1-Acyl-4-benzylpyridinium Tetrafluoroborates: Stability, Structural Properties, and Utilization for the Synthesis of Acyl Fluorides

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Keywords: 4-Alkylidene-1,4-dihydropyridines / 1-Acyl-4-benzylpyridinium tetrafluoroborates / Carboxylic acid fluorides / X-ray structures / Ab initio calculations / Density functional calculations

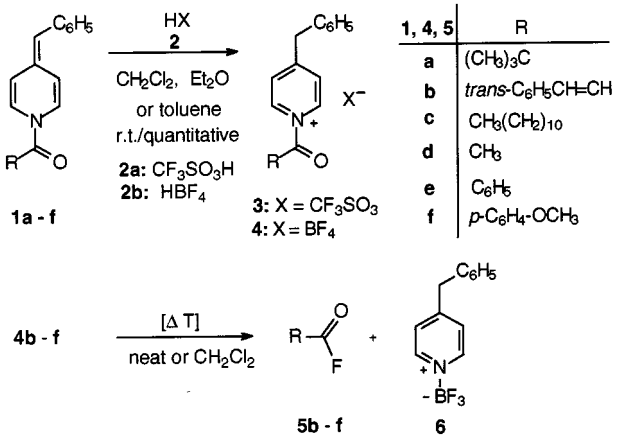
1-Acyl-4-benzylpyridinium salts **4** containing nonnucleophilic anions X^- such as $CF_3SO_3^-$, FSO_3^-, and BF_4^- can be generated quantitatively and in situ from 1-acyl-4-alkylidene-1,4-dihydropyridines **1a–f** and the corresponding acid, HX. The BF_4^- salts reveal an interesting and unexpected thermal instability which allows the convenient synthesis of carboxylic acid fluorides **5b–f**. This procedure offers advantages over known methods: All operations can be performed in a standard glass apparatus and do not require high pressures. The formation of RCOF **5** is assisted by the pyridine moiety of **4**, which splits off and functions as a Lewis base to intercept the BF_3 acid. The structural and electronic relationships as well as dominating differences between the very reactive cations of **4** and their almost "inert" uncharged precursors, the dihydropyridines **1**, are discussed both on the fundament of experimental evidence (X-ray structures of **1f** and the extremely reactive and very labile **4f**) and theoretical investigations (ab initio and DFT MO calculations).

Introduction

Acyl fluorides are conventionally prepared from the corresponding halides or anhydrides. Various reagents can be utilized for this transformation. Without thought of completeness, we summarize some examples: Frequently used inorganic salts like potassium fluoride,[1] potassium hydrogen fluoride,[2] or potassium fluorosulfinate[3] are just as suitable as sulfur tetrafluoride,[4] benzoyl fluoride,[5] dialkylaminosulfur trifluorides,[6] or 1,3-dimethyl-2-fluoropyridinium salts.[7] In some cases it is possible to obtain aroyl fluorides from aryl halides which had been treated with carbon monoxide and an alkali metal fluoride in the presence of palladium phosphane complexes.[8] Since use of anhydrous hydrogen fluoride as the fluorinating agent generally requires superatmospheric pressure, modern fluorination reactions alternatively employ the less volatile pyridinium poly(hydrogen fluoride)[9] or cyanuric fluoride.[10][11]

Although carboxylic acid chlorides and bromides can be utilized for standard acylation reactions, the corresponding fluorides are a useful class of compounds. In special cases, Friedel–Crafts reactions proceed with better or even reversed regioselectivity if an acyl fluoride/BF_3 system is used instead of an acyl chloride/$AlCl_3$.[12] Furthermore, there is considerable current interest in the smooth formation of amino acid fluorides from FMOC-protected[13] amino acid chlorides. These fluorides are relatively stable to hydrolysis and reactive towards amines, thus providing an effective peptide coupling method.[14] Another application of acyl fluorides is the stereoselective formation of α- and β-glycosyl esters in the presence of cesium fluoride.[15]

Recently, we reported the synthesis and reactivity of the 1-acylpyridinium salts **3** and **4**, which are quantitatively obtained from the readily available and stable 1-acyldihydropyridine precursors **1** by protonation with strong protonic acids **2a**,**b** (Scheme 1).[16]



Scheme 1. Synthesis of acylfluorides **5** from 1-acyl-4-benzylpyridinium tetrafluoroborates **4**

The anion X^- significantly controls the properties of these compounds. The reactive trifluoromethanesulfonates **3** were especially suitable for the acylation of sensitive chiral (secondary) alcohols, while the use of the analogous (even more reactive) tetrafluoroborates **4** generally resulted in low yields of the desired esters. A more detailed analysis of the crude reaction mixtures indicated that this must be due to

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  1434–193X/99/0909–2383 $ 17.50+.50/0

Table 1. Acyl fluorides **5b**−**f** prepared (cf. Scheme 1)

No.	R	method	melt.[a] *T* [°C]	decomp.[a] *T* [°C]	yield[b] [%]	b.p. [°C(mbar)]	ref.
5b	*trans*-$C_6H_5CH=CH$	**A**	>116	120	85	65 − 67 (0.7)	[7], [10]
		B			45		
5c	$CH_3(CH_2)_{11}$	**A**	> 76	85	77	84 − 85 (0.2)	[3], [7]
		B	−	−	55		
5d	CH_3	**A**	> 110	124	64	20 (1013)	[9]
5e	C_6H_5	**A**	> 120	127	74	31 (0.5)	[9]
		B	−	−	48		
5f	*p*-$CH_3OC_6H_4$	**B**	−	−	84	78 − 80 (0.3)	[53]

[a] Bath temperature. − [b] Yields of isolated and purified substances, structures confirmed by ^{1}H- and ^{13}C-NMR spectra (purity ⩾ 98%), other analytical data are in accordance with those given in the literature.

an unexpectedly enhanced tendency of the BF_4^- anion to decompose to F^- and BF_3. This decomposition is facilitated by the assistance of a Lewis base.

Results and Discussion

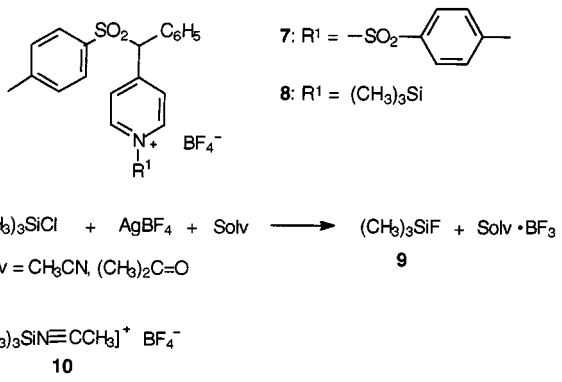
The observation that the salts **4** are thermally unstable was the starting point for the development of a synthetically useful method for the preparation of acyl fluorides **5b**−**f** in good yields, Scheme 1.

In general, the extremely moisture-sensitive and reactive salts **4a**−**f** were synthesized just prior to use, isolated if possible, and heated under normal pressure (fluorides with low boiling points) or in vacuo (higher boiling fluorides). At their specific oil bath temperature (Table 1), the solid materials melted with the formation of an orange liquid. At this point, the fluorides **5b**−**f** were distilled off immediately (Method **A**). Alternatively, the thermal lability of these pyridinium salts can be used for an in situ decomposition (Method **B**) of the compounds **4a**−**f**. This method is superior for salts **4** which can neither be crystallized nor isolated due to their sensitivity. Furthermore, Method **B** is advantageous if the RCOF product stability demands moderate temperatures. This is the case when additional functional groups are present. Both methods are suitable for the synthesis of alkyl, aryl and α,β-unsaturated acyl fluorides and thus appear to be generally applicable. The experimental results for acyl fluorides **5b**−**f**, obtained either according to Method **A** or **B**, are summarized in Table 1.

In the course of our investigations, we detected a limitation. If the 1-pivaloyl derivative **4a** was employed, no fluoride **5a** was detected in the distilled material obtained after decomposition. This was independent of the decomposition method employed. Instead nearly (NMR analytical) pure 4-benzylpyridinium tetrafluoroborate (**7**) was obtained as the only residue. The *tert*-butyl moiety was completely destroyed.[17]

Although the BF_4^- anion normally behaves as a relatively stable and weakly nucleophilic species, its stability is sometimes overestimated. Some tris(3-*tert*-butylpyrazolyl)hydroborato MCl (Mn, Fe, Co, Ni) complexes have been employed by Gorrell and Parkin for the facile abstraction of the fluoride from BF_4^- ion of $AgBF_4$.[18] Comparable reactions have been reported by Winter et al. They obtained special titanocene difluorides (containing silylated cyclopentadienyl ligands) from the corresponding titanocene dichlorides after reaction with $AgBF_4$ at room temperature.[19] A related example for the potential abstraction of F^- from BF_4^- has been investigated by Caputo et al.[20] They reported that use of acetonitrile as the solvent resulted in the trimethylsilylnitrilium tetrafluoroborate **10**. This result was refuted, however, by Bassinndale et al.[21] who proved the nonexistence of **10** as they managed to synthesize **9** quantitatively from a mixture of trimethylchlorosilane and $AgBF_4$ in both solvents. In this reaction, BF_3 was obtained as a by-product which was weakly coordinated to the solvent molecules (Scheme 2). These results as well as the earlier investigations by Lawton and Levy[22] are not surprising, since the formation of the extremely strong silicon fluorine bond[21] is the driving force for course of this reaction.

Previous investigation of 1-(4-methylphenyl)sulfonyl- and 1-trimethylsilyl-4-benzylpyridinium tetrafluoroborate (**7**) and (**8**) verified the lability of such compounds. In case of salt **7** (Scheme 2), the decomposition reaction is slow at room temperature and both sulfonic acid esters RSO_3R^1 and fluorides RSO_2F are formed in competition when **7** is treated with alcohols.[23] The existence of compound **8** has been doubted, as there is, as yet, no evidence for its intermediacy.[24] Actually, the sulfonyl fluorides were identified by mass spectroscopy and the suspected formation of trimethylfluorosilane (**9**) was derived from ^{1}H-NMR spectroscopic data. Both decomposition reactions have therefore never been utilized for preparative purposes.

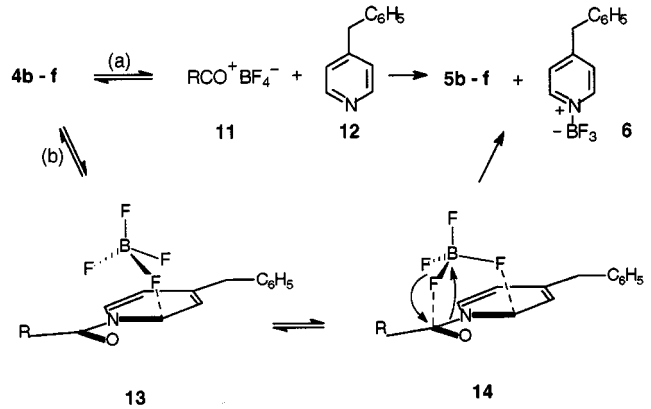


Scheme 2. Lability of some tetrafluoroborates

At first sight, the properties of the title compounds **4** (an X-ray structure is available for the 1-aroylpyridinium salt **4f**, vide infra for a detailed discussion), might be compared to those of the $TMSBF_4$ derivative **10**. The relatively long N^+-CO-bond [151.4(14) pm] could lead to the assumption that the labile salts **4** may dissociate into acylium tetrafluoroborates **11b−f**, which then decompose giving the acyl fluorides **5b−f** and the adduct **6** [Scheme 3, pathway (a)]. Such complexes **11** do indeed exist at low temperatures in a more or less nonnucleophilic environment and have been intensively investigated by Olah et al.[25] and Seel.[26] Nevertheless, pathway (a) in Scheme 3 seems to be not very realistic since the intermediate existence of extremely reactive acyl cations **11** in the presence of aromatic and nucleophilic compounds such as **12** would cause a manifold of side reactions. At least the reverse reaction (**11** + **12** → **4**) appears to be more plausible.

Another related example is given in the literature. Akaba et al.[27] irradiated aryl-alkyl ketones such as $(C_6H_5)_2CHCOC_6H_5$ in the presence of 2,4,6-triphenylpyrylium salts and molecular oxygen. Both the BF_4^-- and the PF_6^--containing sensitizers formed significant yields of benzoyl fluoride (**5e**). If pyrylium perchlorate was added, benzoic acid was detected as an oxygenated product since no fluorine was available. It was pointed out that the generation of benzoyl fluoride "could be very complex" and the intermediate formation of a benzoyl cation that degrades the BF_4^- moiety is only one of many conceivable alternatives.

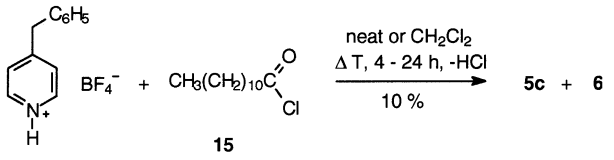
The formation of **6** was proven in the course of the decomposition of **4c** in $CDCl_3$. After heating this solution to 50°C (0.5 h), together with the signals of **5c**, a singlet appeared in the ^{1}H-NMR spectrum at $\delta = 4.14$ which was assigned to the BF_3 adduct **6**. Compound **6** was independently identified by comparing its spectra with those of a sample directly prepared from 4-benzylpyridine and $Et_2O{\cdot}BF_3$ (^{1}H, ^{13}C, ^{19}F, ^{11}B NMR).



Scheme 3. Proposed reaction mechanism for the formation of acylfluorides **5** from salts **4**

Based on the assumption that the process might be an equilibrium reaction (cf. Scheme 3), equimolar amounts of acyl fluoride **5c** and **6** were mixed together in $CDCl_3$ solution. The progress of the reaction was then monitored by ^{1}H-NMR spectroscopy. The components remained unchanged upon standing for 4 days at 50 °C. No trace of salt **4c** was detected. We therefore draw the conclusion that the decomposition is not an equilibrium reaction but that the rate constant is significantly temperature-dependent. The reaction was completed after 18 h, when a sample of **4c** in $CDCl_3$ was kept at 50 °C. Only traces of salt **4c** could be detected after this period. This provides an indication that yields obtained according to method **B** might be increased by prolonged heating.

We concluded from these results that the tendency of fluoride abstraction from BF_4^- is not only due to the activation of the *carbonyl group* bonded to the pyridinium nitrogen, but might also be an effect of the pyridinium moiety itself. To check this assumption, we investigated the fluorinating potential of 4-benzylpyridinium tetrafluoroborate and HBF_4 (**2b**) towards lauroyl chloride (**15**) under the same conditions as previously described for the Methods **A** and **B** (Scheme 4).



Scheme 4. Fluorination of an acyl chloride **15** with 4-benzylpyridinium tetrafluoroborate

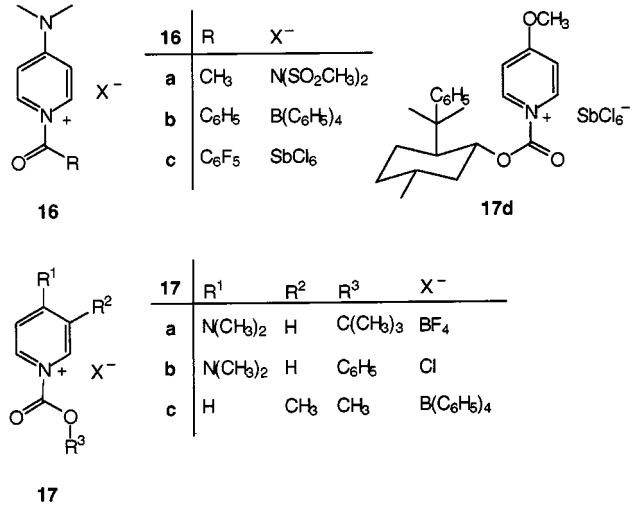
Surprisingly, an equimolar mixture of 4-benzylpyridinium tetrafluoroborate and **15** in CH_2Cl_2, which was heated for 24 h, afforded fluoride **5c** in 10% yield. The heating of the salt above its melting point (130°C) in the presence of acyl chloride **15** gave the same result. A mixture containing 12% of fluoride **5c** and 88% of chloride **15** was distilled off (in both cases the yields were determined by ^{1}H-NMR spectroscopy). For completeness, we investigated the behavior of HBF_4 (**2b**) against **15**. Already at room temperature, as shown by an ^{1}H-NMR experiment, the fluoride **5c** was initially formed − but disappeared completely after ca. 50 min. Thus, from a practical point of view, both fluorination reactions do not seem to be alternatives to the title reaction presented in this paper.

At present, we conclude that the decomposition of **4** proceeds via pathway (b) (Scheme 3) which is initiated by the formation of a loose complex **13** as found in the X-ray structure in which a BF_4^- is presumably in weak contact with either C(10) or C(11). After an energetically inexpensive internal rearrangement under inclusion of the carbonyl C atom, the species **14** (an intermediate or transition structure) is formed, in which one of the BF_4^- fluorines is properly positioned in order to allow the complex to collapse into the products **5** and **6**. This pathway avoids the dissociation step under formation of **11** and **12**. This step has been modeled by DFT calculations.[28] 4-Benzylpyridine (**12**) serves as an internal proton acceptor in the case of acylation reactions with the trifluoromethane sulfonates **3** and alcohols. In the course of the formation of the acyl fluorides **5b−g**, the pyridine derivative **12** remembers its Lewis base properties. This should be important for the suc-

cessful formation of aromatic acyl fluorides. Without the synchronous formation of the equimolar amount of the Lewis base, the free BF_3 will catalyze the acylation of the aromatic ring moieties.[25]

Crystal Structure and Ab initio Calculations

In spite of their great significance in preparative organic synthesis, only a few crystal structures of 1-acylpyridinium salts are available (Scheme 5). The first structure of such a compound was that of 1-acetyl-4-dimethylaminopyridinium dimesylamide (**16a**).[29] This is not surprising since 1-acyl DMAP derivatives are important acylating reagents.[30] We regard C4-heteroatom-substituted salts such as **16**[31] as "stabilized" representatives of cations in which the $C-N^+$ bond is stronger than in the salts **3** and **4** presented in this work. In contrast to the 4-$N(CH_3)_2$ group, the 4-benzyl substituent of **3** and **4** has almost no influence on the stability of the remote $C-N^+$ bond. Another category of stabilized pyridinium salts are the 1-acyloxy derivatives **17**.[32] To the best of our knowledge, Figure 2 shows the first crystal structure of an 1-acyl-4-alkylpyridinium salt reported in the literature.



Scheme 5. Available crystal structures of 1-acylpyridinium salts

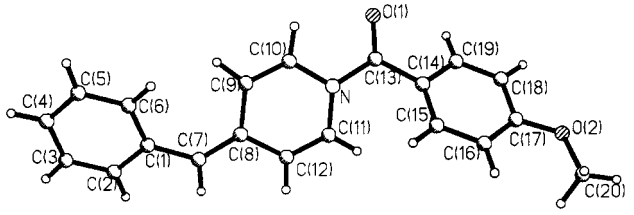


Figure 1. Crystal structure of **1f**, the precursor of **4f**

In the solid-state structure two BF_4^- anions are found to be in contact with the positively charged (cf. Table 4) C(10) and C(11) carbons [3.01(2) and 3.17(2) Å]. Both distances are shorter than or equal to the sum of the van der Waals radii of C and F (3.17 Å).[31c] The fluorine F(2A) seems to prefer contact with C(11) over coordination with the carbonyl C atom C(13) [distance: 3.29(2) Å]. Unfortunately, the estimated standard deviation of this structure is relatively large. Due to the experimental error, these interpretations should be treated with caution.

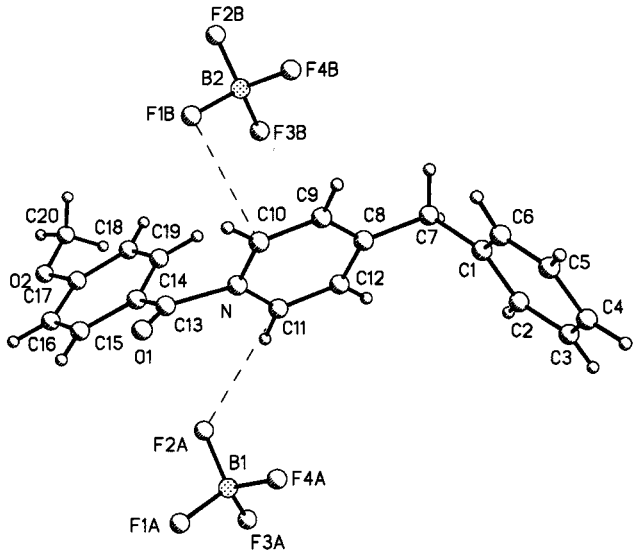


Figure 2. Crystal structure of **4f**, one of the title compounds. Two BF_4^- anions are interacting with the 1-acylpyridinium cation via the C10/F1B atoms [distance: 3.01(2) Å] and C11/F2A [distance: 3.17(2) Å]. The distance C13/F13 [3.29(2) Å] is slightly larger than the sum of the F and C van der Waals radii (3.17 Å)

The investigation of solid-state structures of type **4f**[33] is part of our ongoing studies on the *selective* bond lengthening caused by cation formation. Since the X-ray refinement of structure **4f** shows relatively large error bars, an X-ray-based comparison of structural changes during protonation of the dihydropyridine **1f**[34] producing the species **4f** could lead to misinterpretations. In order to obtain further insight into the properties of these interesting compounds, we have modeled the cation of **4f** and its neutral precursor **1f** with MO methods (AM1,[35][36] PM3,[37] HF/6-31+G*,[38][39] and B3LYP/6-31+G*[40]).

Table 2 clearly indicates that the B3LYP/6-31+G* optimized gas-phase structure of **1f** is in very good agreement with the geometry obtained from the excellent crystallographic analysis. In addition, all relevant structural properties of the B3LYP/6-31+G* calculated geometry of **4f** correspond well with those obtained from its poor X-ray analysis (Table 3). Therefore, B3LYP is a suitable method for describing both the uncharged precursor **1f** and its cationic form **4f**. The gas-phase data in combination with the X-ray results provide a reliable foundation for structure discussions.

Protonation of dihydropyridine **1f** giving structure **4f** leads to a *selective lengthening* of the exocyclic C(13)−N *single bond* [139.9(2) pm to 151.4(14) pm by X-ray analysis, 141.4 pm to 152.7 pm by B3LYP/6-31+G* calculations]. In addition, these structural changes parallel the significant changes in calculated atomic charges (resulting from a Natural Population Analysis [NPA],[41] Table 4). The attractive charge difference between C(13) and N decreases from 1.15 (**1f**) to 1.08 (**4f**). Furthermore, the Wiberg-Bond-

Table 2. Selected bond distances and bond angles of structure **1f**, determined by X-ray structure analysis, and derived from semiempirical, ab initio, and DFT calculations

Atoms[a]	X-ray[b]	AM1[b]	PM3[b]	HF/6-31+G*	B3LYP/6-31+G*
N−C(13)	139.9(2)	144.1	144.0	139.1	141.4
C(13)−O(1)	122.1(2)	124.3	121.9	119.8	122.6
N−C(11)	140.9(2)	140.2	142.5	140.0	140.4
N−C(10)	140.0(2)	140.6	142.6	139.9	140.2
C(11)−C(12)	133.2(2)	135.6	134.6	132.8	134.9
C(9)−C(10)	133.2(2)	135.6	134.7	133.0	135.0
C(8)−C(9)	145.6(2)	145.7	145.8	146.8	145.9
C(8)−C(12)	145.7(2)	145.3	145.2	146.8	145.9
C(7)−C(8)	136.0(2)	135.2	135.2	134.0	137.0
C(1)−C(7)−C(8)	131.1(2)	126.5	128.5	128.1	129.7
C(7)−C(8)−C(9)	127.3(2)	124.8	125.6	126.3	126.5
C(9)−C(8)−C(12)	112.3(14)	114.4	115.1	112.6	112.9
N−C(13)−O(1)	119.5(14)	119.4	118.5	120.4	119.9

[a] Numbering cf. X-ray, Figure 1. − [b] Bond lengths in [pm], angles in [°].

Table 3. Selected bond distances and angles of structure **4f**, determined by X-ray structure analysis and derived from semiempirical, ab initio, and DFT calculations

Atoms[a]	X-ray[b]	AM1[b]	PM3[b]	HF/6-31+G*	B3LYP/6-31+G*
N−C(13)	151.4(14)	148.4	153.4	148.7	152.7
C(13)−O(1)	120.7(13)	122.7	120.1	117.9	120.6
N−C(11)	134.3(13)	137.1	137.8	134.7	135.8
N−C(10)	137.6(14)	137.3	137.8	134.3	135.6
C(11)−C(12)	138.(2)	139.4	138.6	136.4	138.0
C(9)−C(10)	134.(2)	139.5	138.8	137.0	138.2
C(8)−C(9)	143.(2)	140.6	140.1	139.5	140.5
C(8)−C(12)	135.7(14)	140.9	140.3	140.4	140.9
C(7)−C(8)	145.0(2)	148.6	149.4	151.6	151.7
C(1)−C(7)−C(8)	114.0(10)	114.1	109.9	116.2	116.2
C(7)−C(8)−C(9)	120.8(12)	122.2	120.7	123.5	122.9
C(9)−C(8)−C(12)	118.0(11)	117.9	118.6	117.5	117.2
N−C(13)−O(1)	116.0(10)	115.3	113.5	115.5	114.9

[a] Numbering cf. X-ray, Figure 2. − [b] Bond lengths in [pm], angles in [°].

Indices[42] (Table 5) from the NBO analysis clearly support the existence of this effect (bond-order N−C(13): **1f** 1.03; **4f** 0.80). No other bond (except the exocyclic double/single bond change: from 136.0(2) pm to 145.0(2) pm by X-ray analysis and from 137.0 pm to 151.0 pm by B3LYP/6-31+G* calculations; bond orders: from 1.61 to 1.02) is characterized by such a significant change.[28]

The smaller changes in the bond relations in the central pyridinium ring [N, C(8), C(9), C(10), C(11), and C(12)] are in accord with what one would expect. Furthermore, it is noteworthy that all quantum-mechanical methods predict a bond-shortening of the C(13)−O(1) bond by protonation of **1f** [**1f** 122.1(2) pm and **4f** 120.7(13) pm by X-ray analysis; **1f** 122.6 pm and **4f** 120.6 pm by B3LYP/6-31+G* calculations; bond orders: **1f** 1.68, **4f** 1.80], which is in excellent agreement with the X-ray analysis. This shortening can be explained by a slight delocalization of one lone pair of the O(1) under the influence of the adjacent acyl C(13) carbon atom. The decrease of negative charge at the equivalent O(1) reflects this effect (**1f** −0.60, **4f** −0,.50)

Conclusion

The method described here represents a new and versatile preparative route to carboxylic acid fluorides **5**. There is no need for high pressure and/or polyethylene equipment and no hazardous gases are involved. All transformations can therefore be performed in conventional glass flasks. The source of fluorine is the inexpensive tetrafluoroboric acid (**2b**), similar to the historical *Schiemann* reaction.[43] These reactions can be performed on normal laboratory scales. The conditions employed are mild (especially those of method **B**), and the yields are satisfactory relative to those of the other fluorination reactions mentioned above and additional methods with perfluoro compounds,[44] cesium fluoroxysulfate[45] and the most used potassium fluoride, whose major drawback is its very low solubility in all but a few protic solvents.

With the evidence provided in this work that the BF_4^- ion formally decomposes to fluoride and BF_3, a more general synthetic problem appears to be illuminated. Some au-

Table 4. Selected NPA-charges (B3LYP/6-31+G*) of structures **1f** and **4f**

	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	N	C(13)	O(1)
1f [a]	−0.25	−0.08	−0.27	−0.01	−0.02	−0.25	−0.46	+0.69	−0.60
4f [a]	−0.50	+0.10	−0.25	+0.09	+0.07	−0.25	−0.38	+0.70	−0.50

[a] Numbering cf. X-ray, Figures 1 and 2.

Table 5. Specific Wiberg-Bond-Indices B3LYP/6-31+G*, structures **1f** and **4f**

	C(7)−C(8)	C(8)−C(9)	C(9)−C(10)	C(10)−N	N−C(13)	C(13)−O(1)
1f [a]	1.61	1.11	1.75	1.04	1.03	1.68
4f [a]	1.02	1.37	1.48	1.24	0.80	1.80

[a] Numbering cf. X-ray, Figures 1 and 2

thors who tried to utilize *N*-acyl-N^+ tetrafluoroborates derived both from pyridines and aliphatic tertiary amines complained about the limited applicability of such compounds but failed to give a plausible explanation for the instability of such cations.[46] Obviously, the reactivity of fluoride ions as intermediates always has to be taken into account in the presence of BF_4^- and quaternized nitrogens as they could cause a rapid formation of a variety of fluorinated or deprotonated products. Ketenes are typical examples. For efficient acylation reactions we recommend, in accord with our recent results,[16a] the exclusive use of the trifluormethanesulfonates **3**.

Experimental Section

General: All reactions were carried out under a positive pressure of purified N_2. Standard syringe techniques were used to transfer solvents and to add liquid reagents. Glassware was flame-dried and flushed with N_2 before use. − The dihydropyridines **1a**,**d**−**f** and the 1-acylpyridinium tetrafluoroborates **4a**,**d**−**f** are either known in the literature or derivatives **1c** and **4c** were synthesized according to literature procedures. All acyl fluorides **5b**−**f** prepared are known compounds, and their physical properties agree with those reported in the literature (cf. Table 1). HBF_4 (**2b**) was taken from original containers (Fluka) and had a content of 54% in Et_2O. Diethyl ether and toluene were distilled from sodium benzophenone ketyl; CH_2Cl_2 was purified by column chromatography (alumina). − ^{11}B-, ^{13}C-, and ^{1}H-NMR spectra were determined with Bruker DRX400 operating at 128.4, 100.6 and 400 MHz. Chemical shifts (δ) are reported relative to $CDCl_3$ (δ_H = 7.24, δ_C = 77.0) or [D_6]DMSO (δ_H = 2.49, δ_C = 39.7) as an internal standard and are given in ppm; the standard for ^{11}B-NMR spectroscopy was $BF_3 \cdot Et_2O$. ^{19}F-NMR spectra were determined with a Bruker AC200 operating at 188.3 MHz and chemical shifts (δ) are reported relative to CCl_3F as an external standard. Coupling constants *J* are given in Hz. − IR spectra were recorded with a Nicolet Impact 400 spectrophotometer. − Microanalysis were obtained with a LECO CHNS-932 element analyzer. − Melting points were taken with a copper block apparatus (Linström) and are uncorrected.

Crystal Structure Analysis of 1f and 4f: Data Collection: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation and the φ-scan technique (180 frames, 30 s per frame, Δφ = 1°) at −90°C. Data were corrected for Lorentz and polarization effects, but not for absorption.[47] *Structure Solution and Refinement:* The structures were solved by direct methods (SHELXS[48]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97[49]). The hydrogen atoms for **1f** were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms for **4f** were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

4-Benzylidene-1-lauroyl-1,4-dihydropyridine (1c): Yellow crystals, m.p. 83−84 °C (acetone).− IR (KBr pellet): $\tilde{\nu}$ = 1678, 1655 cm^{-1} (C=O, C=C). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86 (t, 3 H, CH_3), 1.19−1.31 (m, 16 H, $(CH_2)_8$), 1.70 (m, 2 H, $COCH_2CH_2$), 2.49 (t, 2 H, $COCH_2$), 5.87, 6.44, 6.76, 7.31 (br, 4 H, dihydropyridine-moiety: both rotamers), 5.85 [s, 1 H, C=CH(α)], 7.12−7.29 (m, 5 H, PhH). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.03 (CH_3), 22.65, 24.43, 29.17, 29.30, 29.32, 29.43, 29.56, 29.57, 31.86, 33.12 (CH_2), 109.87, 110.51, 116.74, 117.50, 122.45, 123.35, 124.42, 125.38 (br, C-2, C-3, C-5, C-6, dihydropyridine-moiety: both rotamers), 115.83 [C(α)], 125.76, 127.68, 128.30, 129.33, 137.86, 168.28 (C=O). − $C_{24}H_{33}NO$ (351.5): calcd. C 82.00, H 9.46, N 3.98; found C 82.25, H 9.66, N 3.91

4-Benzyl-1-lauroylpyridinium Tetrafluoroborate (4c): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.84 (t, 3 H, CH_3), 1.22−1.27 (m, 14 H, $(CH_2)_7$), 1.36 (m, 2 H, $COCH_2CH_2CH_2$), 1.77 (m, 2 H, $COCH_2CH_2$), 3.30 (t, 2 H, $COCH_2$), 4.30 [s, 2 H, C(α)H_2], 7.15−7.32 (m, 5 H, PhH), 7.87 (d, 2 H, Py H-3, H-5), 9.11 (d, 2 H, Py H-2, H-6). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.02, 22.58, 23.79, 28.36, 29.13, 29.27, 29.33, 29.43, 29.53, 31.81, 33.39; 41.98 [C(α)], 127.32 (Ph C-*p*), 127.76 (Py C-3, C-5), 129.32, 129.38 (Ph C-*o*,*o*′, C-*m*,*m*′), 135.16 (Ph C-*i*), 139.07 (Py C-2, C-6), 168.51 (Py C-4), 169.82 (C=O).

Acyl Fluorides 5b−g; General Procedures

Method A: Freshly prepared 1-acylpyridinium tetrafluoroborates **4a−g** were weighed into a 100 mL flask which was connected to a microdistillation apparatus. The salt was heated by means of an oil bath to slightly above the melting point and a clear orange solution was formed. Then the temperature slowly was raised until distillation was complete.

Method B: The dihydropyridines **1a−g** were dissolved in 100 mL of CH_2Cl_2 and the equimolar amount of HBF_4 (**2b**) was added. The mixture was brought to reflux and heated for 3.0 to 4.0 h.

Then CH_2Cl_2 was evaporated off and the residue was dissolved in 30 mL of Et_2O. The insoluble components were filtered off, the solvent was removed with a rotatory evaporator and the crude product was distilled.

From theses residues (both methods), benzylpyridine (**12**) was recovered in 85−90% yield after distillation of the acyl fluorides: As exemplified for the synthesis of **5c**,**e**,**f**, the residue was dissolved in 200 mL of half conc. HCl and then washed with 2 × 100 mL of Et_2O . The aqueous solution was made alkaline with conc. NaOH solution and extracted with 3 × 100 mL of CH_2Cl_2. The organic layer was dried (Na_2SO_4), then the solvent was evaporated and finally the crude product was purified by distillation.

Cinnamoyl Fluoride (5b): Method **A**: from pyridinium salt **4b** (11.2 g, 24.3 mmol), yield: 3.1 g (85%), m.p. = 31.5°C. − Method **B**: from dihydropyridine **1b** (10.2 g, 34.1 mmol) and 4.6 mL of HBF_4 (**2b**) in CH_2Cl_2 (150 mL), heating: 4.0 h, yield: 2.3 g (45%). − ^{1}H NMR ($CDCl_3$, 400 MHz)[50]: δ = 6.36 (dd, $^3J_{HF}$ = 7.4 Hz, $^3J_{HH}$ = 16.0 Hz, 1 H, CH=C*H*COF,); 7.39−7.50 (m, 3 H, Ph H-*p*-,H-*m*,*m*′); 7.54−7.62 (m, 2 H, Ph H-*o*, *o*′); 7.82 (d, $^3J_{HH}$ = 16.0 Hz, 2 H, C*H*=CHCOF,). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 111.71 (d, $^2J_{CF}$ = 67.1 Hz, CH=*C*HCOF), 128.26 (Ph C-*o*,*o*′), 128.90 (Ph C-*m*,*m*′); 131.12 (Ph C-*p*), 132.84 (d, $^4J_{CF}$ = 0.8 Hz, C-*i*), 151.22 (d, $^3J_{CF}$ = 6.14 Hz, *C*H=CHCOF), 156.94 (d, $^1J_{CF}$ = 338.2 Hz, COF).

Lauroyl Fluoride (5c): Method **A**: from pyridinium salt **4c** (8.5 g, 19.35 mmol), yield: 3.0 g (77%). − Method **B**: from dihydropyridine **1c** (10.8 g, 30.7 mmol) and 4.2 mL of HBF_4 (**2b**) in 100 mL of CH_2Cl_2, heating: 4.0 h, yield: 3.4 g (54.8%). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86 (t, 3 H, CH_3), 1.15−1.40 (m, 16 H, $(CH_2)_8$), 1.65 (m, 2 H, β-CH_2), 2.47 (dt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HF}$ = 1.1 Hz, 2 H, α-CH_2). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.00 (s, CH_3), 22.59, 23.84 (d, $^3J_{CF}$ = 1.7 Hz, β-CH_2,), 28.61 (s, δ-CH_2), 28.98 (s, γ-CH_2), 29.22, 29.25, 29.44, 29.48, 31.80, 32.04 (d, $^2J_{CF}$ = 32.0 Hz, α-CH_2,), 163.55 (d, $^1J_{CF}$ = 360.7 Hz, COF). − ^{19}F NMR ($CDCl_3$, 188.3 MHz)[51]: δ = 44.9.

Acetyl Fluoride (5d): Method **A**: from pyridinium salt **4d** (9.0 g, 30.0 mmol), yield: 1.2 g (64%). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.23 ($^3J_{HF}$ = 7.1 Hz). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 18.7 (d, $^2J_{CF}$ = 58.3 Hz, CH_3), 160.8 (d, $^1J_{CF}$ = 354.4 Hz, COF).

Benzoyl Fluoride (5e): Method **A**: from pyridinium salt **4e** (5.9 g, 16.3 mmol), yield: 1.5 g (74%). − Method **B**: from dihydropyridine **1e** (9.2 g, 33.7 mmol) and 4.6 mL of HBF_4 (**2b**) in CH_2Cl_2 (150 mL), heating: 3.5 h; yield: 2.0 g (48%). − ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 7.61 (m, 2 H, H-*m*,*m*′), 7.81 (m, 1 H, H-*p*), 8.00 (m, 2 H, H-*o*,*o*′). − ^{13}C NMR ([D$_6$]DMSO, 100.6 MHz): δ = 124.9 (d, $^2J_{CF}$ = 60.5 Hz, C-1), 129.0 (d, $^4J_{CF}$ = 1.13 Hz, C-3, C-5), 131.4 (d, $^3J_{CF}$ = 4.1 Hz, C-2, C-6), 135.3 (s, C-4), 157.34 (d, $^1J_{CF}$ = 344.3 Hz, COF). − ^{19}F NMR ($CDCl_3$, 188.3 MHz): δ = 17.52.

Anisoyl Fluoride (5f): Method **B**: from dihydropyridine **1f** (9.85 g, 32.5 mmol) and 4.4 mL of HBF_4 (**2b**) in CH_2Cl_2 (90 mL), heating 4.0 h, yield 4.2 g (84%). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.86 (s, 3 H, OCH_3), 6.96 (m, 2 H), 7.94 (m, 2 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz)[52]: δ = 56.59 (s, OCH_3), 115.37 (d, $^4J_{CF}$ = 1.3 Hz, C-3, C-5), 117.12 (d, $^2J_{CF}$ = 61.8 Hz, C-1), 134.69 (d, $^3J_{CF}$ = 4.2 Hz, C-2, C-6), 158.23 (d, $^1J_{CF}$ = 339.7 Hz, COF); 166.18 (s, C-4). − ^{19}F NMR ($CDCl_3$, 188.3 MHz): δ = 15.40.

Preparation of Borontrifluoride Pyridine Complex 6 as a Reference Compound: A solution of 8.5 g (50.2 mmol) of 4-benzylpyridine (**12**) in 100 mL of Et_2O was cooled with an ice bath. Then 13.6 mL (50.2 mmol) of $BF_3 \times OEt_2$ (48% in Et_2O) was added and the mixture was stirred for 1 h. A yellowish oil precipitated which crystallized upon cooling to −40°C. The solid was filtered off, washed with 20 mL of dry Et_2O, and dried in vacuo giving 11.0 g of **6** (92%), colorless solid. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.15 (s, 2 H, CH_2), 7.09−7.40 (m, 5 H, benzylic H), 7.51 (d, *J* = 6.3 Hz, 2 H, Py H-3, H-5), 8.53 (d, *J* = 6.3 Hz, 2 H, Py H-2,H-6). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 41.11 (s, CH_2), 126.19 (s, Py C-3, C-5), 127.22, 129.14, 129.40, 136.45 (s, benzylic C), 142.85 (s, Py C-2, C-6), 163.54 (s, Py C-4). − ^{19}F NMR ($CDCl_3$, 188.3 MHz): δ = −152.0 (q, *J* = 11.3 Hz, N-BF_3). − ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ = 3.57 (q, *J* = 10.9 Hz, N-BF_3).

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and by the Thüringer Ministerium für Wissenschaft, Forschung und Kultur (Erfurt, Germany) is gratefully acknowledged. We thank the Hewlett−Packard Company for providing us with CPU time. We thank Dr. M. Kunert and A. Jansen of the Max Planck Gesellschaft, Forschungsgruppe CO_2-Chemie, Jena for the performance of ^{19}F-NMR measurements. We thank Dr. Jennie Weston (Jena) for useful discussions.

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[34] *Crystal Data for* **1f**: $C_{20}H_{17}NO_2$, *M*r = 303.35 gmol^{-1}, colourless prism, size 0.35 × 0.20 × 0.10 mm, monoclinic, space group $P2_1/c$, a = 17.0256(9), b = 14.6550(8), c = 6.1546(3) Å, β = 92.397(3)°, V = 1534.29(14) Å^3, T= −90°C, Z = 4, $r_{calcd.}$ = 1.313 gcm^{-3}, μ(Mo-K_α) = 0.85 cm^{-1}, F(000) = 640, 4056 reflections in h(−18/18), k(−16/16), l(0/6), measured in the range 3.59° ≤ Θ ≤ 23.28°, 2198 independent reflections, R_{int} = 0.033, 1811 reflections with $F_o > 4\sigma(F_o)$, 277 parameters, $R1_{obs}$ = 0.0380, wR^2_{obs} = 0.0968, $R1_{all}$ = 0.049, wR^2_{all} = 0.105, GOOF = 1.046, largest difference peak and hole: 0.165/−0.226 e Å^{-3}.

Further details of the crystal structure investigations are available on requests from CCDC, 12 Union Road, Cambridge CB 21 EZ, U.K., on quoting the depository number CSD-410404 (**1f**) and CSD-410405 (**4f**), the names of the authors, and the journal citation.
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Received November 6, 1998
[O98500]