underline{H}_3$C	4.26 s	3.23 dxq	2.49 m	1.0	
(Z)-**9**	H$_3$C–C$\underline{H}_2$	4.55 q	2.98 dxq	2.44 dxq	0.9	1.7

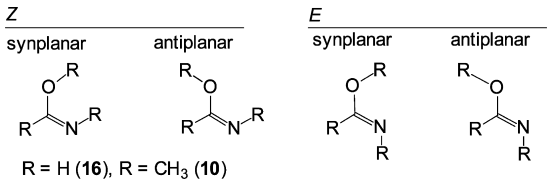
Scheme 3



Upon deprotonation the (Z)-alkoxyiminium salts (Z)-**8**, (Z)-**9**, and (Z)-**14** isomerize to the (E)-N-methylalkoxyimines (E)-**10**, (E)-**11**, and (E)-**15**, respectively. According to detailed NMR analyses by Kessler and others, the (Z)- to (E)-isomerization occurs via in-plane inversion at the N center.[28,29]

Computational Aspects. The structures of the stereoisomers of the (Z/E)-alkoxyimine **10** and of the (Z/E)-alkoxyiminium cations of **8** are to be discussed in terms of the two configurations, including the syn(peri)- and anti(peri)-planar conformations of the methoxy group (Scheme 4).

Scheme 4. The Z/E Configurations Including the Synplanar/Antiplanar Conformations of Hydroxyformimine 16 and N-Methyl-methoxyacetimine 10



First we repeated Pople's ab initio calculations[30] on hydroxyformimine (**16**) at the B3LYP/6-31+G(2d,2p) level of theory using Gaussian09.[31] Our computational results confirm that E_{sp} is the stable isomer although Z_{sp} and Z_{ap} are inverted (Table 5). All isomers have C_s symmetry.

We calculated the diastereomeric structures including the conformations of N-CH_3-methoxyacetimine (E/Z)-**10** and their protonated congeners (E/Z)-**8** at the same level of theory (see Table 5). The iminoester **10** has a similar order of stabilities as

Table 5. Relative Energies (kcal/mol) for the Z/E Diastereomers of Hydroxyformimine 16, the Iminoester (Z/E)-10, the N-CH_3-methoxyacetiminium Cation (Z/E)-8, and Their Antiperiplanar (ap)/Synperiplanar (sp) Conformations (in parentheses, the results from ref 30 for 16)

	Z sp	Z ap	E sp	E ap
16	3.1 (6.7)	3.8 (3.8)	0.0	6.6 (8.3)
10	7.8	4.1	0.0	8.8
8	7.0	0.0	2.3	2.1

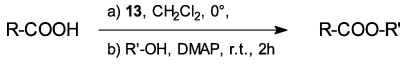
16, with E_{sp} being the most stable isomer and E_{ap} being the least stable structure, thus supporting the experimental results for **4**,[20] discussed above. In the protonated series, **8**, the stable structure is Z_{ap} with an antiplanar conformation. Z_{sp} (**8**) is associated with the highest energy as for **10**. This configuration has been observed in the substructure of **3**. Interestingly, all the *synplanar* conformers are associated with stationary points in C_1 symmetry, slightly distorted out of C_s. The *antiplanar* conformers are stable in C_s symmetry, with the exception of E_{ap} **10**, which has C_1 symmetry. The reason of distortion from planar symmetry in **10**, at variance from **16**, must be due to the larger steric hindrance of the methyl groups.

Nitrilium Salts as Reagent. It is well-known that nitrilium salts, most often prepared in situ, are useful building blocks in preparations of a variety of compounds.[3,5,6,32,33] We have explored reactions where a nitrilium salt serves as reagent for esterifications under mild conditions (Scheme 5).

Addition of an acid to the nitrilium salt **13** leads to an intermediate, which is an iminium analogue of a protonated

dx.doi.org/10.1021/jo301983s | J. Org. Chem. 2013, 78, 1965−1970

Scheme 5



anhydride and may thus show an enhanced reactivity. (The configuration of this intermediate salt has not been determined.) Reaction of an alcohol at rt for 2 h led to the appropriate ester; the reactions were not optimized (Table 6).

Table 6. Nitrilium Salt 13 as Reagent for Formation of Esters from Acids and Alcohols (Scheme 5)

exp	acid **17** R =	R′OH	yield **18** (%)
a	CH_3-	butan-2-ol	39
b	CH_3-	phenol	94
c	H_5C_6-	phenol	30
d	H_5C_6-CH_2-	geraniol	61
e	CH_3-	geraniol	47

CONCLUSIONS

Detailed NMR-analyses were used to determine the stereoselectivity of additions of simple alcohols to the nitrilium salts **7** and **13**. It is concluded that these additions proceed preferentially via an anti addition to *N*-methyl-alkoxyacetiminium salts with Z-configuration. These assignments are based on $^5J_{HH}$ coupling constants reported for *N*-methyl alkoxyacetimines which were transferred to the iminium cations prepared by protonation of these iminosters and addition of alcohols to the nitrilium salts, respectively. $^3J_{^{13}C-H}$ coupling constants ($(R)_3\underline{C}$—C═N$\underline{H}^+(CH_3)$) were correlated with the $^5J_{HH}$ coupling constants to show that the addition of methanol to the nitrilium salt **13** also occurs with a high stereoselectivity. Finally it should be mentioned that *N*-alkyl-methoxyacetiminium salts can also be generated by alkylation of *N*-methylacetamide with FSO_3CH_3. Since it is known that *N*-methylacetamide exists exclusively in the "peptide" configuration ((*Z*)-arrangement),[26] it is not surprising that this compound gives exclusively the *N*-methylmethoxy-acetiminium (*Z*)-**8**.

EXPERIMENTAL PART

General. All experiments were conducted under N_2. Solvents: the most relevant solvents were distilled prior to use. FSO_3CH_3: Fluka pract. distilled under Ar; FSO_3H: Fluka pract. distilled under Ar; DMAP: Fluka purum; Cu(I)CN: Siegfried purum; CH_2Cl_2: distilled over P_2O_5; $(n\text{-}Bu)_4N^+Cl^-$: Fluka techn. crystallized from CCl_4. Other reagents were used as obtained. For work up sat. $NaHCO_3$, 2 N $NaHCO_3$, NaCl sat., and 2 N HCl were used. The solutions were dried over $MgSO_4$. For CC silica gel 60 (Merck) was used. GC: analytical: column length 2 m, diameter 2 mm; preparative: column length 3.6 m, diameter 10 mm. Mp. were measured in an open capillary and are uncorrected. Bp. are not corrected, for Kugelrohr distillations the temperature of the oven is given. IR spectra (cm^{-1}) were measured in $CHCl_3$; only the most intensive signals are reported, sh (shoulder). ^1H NMR spectra (δ in ppm) were recorded in $CDCl_3$; otherwise, the solvent is given. The coupling constants *J* are given in Hz, with the following abbreviations: s(inglet), d(oublet), t(riplet), q(uartet), S(eptet), m(ultiplet), br (broad). ^{13}C NMR spectra were recorded at 25.2 MHz. MS were measured at 70 eV, direct inlet, source temp. 250°. The temp. of the sample is given in brackets. The peaks are reported as *m*/*z* %; intensities relative to the strongest peak.

Computations. All calculations were carried out with Gaussian 09,[30,31] at density functional level (with hybrid B3LYP functional), using the 6-31G+(2d,2p) basis set. For some compounds, the results were compared against those at MP2 level, to detect possible ambiguities of DFT calculations.

For the two conformations of each of the (Z)- and (*E*)-configurations of **8** and **10**, molecular geometry optimizations were carried out, searching for true minima on the potential energy surface (PES) by calculation of the frequencies. An initial guess was obtained from molecular mechanics simulations. All simulations do not include temperature effects.

***N*-Methyl-acetonitrilium Fluorosulfonate 7.** To freshly distilled FSO_3CH_3 (11.4 g, 0.1 mol) was added 1.37 g (33.3 mmol) of CH_3CN in one batch under N_2. After stirring the mixture for 1 h at 50 °C, the excess of FSO_3CH_3 was removed in high vacuo to give 4.05 g (79%) of a clean, white salt, which was stable for several weeks at −20 °C.

Mp 84−90 °C (sealed tube); IR (cm^{-1}; Nujol, 10% suspension): 3290m, 3190 (sh), 2640 (sh), 2410, 1280, 1155, 1105, 1075, 735, 655, 580; additional signals at 1680 and 1635; probably C═N stretch vibrations. ^1H NMR (60 MHz, CD_3CN): 2.82 (m, 3H), 3.75 (m, 3H) [2.67, 3.66 and coupling constants;[34b] 2.78, 3.71[34] both for the BF_4^- salt); additional signal at 2.43 (ca. 0.3 H). ^{13}C NMR (CD_3CN): 8.33 (q, J = 140.6 Hz) broadend by $^4J \sim 1.0$ Hz), 39.46 (qxt, ^1J = 150.89 Hz; ^1J ($^{13}C-^{15}N$) = 7.35 Hz), 113.47 (t, ^1J ($^{13}C\equiv^{15}N$) = 47.47 Hz); $C_3H_6FNO_3S$; calc. C 23.22, H 3.90, N 9.03, found: C 23.01, H 3.73, N 8.85.

Addition of Alcohols to *N*-Methylacetonitrilium Fluorosulfonate 7. General procedure. A weighted amount of the nitrilium salt 7 in a flame-dried NMR tube was dissolved in CD_3CN and treated with an equivalent amount of the alcohol at −30 °C. The tube was attached to a vibromixer and vibrated for 5 min at −20 °C. The ^1H- and ^{13}C NMR spectra were subsequently recorded at rt.

(*Z*)-*N*-Methyl-methoxyacetonitrilium Fluorosulfonate [(*Z*)-8]. ^1H NMR (CD_3CN) (100 MHz): 2.49 (m, 3H), 3.23 (dxq, ^3J (H−CH_2−N^+−H) 5.0, 3H), 4.26 (s, 3H) for further data, see Table 2; ^{13}C NMR: 17.6, 29.5, 60.7, 177.6.

(*Z*)-*N*-Methyl-ethoxyacetonitrilium Fluorosulfonate (*Z*)-9. ^1H NMR (CD_3CN) (100 MHz): 1.44 (t, J = 7.2 Hz, 3H), 2.44 (dxq, $^5J_{HH}$ = 0.95, ^4J (H−CH_2−C═N^+−H) = 0.78, 3H), 2.98 (dxq, $^5J_{HH}$ = 0.9 Hz, $^3J_{HH}$ = 5.0 Hz, 3H), 4.55 (J = 7.2 Hz, 2H), 11.80 (br); ^{13}C NMR (CD_3CN): 14.41 (qxt, ^1J = 128 Hz, ^2J(^{13}C−C−H) = 3 Hz, 18.12 (qxm), ^1J = 132 Hz, ^3J(^{13}C—C═N^+—H) = 1.7 Hz, 29.37 (qxm, ^1J = 142 Hz), 71.66 (txqxm), ^1J = 150 Hz, $^2J_{CH}$ = 4 Hz) 178.1; additional couplings are not resolved.

N-CH_3-Alkoxyacetimines **10** and **11** by deprotonation of the *N*-CH_3-alkoxyacetonitrilium salts **8** and **9**.

(*E*)-*N*-Methyl-methoxyacetimine [(*E*)-10].[35] In a 25 mL three-necked flask equipped with a N_2 valve and a stirring bar, 1.9 g (12.3 mmol) of nitrilium salt (**7**) was dissolved in 50 mL of CH_3CN and cooled to −20 °C. The solution of an equimolar amount of the alcohol in acetonitrile was slowly added. After removal of CH_3CN under N_2 at the rotary evaporator, the residue was taken up in CH_2Cl_2 and cooled to 0 °C. After addition of an equimolar amount of $(i\text{-}Pr)_2NH$ in CH_2Cl_2, the solution was stirred for 1 h. The soluble compounds were distilled off into a cooling trap at 300 Torr and fractionated under normal pressure. The residue was purified by GC. Yield: 0.27 g (25%), GC-purity 99.7% [GC: Carbowax 1900, 5% on Chromosorb, 60°, 20 mL of N_2/min] t_R: 6.3 min.] IR (cm^{-1}): 2950 s, 2910, 1685 (1675 [33]), 1435, 1370, 1265, 1050; ^1H NMR (100 MHz): 1.88 (q, $^5J_{HH}$ = 0.51, 3H), 3.00 (q, $^5J_{HH}$ = 0.51, 3H), 3.62 (s, 3H); ^{13}C NMR: 14.3, 36.05, 52.08, 162.7.

(*E*)-*N*-Methyl-ethoxyacetimine (*E*)-11. *This Alkoxyimine Was Prepared Analogously.* Yield after GC-separation [Carbowax 20M, 20% on Chromosorb A, 60 °C, 254 mL N2/min] t_R 34 min: 0.006 g (5%); IR (cm^{-1}): 2960, 1670, 1370, 1265, 10.50; ^1H NMR (CD_2Cl_2): 1.26 (t, J = 7, 3H), 1.87 (q, $^5J_{HH}$ = 0.49, 3H), 2.98 (q, $^5J_{HH}$ = 0.49 Hz, 3H), 4.03 (q, J = 7 Hz, 2H); ^{13}C NMR: 14.37, 14.42. 35.96, 60.17, 161.97; MS (20°): 101(14, M^+), 86 (11), 73(58), 58(44), 57(100), 56(92), 43(53), 42(86); $C_5H_{11}NO$: calc. 59.37, H 10.96. N 13.85; found: C 59.43, H 11.18, N 13.72.

dx.doi.org/10.1021/jo301983s | J. Org. Chem. 2013, 78, 1965−1970

Addition of FSO_3H to (*E*)-Alkoxyacetimines (*E*)-10 and (*E*)-11. General procedure. A weighted amount of FSO_3H in a dried NMR tube under N_2 was dissolved in CD_2Cl_2 and cooled to −78 °C. A solution of the iminoesters (*E*)-**10** and (*E*)-(**11**) (~99% of 1 mol equiv) in CD_2Cl_2 was slowly added, and the mixture was vibrated for 5 min at −78 °C. The protonated iminoesters (*E*)-**8** and (*E*)-**9** were characterized by their ^1H and ^{13}C spectra.

(*E*)-*N*-Methyl-methoxyacetonitrilium Fluorosulfonate [(*E*)-8]. ^1H NMR (CD_2Cl_2) (80 MHz): 2.44 (m, 3H), 3.29 (dxq, $^3J_{HH}$ = 5 Hz, $^5J_{HH}$ = 0.46 Hz, 3H), 4.19 (s, 3H, 10.12 (br), coupling constants were extracted from an experiment with inverse addition at rt); ^{13}C NMR (CD_2Cl_2) (80 MHz): 18.1, 32.4, 59.1. 177.6.

(*E*)-*N*-Methyl-ethoxyacetonitrilium Fluorosulfonate [(*E*)-9]. ^1H NMR (CD_2Cl_2) (80 MHz): 1.50 (t, *J* = 7.2, 3H), 2.41 (m, $^5J_{HH} \leq$ 0.3 Hz, 3H), 3.28 (dxq, $^3J_{HH}$ = 5 Hz, $^5J_{HH} \leq$ 0.3 Hz, 3H), 4.48 (q, *J* = 7 Hz, 2H), 9.96 (br); ^{13}C NMR (CD_2Cl_2) (80 MHz): 13.4 (qxt, ^1J = 128.8 Hz, $^2J(^{13}\underline{C}\text{-CH-}\underline{H})$ = 3.1 Hz), 17.8 (qxd, ^1J = 132.6 Hz, $^3J_{trans}$ ($^{13}\underline{C}$—C═N^+—$\underline{H}$ = 4.7)), 32.2 (q, ^1J = 143.4 Hz), 69.4 (txq, ^1J = 150.1 Hz, $^2J(^{13}\underline{C}H_2\text{—}CH_2\text{—}\underline{H})$ = 4.3 Hz), 176.8.

***N*-Methyl-2,4,6-trisisopropylbenzonitrilium Fluorosulfonate 13.** 2,4,6-Trisisopropyl-benzonitril (**18c**) was prepared from 1,3,5-trisisopropylbenzene (**12a**) in two steps via (**12b**).[36,37] The reaction mixture, prepared from 18.32 g (80 mmol) (**12c**) and 27.28 g (0.24 mol) of FSO_3CH_3 was stirred at 45° for 45 h. The excess of FSO_3CH_3 was pumped off in high vacuo and the colorless salt left under high vacuo for 20 h.

Yield: 25.04 g (91%). Mp: 86−90° (sealed tube). IR (Nujol, cm^{-1}): 2960, 2320, 2250, 1595, 1275, 1215, 1065, 575; ^1H NMR (60 MHz): 1.28 (d, *J* = 7.2 Hz, 6H), 1.37 (d, *J* = 7.2 Hz, 12H), 3.13 (S, *J* = 7.2 Hz, 3H), 4.33 (s, 3H), 7.17 (s, 2H); ^{13}C NMR: 23.2 q, 23.5 q, 32.7 q, 33.4 d, 35.2 d, 98.7 s, 105.7 s (br), 122.7 d, 158.3 s, 161.1 s.

(*Z*)-*N*-Methyl-methoxy-2,4,6-trisisopropylbenziminium Fluorosulfonate (*Z*)-14. This product was prepared as described above for **8** and **9**; $CDCl_3$ was used as solvent for better solubility. ^1H NMR (60 MHz): 1.20−1.31 (d, *J* = 7.5 Hz, 18H), 2.34 (~S, *J* = 7.5 Hz, 1H), 3.33 (d, *J* = 5.0 Hz, 3H), 3.97 (s, 3H), 7.15 (s, 2H), 11.30 (bro); disturbing signal at 4.30. ^{13}C NMR: 23.3 q, 23.6 q, 24.7 q, 30.2 q, 32.2 d, 34.4 d, 61.3 q, 118.9 s, 122.4 d, 146.1 s, 154.5 s, 177.1 s; Coupling constants after selective decoupling of the o-$C\underline{H}(C_3H_7)_2$ signals: C_{ipso}: $^3J_{^{13}C\text{—}C=N^+H} \approx$ 1.5, $^3J_{^{13}C\text{—}CC(meta)H}$ ca. 4.9, C_{meta} dxd: ^1J = 98 Hz, ^3J = 4.1 Hz, $C_{iminium}$: $^2J_{C=N^+H}$ 3.62.

(*E*)-*N*-Methyl−methyloxy-2,4,6-trisisopropylbenzimine [(*E*)-15]. To a solution of the *N*-methyl-nitrilium salt (*Z*)-**14** (5.37 g, 15.66 mmol) in CH_2Cl_2, cooled to −78°, was dropped 0.5 g (15.66) mmol) of CH_3OH. The organic phase was shaken 3× with 2 N Na_2CO_3 and was dried over Na_2SO_4. CC with *n*-pentane−Et_2O = 1:1 as eluent gave 2.75 g (64%) of (*E*)-**15**, which was crystallized from pentane at −20 °C and sublimed at 6 × 10^{-5} Torr to give GC pure product. Mp 37−39 °C. R_f (*n*-pentane−Et_2O = 1:1): 0.48; GC (anal.), t_R: 12.8 min; XF-1150, 5% on chromosorb, 100 °C, 30 mL N_2/min; IR (cm^{-1}): 2960, 2870, 1670, 1460, 1285, 1255, 1040, 870; ^1H NMR (80 MHz): 1.19 (d, *J* = 7, 12H), 1.24 (d, *J* = 7, 6H), 2.74 (~S, *J* = 7, 3H), 2.78 (s, 3H), 3.73 (s, 3H, 7.00 (s, 2H)); ^{13}C NMR: 23.7 q, 23.9 q, 24.7 q, 31.25 d, 34.3 d, 37.2 q, 52.3 q, 120.7 d, 128.5 s, 145.1 s, 149.5 s, 163.8 s; MS (20°) 276(7), 275 (35, M+), 274(3), 261(21), 260(100), 245(18), 244(11), 229(16); EA $C_{18}H_{29}NO$: calc. C 78.49, H 10.61, N 5.09; found: C 78.48, H 10.60, N 5.06.

(*E*)-*N*-Methyl-methoxy-2,4,6-trisisopropylbenziminium Fluorosulfonate (*E*)-14. As described above for the protonation of **9** and **10**, (*E*)-**15** was treated with FSO_3H in $CDCl_3$ ^1H NMR (60 MHz): 1.10−1.40 (2d, 18H), 2.54 (~S, *J* = 7 Hz, 2H), 2.96 (m, *J* = 7 Hz, 1H), 3.14 (d, *J* = 5.0 Hz, 3H), 4.40 (s, 3H), 7.16 (s, 2H), 11.2 (br); ^{13}C NMR (−10°): 23.5 (qxm, ^1J = 126 Hz), 23.7 (qxm, ^1J = 126 Hz), 24.9 (qxm, ^1J = 126 Hz), 31.7 (qxm, ^1J = 124 Hz), 33.6 (q, ^1J = 143.8 Hz), 34.4 (dxm, ^1J ~ 110 Hz), 59.9 (q, ^1J = 151 Hz), 119.8 (s, br), 122.2 (dxt, ^1J = 157 Hz), 145.5 (m*), 153.9 (m), 176.7 (m); (*) coupling constants after decoupling of the $-\underline{H}C(CH_3)_2$ at 2.53 ppm: C_{ipso} 145.5 (q): $^3J_{^{13}C\text{—}C\text{—}C\text{—}H} = {}^3J_{^{13}C\text{—}C=N^+\text{—}H}$ = ca. 5.4 Hz). Excitation at 7.16 ppm (2 H_{meta}) gives C_{ipso} at 145.5 ppm) as q.

Esterification with the *N*-Methyl Nitrilium Salt (13) as Reagent. Method A for exp. a−e: To a solution of the acid and DMAP (ca. 20 mol %) in CH_2Cl_2 was dropped a solution of **13** in CH_2Cl_2 at 0 °C. After addition of the alcohol (2 mol equiv) at rt, the mixture was left for 20 h. Diluted with CH_2Cl_2, the organic phase was washed 2× each with 0.5 N HCl and sat. $NaHCO_3$ solution. Work up gave the appropriate ester, which was purified and identified by comparison of its ^1H NMR spectrum with the published one.[38]

(a) The crude product was distilled in a Kugelrohr apparatus at normal pressure. bp 112°, ^1H NMR identical with Sadtler, Nr. 6787. (b) The crude product was distilled at 100 °C (15 Torr); ^1H NMR: identical with Sadtler 6777. (c) Purified via CC (pentane−ether = 4:1); ^1H NMR: identical with Sadtler 3173. (d) ^1H NMR corresponds to Sadtler 4240; (e) ^1H NMR corresponds to Sadtler Nr. 9479.

(*Z*)-*N*-Methylmethoxyacetonitrilium Fluorosulfonate ((*Z*)-8) from *N*-Methylacetamide. To FSO_3CH_3 (0.04 g, 0.35 mmol) in a NMR tube was added a solution of 0.026 g (0.35 mmol) *N*-CH_3-acetamide in CD_3CN, and the reaction mixture was kept for 24 h. The ^1H NMR spectrum was identical to that obtained by addition of CH_3OH to 7.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H spectra and Cartesian coordinates and absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Swiss National Science Foundation, a stipend of the Foundation of the Chemical Industry Basel, and the Canton of Bern. We thank Dr. U. Voegeli for many detailed NMR analyses.

■ DEDICATION

In memoriam: Howard E. Zimmerman, dedicated scientist with great enthusiasm and achievements.

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