



Preparations and reactions of 2-trifluoromethylketenimines

Toshimasa Katagiri*, Michiharu Handa, Hiroyuki Asano, Teppei Asanuma, Tomohiro Mori, Tatsuya Jukurogi, Kenji Uneyama

Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushimanaka 3-1-1, Okayama 700-8530, Japan

ARTICLE INFO

Article history:

Received 21 April 2009

Received in revised form 13 May 2009

Accepted 14 May 2009

Available online 11 June 2009

Keywords:

Trifluoromethylketenimine

Imidoyl halide

β -Amino acid

Fluorinated building block

ABSTRACT

Preparations and reactions of a series of 2-trifluoromethylketenimines are described. Trifluoromethylketenimines were prepared from trifluoropropanoic acids via corresponding imidoyl chlorides in good yields. 2-Trifluoromethylketenimine was functionalized at its β -position by electrophilic addition of halide, followed by dehydrohalogenation. Addition of nucleophile at α -position gave trifluoroethylated β -amino acid derivative via 1,3-proton shift.

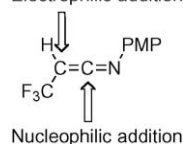
© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Fluorinated building blocks are of importance in preparation of biologically active organic molecules [1]. Among them, building blocks with unsaturated bonds gain much interest for their electronic structures of the π -system, thus their unique reactivities by the strong electron withdrawing effect of the fluorine atom(s) and/or fluoroalkyl group(s) [1,2]. Similar to the fluoroalkylated imines [1,3], fluoroalkylated ketenimines would be highly talented class of compounds in the field of synthetic organic chemistry. They could undertake nucleophilic additions at sp carbon (α -position) and electrophilic additions at sp^2 carbon (β -position) [4]. However, they are less explored than the fluoroalkylated imines, because of their low availability.

To date, a few reports have described preparations of fluoroalkylated ketenimines. Bis(trifluoromethyl)ketenimines have been prepared by perfluoroisobutene or its analogs [5]. More complicated ketenimine has been prepared by the reaction of perfluoro(3,4-dimethylhex-3-en-2-one) with *tert*-butylamine [6], the reaction of perfluoro(2-methyl-2-pentene) with amines [7], and the reaction of 3,4-dicyano-1,1,1,4,4,4-hexafluoro-2-butene with thiadiazoline [8]. These ketenimines react with nucleophiles to give aldimines [9], heterocyclic compounds [5b,6,10], and metal complex [11]. To date, no electrophilic addition at sp^2 carbon of fluoroalkylated ketenimine has been reported.

Electrophilic addition



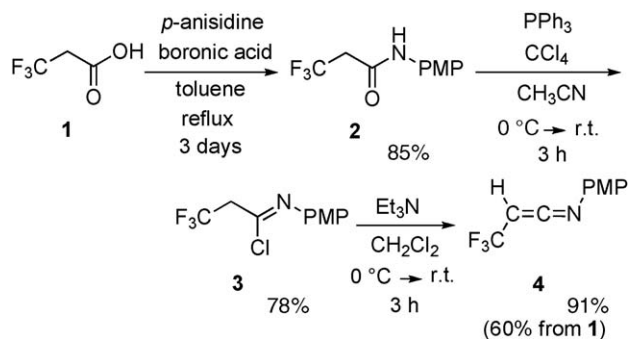
Here, we report a facile preparation of β -trifluoromethylketenimines from the corresponding commercially available carboxylic acids via imidoyl halide [12]. We also report modifications of β -position (sp^2 ketenimine carbon) by electrophilic addition – dehydrohalogenation, as well as a nucleophilic addition at α -position to give trifluoroethylated β -amino acid derivative (dimethyl 2-{1-(*p*-anisyl)amino-3,3,3-trifluoropropylidene}malonate) via 1,3-proton shift.

2. Results and discussion

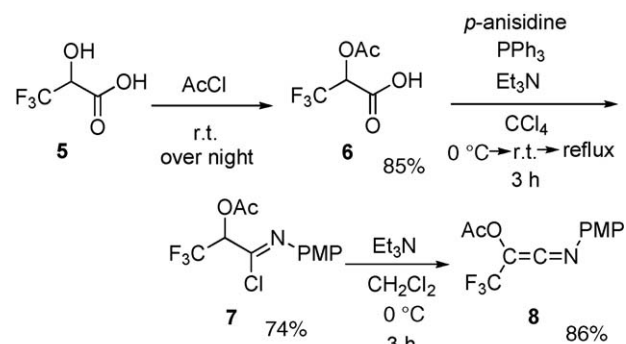
2.1. Preparations of ketenimines

Conventionally, fluorinated ketenimines were prepared by nucleophilic substitution (addition-defluorination) of olefinic fluorine of perfluoroisobutene derivatives with amines [3]. Although imidoyl halides have been frequently used as starting materials for non-fluorinated ketenimines [12], these compounds have not been used as intermediates of trifluoromethylketenimines, yet. The preparation of trifluoromethylated ketenimine from imidoyl halide would experience a tentative generation of α -trifluoromethylated carbanion, which is well known for its instability to leave β -fluoride [13]. Previously, we reported a

* Corresponding author. Tel.: +81 86 251 8605; fax: +81 86 251 8021.
E-mail address: tkata@cc.okayama-u.ac.jp (T. Katagiri).



Scheme 1.



Scheme 2.

racemization of imidoyl halide of the trifluorolactate [3b]. These racemizations would also undergo via tentative α -trifluoromethylated carbanion intermediates or via β -trifluoromethylketenes. These observations encouraged us to prepare the β -trifluoromethylated ketenimines from the corresponding β -trifluoropropanoic acids via imidoyl chlorides.

The trifluoropropioimidoyl halide **3** was prepared from corresponding trifluoropropanoic amide **2** by one pot reaction with triphenylphosphine and carbon tetrachloride, as previously reported [14]. Then dehydrochlorination of the imidoyl chloride **3** with triethylamine gave the aimed ketenimine **4** in over all 60% yield from the commercially available trifluoropropanoic acid **1** (Scheme 1).

2-Acetoxy-2-trifluoromethylketenimine, **8** was prepared from commercially available trifluorolactic acid **5** in 54% yield [15]. The carboxylic acid **6** was directly converted to imidoyl chloride **7**, followed by dehydrochlorination to the ketenimine **8** (Scheme 2) [3b,14].

2.2. Electrophilic modification of the β -position

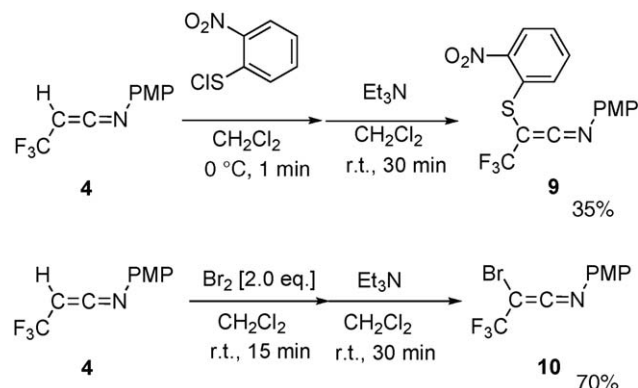
Electrophilic addition of halides to the ketenimine **4**, followed by dehydrohalogenations with triethylamine, gave β -substituted- β -trifluoromethylketenimines (**9** and **10** in Scheme 3).

Similarly, addition of TMS-OTf to the ketenimine **4**, followed by detriflation gave β -trimethylsilyl- β -trifluoromethylketenimine **11** (Scheme 4).

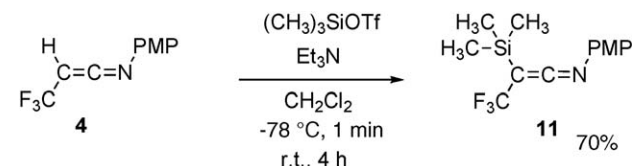
As shown in these examples, these electrophilic modifications of the ketenimine **4** would give a variety of β -substituted- β -trifluoromethylketenimines.

2.3. Nucleophilic addition to the α -position

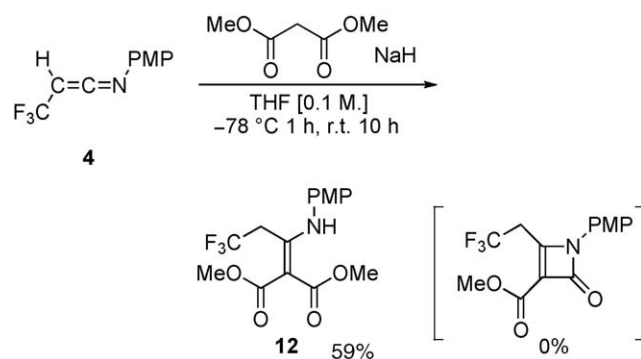
Nucleophilic C–C bond formation of the ketenimine **4** with enolates would give β -lactams via following amide formation.



Scheme 3.



Scheme 4.



Scheme 5.

However, the reaction of malonate resulted in formation of α,β -unsaturated carboxylate **12** as a sole product, without formation of the aimed β -lactam (Scheme 5).

It is noteworthy that, a 1,3-shift of the hydrogen of active methylene to α -position of trifluoromethyl group seemed to be undertaken in the course of the reaction [16]. The double bond would put carbonyl group too far to attack by nitrogen nucleophile. Moreover, the larger strain energy of β -lactam with double bond would make the β -lactam too reactive to isolate.

3. Summary

In summary, we prepared a β -trifluoromethylketenimine **4** via corresponding imidoyl halide. Electrophilic addition of halides to the ketenimine **4** gave β -substituted- β -trifluoromethylketenimines, also via corresponding imidoyl halides or its synthon. Nucleophilic addition of active methylene compound unexpectedly produced α,β -unsaturated carboxylate **12** which could be a precursor of β -amino acids. Further studies, especially for the reaction of the α,β -unsaturated carboxylate **12** for preparations of β -amino acids, would enable to prepare a variety of trifluoroethylated β -amino acids.

4. Experimental

4.1. General

4.1.1. Spectroscopic measurements

NMR spectra: All NMR spectra were recorded as CDCl₃ solutions. ¹H and ¹⁹F NMR spectra were recorded at 300 and 282 MHz respectively with Varian MERCURY 300 instrument. The chemical shifts are reported in δ (ppm) related to the CHCl₃ (7.26 ppm for ¹H NMR) and C₆F₆ (0 ppm for ¹⁹F NMR: The relative chemical shift of C₆F₆ to CFCl₃ is –162.2 ppm.). Coupling constants (*J*) are reported in hertz (Hz).

IR spectra: Infrared spectra were recorded on a Hitachi 270-30 spectrometer. Only selected absorbances are reported (ν in cm^{–1}).

MS analysis: MS analyses were performed on a Shimadzu GCMS-QP5050A.

Elemental analysis: A Perkin-Elmer series II CHNS/O Analyzer 2400 was employed for elemental analysis.

4.1.2. Chemicals

CH₂Cl₂, triethylamine were distilled from CaH₂ and stored under an argon atmosphere. Acetonitrile was dried over P₂O₅, distilled, and stored under an argon atmosphere. Other reagents and solvents were employed without further purification.

3,3,3-Trifluoro-*N*-(4-methoxyphenyl)propanamide **2** was prepared from 3,3,3-trifluoropropanoic acid and anisidine with boronic acid catalyst. 2-Acetoxy-3,3,3-trifluoropropanoic acid **6** was prepared by an acetylation of 3,3,3-trifluorolactic acid [17].

4.2. Preparation of *N*-*p*-methoxyphenyl-3,3,3-trifluoropropanimidoyl chloride (Scheme 1, compound 3)

To a mixture of *N*-*p*-methoxyphenyl-3,3,3-trifluoropropanamide (**2**) (1.16 g, 5.0 mmol) and PPh₃ (1.57 g, 6.0 mmol) in CH₃CN (10 ml) was added CCl₄ (0.577 ml, 6.0 mmol) at 0 °C under an argon atmosphere, then was stirred for 3 h at room temperature. The solvent was removed under reduced pressure from reaction mixture. The residue was immediately purified by Kugelrohr distillation at 130 °C/0.2 Torr. The colorless oil of *N*-*p*-methoxyphenyl-3,3,3-trifluoropropanimidoyl chloride (**3**) (0.978 g, 3.9 mmol, 78%) was obtained.

¹⁹F NMR δ 99.2 (t, *J* = 9 Hz, 3F) ppm; ¹H NMR δ 2.94 (q, *J* = 9 Hz, 2H), 3.26 (s, 3H), 6.67 (d, *J* = 9 Hz, 2H), 6.90 (d, *J* = 9 Hz, 2H) ppm; IR (neat) 3010, 2950, 1690, 1610 cm^{–1}; MS *m/z* (GC-El) 253 (M⁺, tr.), 251 (10), 215 (100), 200 (58), 152 (12), 77 (53); elemental analysis: Calcd for C₁₀H₉ClF₃NO: C, 47.73; H, 3.61; N, 5.57. Found: C, 47.49; H, 3.93; N, 5.26.

4.3. Preparation of *N*-*p*-methoxyphenyl trifluoromethylketenimine (Scheme 1, compound 4)

To a solution of *N*-*p*-methoxyphenyl-3,3,3-trifluoropropanimidoyl chloride (**3**) (0.854 g, 3.4 mmol) in CH₂Cl₂ (5 ml) was added Et₃N (0.71 ml, 5.1 mmol) at 0 °C under an argon atmosphere, then was stirred for 3 h at room temperature. The reaction mixture was filtered and concentrated under reduced pressure. The crude product was immediately purified by Kugelrohr distillation apparatus at 100 °C/0.2 Torr. The colorless oil of *N*-*p*-methoxyphenyl trifluoromethylketenimine (**4**) (0.66 g, 3.1 mmol, 91%) was obtained.

¹⁹F NMR δ 109.8 (d, *J* = 6 Hz, 3F) ppm; ¹H NMR δ 3.18 (s, 3H), 3.98 (q, *J* = 6 Hz, 1H), 6.40–6.55 (m, 2H), 6.93–7.08 (m, 2H) ppm; IR (neat) 2060, 1610 cm^{–1}; MS *m/z* (GC-El) 216 (M⁺+1, 60), 215 (M⁺, 100), 200 (79), 152 (20); elemental analysis: Calcd for C₁₀H₁₈F₃NO: C, 55.82; H, 3.75; N, 6.51. Found: C, 55.71; H, 3.66; N, 6.50.

4.4. Preparation of *N*-*p*-methoxyphenyl-2-acetoxy-3,3,3-trifluoropropanimidoyl chloride (Scheme 2, compound 7)

Two necked round-bottomed flask was charged with PPh₃ (4.4 g, 16.8 mmol), triethylamine (2.3 ml, 17 mmol), CCl₄ (42 ml), and *p*-anisidine (2.06 g, 16.7 mmol). Then, 2-acetoxy-3,3,3-trifluoropropanoic acid (**6**) (2.58 g, 13.9 mmol) was added to the mixture. After stirring at 0 °C for 10 min, the reacting solution was refluxed for 3 h. Solvents were removed under a reduced pressure. The residue was immediately purified by Kugelrohr distillation apparatus at 120 °C/0.05 Torr. The pale yellow oil of *N*-*p*-methoxyphenyl-2-acetoxy-3,3,3-trifluoropropanimidoyl chloride (**7**) (3.19 g, 10.3 mmol, 74%) was obtained.

¹⁹F NMR δ 88.4 (d, *J* = 9 Hz, 3F) ppm; ¹H NMR δ 2.28 (s, 3H), 3.82 (s, 3H), 5.84 (q, *J* = 6 Hz, 1H), 6.92 (dd, *J* = 9, 2 Hz, 2H), 7.09 (dd, *J* = 9, 2 Hz, 2H) ppm; IR (neat) 1770, 1510 cm^{–1}; MS *m/z* (GC-El) 309 (M⁺, 11), 267 (17), 134 (80), 92 (14), 77 (22), 63 (14), 43 (100); elemental analysis: Calcd for C₁₂H₁₀ClF₃NO₃: C, 46.54; H, 3.58; N, 4.61. Found: C, 46.51; H, 3.73; N, 4.61.

4.5. Preparation of *N*-*p*-methoxyphenyl-2-acetoxy-2-trifluoromethylketenimine (Scheme 2, compound 8)

To a solution of *N*-*p*-methoxyphenyl-2-acetoxy-3,3,3-trifluoropropanimidoyl chloride (**7**) (1.84 g, 6.0 mmol) in CH₂Cl₂ (8.21 ml) was added Et₃N (8.3 ml, 59 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred for 3 h at this temperature. The reaction mixture was filtered and concentrated under a reduced pressure. The crude product was immediately purified by Kugelrohr distillation apparatus at 120 °C/0.03 Torr. The pale yellow oil of *N*-*p*-methoxyphenyl-2-acetoxy-2-trifluoromethylketenimine (**8**) (1.39 g, 5.1 mmol, 86%, purity >98%) was obtained.

¹⁹F NMR δ 96.8 (s, 3F) ppm; ¹H NMR δ 2.26 (s, 3H), 3.84 (s, 3H), 6.94 (d, *J* = 9 Hz, 2H), 7.46 (d, *J* = 9 Hz, 2H) ppm; IR (neat) 2040, 1770 cm^{–1}; MS *m/z* (GC-El) 273 (M⁺, 29), 232 (15), 231 (100), 134 (55); elemental analysis: Calcd for C₁₂H₁₀F₃NO₃: C, 52.75; H, 3.69; N, 5.13. Found: C, 52.58; H, 3.61; N, 5.20.

4.6. Preparation of 2-(2-nitrophenyl)sulphenyl-2-trifluoromethylketenimine (Scheme 3, compound 9)

Two necked round-bottomed flask was charged with 2-nitrophenylsulphenyl chloride (0.39 g, 2.1 mmol) in 2 ml of CH₂Cl₂ under an argon atmosphere. Trifluoromethylketenimine (**4**) (0.44 g, 2.04 mmol) was added dropwise and the reaction mixture was stirred for 1 min at 0 °C. Triethylamine (0.38 ml, 2.7 mmol) was added and stirred for 10 min at 0 °C. The reaction mixture was concentrated under reduced pressure. The crude product was purified by triethylamine treated silica gel column chromatography with hexane/ethyl acetate eluent (6/1). The orange oil of 2-(2-nitrophenyl)sulphenyl-2-trifluoromethylketenimine (**9**) (0.265 g, 0.72 mmol, 35%) was obtained.

¹⁹F NMR δ 104.3 (s, 3F) ppm; ¹H NMR δ 3.84 (s, 3H), 6.93 (d, *J* = 9 Hz, 2H), 7.28 (d, *J* = 9 Hz, 2H), 7.36 (ddd, *J* = 2, 7, 8 Hz, 1H), 7.69 (ddd, *J* = 2, 7, 8 Hz, 1H), 7.81 (d, *J* = 8 Hz, 1H), 8.29 (dd, *J* = 2, 8 Hz, 1H) ppm; IR (neat) 2050 cm^{–1}; MS *m/z* (DI) 368 (M⁺, trace), 230 (22), 149 (100), 138 (36), 77 (88), 69 (67); elemental analysis: Calcd for C₁₆H₁₁F₃N₂O₃S: C, 52.17; H, 3.01; N, 7.61. Found: C, 51.95; H, 2.88; N, 7.55.

4.7. Preparation of 2-bromo-2-trifluoromethylketenimine (Scheme 3, compound 10)

Two necked round-bottomed flask was charged with trifluoromethylketenimine (**4**) (0.086 g, 0.40 mmol) in 0.5 ml of CH₂Cl₂

under an argon atmosphere. Bromine (0.041 ml, 0.79 mmol) was added dropwise and the reaction mixture was stirred for 1 min at 0 °C. Water bath was removed and then stirred for another 15 min at room temperature. Then, triethylamine (0.14 ml, 1.0 mmol) was added and stirred for 30 min at 0 °C. The reaction mixture was filtered and concentrated under a reduced pressure. The crude product was immediately purified by Kugelrohr distillation apparatus at 100 °C/0.05 Torr. The orange oil of 2-bromo-2-trifluoromethylketenimine (**10**) (0.082 g, 0.28 mmol, 70%) was obtained.

^{19}F NMR δ 101.5 (s, 3F) ppm; ^1H NMR δ 3.85 (s, 3H), 6.94 (d, J = 9 Hz, 2H), 7.32 (d, J = 9 Hz, 2H) ppm; IR (neat) 2030 cm^{-1} ; MS m/z (GC-EI) 295 (M^+ , 70), 293 (68), 280 (10), 278 (8), 214 (100), 107 (25), 92 (68), 77 (88); elemental analysis: Calcd for $\text{C}_{10}\text{H}_7\text{BrF}_3\text{NO}$: C, 40.84; H, 2.40; N, 4.76. Found: C, 40.67; H, 2.26; N, 4.87.

4.8. Preparation of 2-trimethylsilyl-2-trifluoromethylketenimine (Scheme 4, compound 11)

Two necked round-bottomed flask was charged with trifluoromethylketenimine (**4**) (0.10 g, 0.47 mmol) in 0.5 ml of CH_2Cl_2 . Then, triethylamine (0.25 ml, 1.8 mmol) was added under an argon atmosphere and flask was cooled to -78°C . Trimethylsilyl trifluoromethanesulfonate (0.25 ml, 1.4 mmol) was added dropwise and the reaction mixture was stirred for 1 h at -78°C . An ethanol bath was put off and the reaction mixture was continuously stirred for 5 h at room temperature. The reaction mixture was concentrated under a reduced pressure. The crude product was immediately purified by Kugelrohr distillation apparatus at 100 °C/0.05 Torr. The colorless oil of 2-trimethylsilyl-2-trifluoromethylketenimine (**11**) (0.095 g, 0.33 mmol, 70%) was obtained.

^{19}F NMR δ 113.3 (s, 3F) ppm; ^1H NMR δ 0.25 (s, 9H), 3.82 (s, 3H), 6.90 (d, J = 9 Hz, 2H), 7.20 (d, J = 9 Hz, 2H) ppm; IR (neat) 2040 cm^{-1} ; MS m/z (GC-EI) 287 (M^+ , 67), 272 (95), 176 (80), 77 (100); elemental analysis: Calcd for $\text{C}_{13}\text{H}_{16}\text{F}_3\text{NOSi}$: C, 54.34; H, 5.61; N, 4.87. Found: C, 54.26; H, 5.68; N, 4.91.

4.9. Reaction of ketenimine 4 with enol from malonate: dimethyl 2-(3,3,3-trifluoro-1-(4-methoxyphenylamino)propylidene)malonate (Scheme 5, compound 12)

Two necked round-bottomed flask was charged with NaH (58% in oil, 0.48 g, 1.16 mmol) in 2.0 ml of THF and cooled to -78°C . To the solution dimethyl malonate (0.136 g, 1.03 mmol) was added and reaction mixture was stirred for 20 min at -78°C , ketenimine **4** (0.147 g, 0.68 mmol) dissolved in 3 ml of THF were added dropwise (30 min). The reaction mixture was stirred for 1 h at -78°C , then stirred 10 h at room temperature. Reaction mixture was treated with silica gel. Short column chromatography gave dimethyl 2-(3,3,3-trifluoro-1-(4-methoxyphenylamino)propylidene)malonate **12** (0.133 g, 0.38 mmol, 59%) as a yellowish solid.

^{19}F NMR δ 99.3 (t, J = 10 Hz, 3F) ppm; ^1H NMR δ 3.62 (q, J = 10 Hz, 2H), 3.77 (s, 3H), 3.77 (s, 3H), 3.83 (s, 3H), 6.91 (d, J = 9 Hz, 2H), 7.06 (d, J = 9 Hz, 2H) ppm; IR (neat) 1700, 1600 cm^{-1} ; MS m/z (GC-EI) 295 (M^+ , 70), 293 (68), 280 (10), 278 (8), 214 (100), 107 (25), 92 (68), 77 (88); elemental analysis: Calcd for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{NO}_5$: C, 51.88; H, 4.64; N, 4.03. Found: C, 52.07; H, 4.55; N, 4.03.

Acknowledgments

We thank SC-NMR Laboratory of Okayama University for ^{19}F and ^1H NMR analyses. We also thank Advanced Science Research Center, Department of Instrumental Analysis of Okayama University for elemental analyses.

References

- [1] (a) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, 2006; (b) K. Uneyama, in: V.A. Soloshonok (Ed.), *Fluorine-containing Synthons*, Oxford University Press, Oxford, 2005; (c) T. Hiyama, *Organofluorine Compounds*, Springer, Berlin, 2000; (d) A. Becker, *Inventory of Industrial Fluoro-biochemicals*, Eyrolles, Paris, 1996.
- [2] (a) R.D. Chambers (Ed.), *Top. Curr. Chem.*, vol. 192, Springer, Berlin, 1997; (b) T. Konno, *Syn. Org. Chem. Jpn.* 63 (2005) 26–39; (c) K. Mikami, Y. Itoh, M. Yamanaka, *Chem. Rev.* 104 (2004) 1–16; (d) A.K. Brisdon, K.K. Banger, *J. Fluorine Chem.* 100 (1999) 35–43; (e) W.R. Dolbier Jr., *Acc. Chem. Res.* 24 (1991) 63–69; (f) D.J. Burton, Z.-Y. Yang, P.A. Morken, *Tetrahedron* 50 (1994) 2993–3063.
- [3] (a) T. Billard, S. Gille, A. Barthelemy, C. Christophe, B.R. Langlois, *J. Fluorine Chem.* 126 (2005) 189–196; (b) K. Uneyama, H. Amii, T. Katagiri, T. Kobayashi, T. Hosokawa, *J. Fluorine Chem.* 126 (2005) 165–171; (c) J.P. Begue, D. Bonnet-Delpon, B. Crousse, J. Legros, *Chem. Soc. Rev.* 34 (2005) 562–572; (d) R. Ocampo, W.R. Dolbier Jr., *Tetrahedron* 60 (2004) 9325–9374; (e) S. Fustero, J.F. Sanz-Cervera, J. Piera, M. Sanchez-Rosello, G. Chiva, A. Simons-Fuentes, *J. Fluorine Chem.* 125 (2004) 621–627; (f) M. Liu, M.P. Sibi, *Tetrahedron* 58 (2002) 7991–8035.
- [4] (a) T.T. Tidwell, *Ketenes*, 2nd ed., Wiley, Hoboken, 2006; (b) S. Patai (Ed.), *The Chemistry of Ketenes, Allenes and Related Compounds*, John Wiley & Sons, Chichester, 1980.
- [5] (a) Yu.V. Zeifman, D.P. Del'tsova, I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1976) 591–594; (b) A.B. Shapiro, D.P. Del'tsova, A.I. Kokorin, E.G. Rozantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1980) 413–416; (c) Y.V. Zeifman, D.P. Del'tsova, E.A. Avetisyan, N.P. Gambaryan, I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1973) 1795–1800 (CAN 79:136659).
- [6] P.L. Coe, I.R. Owen, S.J. Till, *Perkin 1* (2000) 1529–1535.
- [7] W.T. Flowers, R.N. Haszeldine, C.R. Owen, A. Thomas, *J. Chem. Soc., Chem. Commun.* (1974) 134–135.
- [8] R. Huisgen, E. Langhals, G. Mloston, T. Oshima, *Heterocycles* 29 (1989) 2069–2074.
- [9] D.P. Del'tsova, N.P. Gambaryan, Y.V. Zeifman, I.L. Knunyants, *Z. Org. Khim.* 8 (1972) 856–860.
- [10] (a) L.A. Simonyan, Z.V. Safronova, N.P. Gambaryan, M.Y. Antipin, Y.T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1980) 358–364; (b) D.P. Del'tsova, N.P. Gambaryan, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1978) 880–883; (c) Y.V. Zeifman, E.G. Ter-Gabrielyan, L.A. Simonyan, N.P. Gambaryan, I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1976) 1813–1817; (d) D.P. Del'tsova, N.P. Gambaryan, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1976) 858–862; (e) D.P. Del'tsova, E.A. Avetisyan, N.P. Gambaryan, I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1973) 355–358; (f) M.H. Mosslemine, I. Yavarib, M. Anary-Abbasinejada, M.R. Nateghia, *J. Fluorine Chem.* 125 (2004) 1497–1500.
- [11] V.G. Andrianov, M.A. Khomutov, I.B. Zlotina, N.E. Kolobova, Y.T. Struchkov, *Koord. Khim.* 5 (1979) 283–286.
- [12] C.L. Stevens, J.C. French, *J. Am. Chem. Soc.* 76 (1954) 4398–4402.
- [13] (a) K. Uneyama, T. Katagiri, H. Amii, *Acc. Chem. Res.* 41 (2008) 817–829; (b) Y. Yamauchi, T. Katagiri, K. Uneyama, *Org. Lett.* 4 (2002) 173–176; (c) Y. Yamauchi, T. Kawate, T. Katagiri, K. Uneyama, *Tetrahedron* 59 (2003) 9839–9847.
- [14] K. Tamura, H. Mizukami, K. Maeda, H. Watanabe, K. Uneyama, *J. Org. Chem.* 58 (1993) 32–35.
- [15] T. Katagiri, F. Obara, S. Toda, K. Furuhashi, *Synth. Lett.* (1994) 507–508.
- [16] (a) V.A. Soloshonok, T. Ono, *J. Org. Chem.* 62 (1997) 3030–3031; (b) V.A. Soloshonok, T. Ono, *J. Org. Chem.* 62 (1997) 7538–7539; (c) V.A. Soloshonok, V.P. Kukhar, *Tetrahedron* 53 (1997) 8307–8314.
- [17] T. Katagiri, T. Kubota, K. Ueki, Kokai Tokkyo Koho JP06065157 (1994) (CAN: 121: 108006).