Journal of Fluorine Chemistry 167 (2014) 135–138

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

# Synthesis of ethyl 3,3,3-trifluoropropionate from 2-bromo-3,3,3-trifluoropropene

Munenori Inoue [a,*], Masahiro Shiosaki [a], Hajime Muramaru [b]

[a] Sagami Chemical Research Institute, 2743-1 Hayakawa, Ayase, Kanagawa 252-1193, Japan
[b] Tosoh Finechem Corp., Shiba-koen First Building 3-8-2, Shiba, Minato-ku, Tokyo 105-0014, Japan

ARTICLE INFO

*Article history:*
Received 18 April 2014
Received in revised form 1 July 2014
Accepted 12 July 2014
Available online 19 July 2014

Dedicated to Dr. Teruo Umemoto on the occasion of his receipt of the ACS Award for Creative Work in Fluorine Chemistry 2014.

*Keywords:*
Ethyl 3,3,3-trifluoropropionate
2-Bromo-3,3,3-trifluoropropene
Bromination
Alkali metal ethoxide

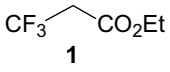
ABSTRACT

A facile synthesis of ethyl 3,3,3-trifluoropropionate is described. Commercially available 2-bromo-3,3,3-trifluoropropene was used as a starting material, which was allowed to react with bromine to produce 2,2,3-tribromo-1,1,1-trifluoropropane. The resulting tribromide was treated with 3 equiv. of potassium ethoxide, giving rise to ethyl 3,3,3-trifluoropropionate in 60% overall yield in 2 steps. The reaction proceeded *via* an alkoxide-induced tandem reaction mechanism.



## 1. Introduction

3,3,3-Trifluoropropionic acid and its esters are useful synthetic intermediates of biologically active compounds [1] and functionalized materials [2]. In addition, since these compounds have three consecutive functional groups including trifluoromethyl, active methylene, and carboxyl groups, they have been utilized as substrates for cyclizations to trifluoromethylated heterocyclic compounds [3], aldol reactions [2c,4] including the asymmetric version [5], Claisen rearrangements [6] and Pd catalyzed allylations [7]. For the purpose of preparation of 3,3,3-trifluoropropionic acid and its esters, several short-step syntheses from commercially available compounds were developed as follows: (i) Arndt-Eistert reaction using 2,2,2-trifluoroacetyl chloride and diazomethane [8a]; (ii) trifluoromethylation of monoethyl malonate with $SF_4$ [8b]; (iii) oxidation of 4,4,4-trifluoro-1-butene prepared from allyl bromide and $CF_3CdBr$ [8c]; (iv) oxidation of 3,3,3-trifluoropropionaldehyde derived from 1-chloro-3,3,3-trifluoropropene and piperidine [8d]; (v) oxidation of 3,3,3-trifluoropropanal dimethyl acetal, synthesized from 1-chloro-3,3,3-trifluoropropene and methanol, by $FeCl_3$ and $H_2O_2$ [8e]; (vi) trifluoromethylation of ketene silyl acetals [3a,8f], and so on [8g]. While several methods to synthesize 3,3,3-trifluoropropionic acid derivatives are available, most of them require expensive materials, and harsh and/or hazardous reaction conditions. Since there remains room to improve the synthetic method of these derivatives, we initiated a project to develop the efficient route leading to ethyl 3,3,3-trifluoropropionate (**1**) (Fig. 1). Herein, we wish to report a facile synthesis of **1** from 2-bromo-3,3,3-trifluoropropene (**2**) in two steps, which is commercially available [9] and also can be easily prepared from 3,3,3-trifluoropropene through a two-step sequence involving bromination and elimination [10].




**1**

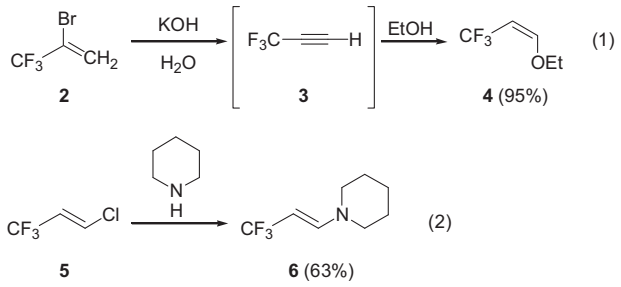
**Fig. 1.** Ethyl 3,3,3-trifluoropropionate (**1**).

## 2. Results and discussion

2-Bromo-3,3,3-trifluoropropene (**2**) has been used as a trifluoromethylated synthetic building block and a precursor of trifluoromethyl-substituted compounds [11]. It was reported that exposure

* Corresponding author. Tel.: +81 467 77 4208; fax: +81 467 77 4113.
*E-mail address:* inoue@sagami.or.jp (M. Inoue).

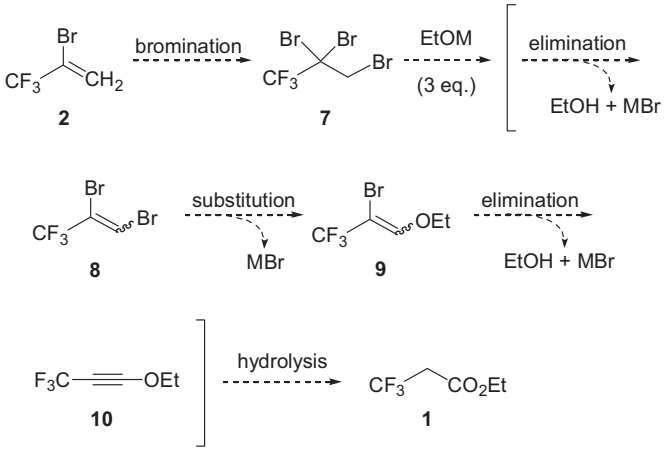
http://dx.doi.org/10.1016/j.jfluchem.2014.07.009
0022-1139/



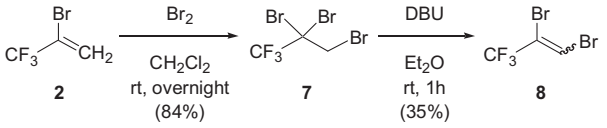

**Scheme 1.** Examples of reactions of the 3,3,3-trifluoropropene derivatives.

of **2** to KOH in the presence of $H_2O$ led to elimination of HBr, giving 3,3,3-trifluoropropyne (**3**) and the reactive C-1 position of **3** was susceptible to addition of EtOH under the alkaline condition to afford a 95% yield of ethyl trifluoropropenyl ether **4** as shown in Eq. (1) of Scheme 1 [12]. Furthermore, it was disclosed that the substitution of the chlorine atom in 1-chloro-3,3,3-trifluoropropene (**5**) by piperidine readily proceeded to furnish 3,3,3-trifluoro-1-piperidinopropene (**6**) in 63% yield (Eq. (2)) [8d]. Inspired by the remarkable reactivity of these 3,3,3-trifluoropropene derivatives, we envisioned that ethyl 3,3,3-trifluoropropionate (**1**) could be derived from known 2,2,3-tribromo-1,1,1-trifluoropropane (**7**), prepared from **2** with $Br_2$ [10], through an elimination-substitution-elimination process triggered by exposure to alkali metal ethoxide as described in Scheme 2. We expected that this tandem reaction would initiate with an alkoxide-induced elimination of HBr from tribromide **7**, followed by substitution of the bromine atom at the C-1 position of dibromopropene **8** by ethoxide ion to furnish the intermediate ethyl trifluoropropenyl ether **9**. Further elimination reaction of **9** would occur to produce ynol ether **10**, which would be eventually hydrolyzed to give the desired product **1** in a single step.

In order to realize the synthetic strategy described above, we initially prepared tribromide **7** by bromination of **2** with bromine in 84% yield as depicted in Scheme 3 [10]. The resulting tribromide **7** was then treated with DBU to provide dibromopropene **8** in 35% yield [13]. When this elimination reaction of **7** to **8** was executed with NaOEt in EtOH at room temperature, fortunately, we detected a small amount of formation of ethyl 3,3,3-trifluoropropionate (**1**) by GC analysis. This result convinced us of the feasibility of the proposed strategy and we then decided to focus on the alkoxide induced one-step conversion of **7** into **1**.




**Scheme 2.** Synthetic strategy for ethyl 3,3,3-trifluoropropionate (**1**).



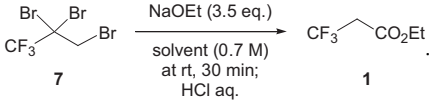

**Scheme 3.** Synthesis of dibromopropene **8**.

As shown in Table 1, the NaOEt-induced transformation of **7** to **1** in various solvents was investigated. Since this reaction required at least 3 equiv. of NaOEt, the reaction was performed upon treatment of **1** with 3.5 equiv. of NaOEt at room temperature for 30 min and quenched with aq. HCl. The initial attempt of the reaction in EtOH produced **1** in 27% GC yield (entry 1). To improve the yield, several solvents were explored under the same reaction condition. In ethereal solvents, such as THF, $Et_2O$, and $Pr^i_2O$, the yield was dramatically increased to 72%, 56%, and 50% yield, respectively (entries 2–4). In aprotic polar solvents, such as DMF, DMSO, and MeCN, the moderate yield of **1** was obtained (entries 5–7). While the reaction in hexane proceeded well (entry 8), the yield was diminished in the case of toluene and $CH_2Cl_2$ (entries 9–10). One should note that it is essential to perform the reaction under anhydrous condition and using fresh reagents, because the decreasing of the yield was observed in the presence of $H_2O$.

Having found a suitable solvent for the reaction, we then investigated the base and reaction temperature as shown in Table 2. At first, treatment of **7** with KOEt in place of NaOEt in THF at room temperature yielded a 75% yield of **1** (entry 1). The reaction proceeded rapidly and cleanly compared with the reaction of **7** with NaOEt. In entries 2 and 3, the reaction temperature was investigated. The reaction executed at 0 °C resulted in the decreased yield of **1** (4%) and the yield of the reaction maintained at 40 °C was slightly reduced (62%). Since the reaction was exothermic, which may accelerate the reaction, cooling the reaction media delayed the reaction. To isolate the product, the reaction was performed in $Et_2O$ in place of THF affording **1** in 72% yield after distillation (entry 4). Although we expected to obtain *tert*-butyl ester **11**, amide **12**, and acid **13**, under the same reaction condition using bases such as $KOBu^t$, $NaNH_2$, and KOAc, respectively, the corresponding trifluoropropionic acid derivatives were not unfortunately produced (entries 5–7). The best result was obtained upon treatment of **7** with KOEt in THF or $Et_2O$ at room temperature and the isolated yield of **1**, produced by the reaction in $Et_2O$, was 72% yield.

The reaction mechanism was not clearly understood, but we assumed the reaction proceeded as follows (Scheme 4). Since

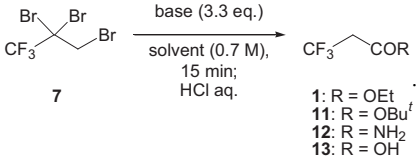
**Table 1**
Synthesis of ethyl 3,3,3-trifluoropropionate **1** from **7** in various solvents.




| Entry | Solvent | Yield (%)[a] |
|---|---|---|
| 1 | EtOH | 27 |
| 2 | THF | 72 |
| 3 | $Et_2O$ | 56 |
| 4 | $Pr^i_2O$ | 50 |
| 5 | DMF | 51 |
| 6 | MeCN | 24 |
| 7 | DMSO | 30 |
| 8 | Hexane | 52 |
| 9 | Toluene | 8 |
| 10 | $CH_2Cl_2$ | 15 |

[a] Determined by GC analysis.

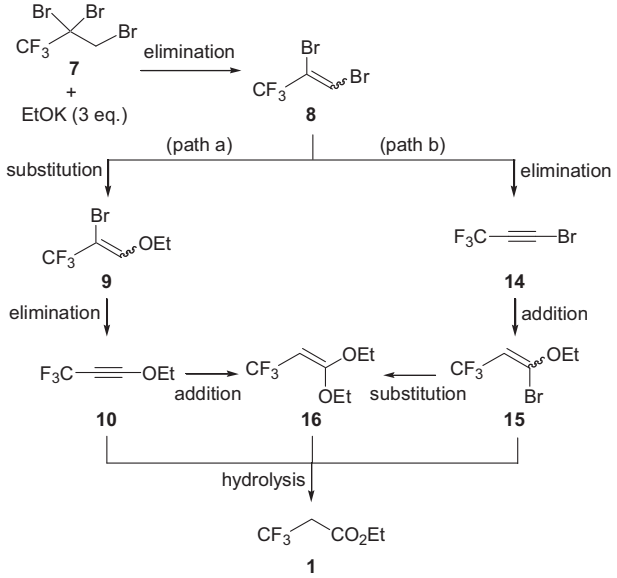
**Table 2**
Synthesis of trifluoropropionic acid derivatives from **7** using various bases.




| Entry | Base | Solvent | Temperature (°C) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | KOEt (R = OEt) | THF | 20 | 75 |
| 2 | KOEt (R = OEt) | THF | 0 | 4 |
| 3 | KOEt (R = OEt) | THF | 40 | 62 |
| 4 | KOEt (R = OEt) | $Et_2O$ | 20 | (72)[b] |
| 5 | $KOBu^t$ (R = $OBu^t$) | THF | 20 | 0 |
| 6 | $NaNH_2$ (R = $NH_2$) | THF | 20 | 0 |
| 7 | KOAc (R = OH) | THF | 20 | 0 |

[a] Determined by GC analysis.
[b] Value in parentheses indicates isolated yield.

treatment of **7** with 1 equiv. of KOEt in THF produced dibromopropene **8** concurrently with the formation of **1**, we thought our developed reaction began with elimination of HBr from **7** and dibromide **8** is the first reaction intermediate. There might be two possibilities to explain the second step of the reaction: replacement of the bromine atom in **8** by ethoxide ion to produce **9** [14] (path a) and/or elimination of HBr from **8**, followed by addition of EtOH to the resulting alkyne **14**, affording alkene **15** (path b). Before quenching of the reaction mixture with aq. HCl, the target compound **1** was not observed by GC-Ms analysis and an unidentified product ($M^+$ = 184) was detected. After hydrolysis, this unidentified compound disappeared with the formation of **1**, which indicated ketene diethyl acetal **16** ($M^+$ = 184) may form as a precursor of the targeted compound **1** during the reaction. We regarded ketene diethyl acetal **16** was produced through elimination of HBr from **9**, followed by addition of EtOH to the resulting ynol ether **10** and/or substitution of the bromine atom in **15** by ethoxide anion.




**Scheme 4.** Plausible mechanism for the formation of **1**.

## 3. Conclusion

In this paper, we described the simple and facile synthesis of ethyl 3,3,3-trifluoropropionate (**1**) from commercially available 2-bromo-3,3,3-trifluoropropene (**2**). Bromination of **2** with $Br_2$ gave 2,2,3-tribromo-1,1,1-trifluoropropane (**7**) and the resulting tribromide **7** was allowed to react with 3 equiv. of KOEt, giving **1** in 60% overall yield in 2 steps. We regarded this one pot sequence involved an ethoxide induced elimination-substitution-elimination-addition pathway (path a) and/or an ethoxide induced elimination-elimination-addition-substitution pathway (path b).

## 4. Experimental

### 4.1. General

All reactions involving air- and moisture-sensitive reagents were carried out using oven-dried glassware and standard syringe-septum cap techniques. Routine monitoring of reaction was carried out and Low-resolution mass (MS) spectra were measured on a Shimadzu GCMS-QP2010. All solvents and reagents were obtained from commercial suppliers and were used without further purification. Infrared (IR) spectral measurements were carried out with a HORIBA FT-720 spectrometer. $^1H$, $^{13}C$, and $^{19}F$ NMR spectra were measured with a Bruker AVANCE III spectrometer. Chemical shifts are expressed in parts per million (ppm) using tetramethylsilane ($\delta$ = 0, $^1H$ NMR) and $C_6F_6$ ($\delta$ = −163.0, $^{19}F$ NMR) as standard substances. Multiplicities are indicated by s (singlet), t (triplet), and q (quartet). $^{19}F$ NMR spectra were recorded without $^1H$ decoupling. High-resolution mass (HRMS) spectra were measured on a JEOL MStation JMS-700 mass spectrometer.

### 4.2. Preparation of 2,2,3-tribromo-1,1,1-trifluoropropane (7)

To a stirred solution of 2-bromo-3,3,3-trifluoropropene (**2**) (30.6 g, 0.175 mol) in $CH_2Cl_2$ (300 mL) was added dropwise bromine (10.8 mL, 0.21 mol) at 0 °C and the resulting solution was stirred at room temperature overnight. The resulting mixture was quenched with 15% aq. $Na_2S_2O_3$ (50 mL) and the aqueous layer was extracted with $CH_2Cl_2$ (50 mL ×3). The extract was washed with brine (40 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by distillation to give **7** (49.1 g, 84%) as a colorless oil. bp. 79–81 °C (80 mmHg). IR (neat): 1419, 1280, 1261, 1236, 1186, 1162, 1054, 933, 912, 894, 817, 775, 732, 705, 674, 651, 644 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 4.17 (s, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 121.4 (q, $J_{CF}$ = 280 Hz, 1C), 57.08 (q, $J_{CF}$ = 33.6 Hz, 1C), 38.26 (s, 1C). $^{19}F$ NMR (376 MHz, $CDCl_3$): $\delta$ −74.4 (s, 3F). HRMS-EI: *m/z* $[M]^+$ calcd for $C_3H_2Br_3F_3$: 331.7659; found: 331.7664.

### 4.3. Preparation of (EZ)-1,2-dibromo-1,1,1-trifluoropropene (8)

To a stirred solution of 2,2,3-tribromo-1,1,1-trifluoropropane (**7**) (2.0 g, 6.0 mmol) in $Et_2O$ (50 mL) was added DBU (1.07 mL, 7.16 mmol) at room temperature and the resulting solution was stirred for 1 h. The resulting mixture was quenched with aq. HCl (1 M, 50 mL) and the organic phase was dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by distillation to give **8** (531 mg, 35%, *E*:*Z* = 1:2.7 by $^1H$ NMR) as a colorless oil. bp. 96 °C (760 mmHg). IR (neat): 1606, 1276, 1141, 933, 919, 815, 782, 752, 717, 674, 609 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.72 (brq, *J* = 1.1 Hz, 1H for *Z*-isomer), 7.13 (s, 1H for *E*-isomer). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 120.3 (q, $J_{CF}$ = 271.3 Hz, 1C for *Z*-isomer), 120.0 (q, $J_{CF}$ = 272.7 Hz, 1C for *E*-isomer), 119.4 (q, $J_{CF}$ = 5.8 Hz, 1C for *Z*-isomer), 118.5 (q, $J_{CF}$ = 37.6 Hz, 1C for *Z*-isomer), 111.4 (q, $J_{CF}$ = 3.1 Hz, 1C for *E*-isomer), 111.0 (q, $J_{CF}$ = 38.4 Hz, 1C for

*E*-isomer). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ −62.11 (s, 3F for *E*-isomer), −67.16 (brd, $J_{HF}$ = 1.1 Hz, 3F for *Z*-isomer). HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_3HBr_2F_3$: 251.8397; found: 251.8395.

### 4.4. Preparation of ethyl 3,3,3-trifluoropropionate (**1**) [8b]

To a stirred suspension of KOEt (5.0 g, 59.4 mmol) in $Et_2O$ (200 mL) was added dropwise a solution of 2,2,3-tribromo-1,1,1-trifluoropropane (**7**) (6.0 g, 17.9 mmol) in $Et_2O$ (50 mL) at room temperature and the resulting mixture was stirred at room temperature for 15 min. The resulting mixture was quenched with aq. HCl (1 M, 50 mL) and stirred for further 30 min. The aqueous layer was extracted with $Et_2O$ (50 mL ×3) and the combined organic phase was washed with brine (40 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by distillation to give **1** (2.0 g, 72%) as a colorless oil. bp. 106 °C (760 mmHg). IR (neat): 2989, 1747, 1384, 1360, 1267, 1216, 1110, 1026, 929, 836, 755, 653 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.24 (q, $J$ = 7.2 Hz, 2H), 3.17 (q, $J$ = 10.1 Hz, 2H), 1.30 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 164.1 (q, $J_{CF}$ = 4.1 Hz, 1C), 123.4 (q, $J_{CF}$ = 274.5 Hz, 1C), 61.7 (1C), 39.5 (q, $J_{CF}$ = 30.8 Hz, 1C), 13.8 (1C). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ −64.8 (t, $J_{HF}$ = 10.1 Hz, 3F). EI-MS *m*/*z* (rel. int.): 156 $[M]^+$ (2.4), 141 $[M-Me]^+$ (1.4), 129 $[M+2H-Et]^+$ (8.2), 111 $[M-OEt]^+$ (100), 91 $[CF_2CHCO]^+$ (12.9), 83 $[CF_3CH_2]^+$ (15.7), 69 $[CF_3]^+$ (7.5), 45 $[EtO]^+$ (41.4).

## Acknowledgement

We greatly thank Tosoh F-Tech, Inc. for the generous gift of 2-bromo-3,3,3-trifluoropropene.

## References

[1] (a) F.A. Romero, S.M. Vodonick, K.R. Criscione, M.J. McLeish, G.L. Grunewald, J. Med. Chem. 47 (2004) 4483–4493;
(b) D.-M. Feng, J.M. Wai, S.D. Kuduk, C. Ng, K.L. Murphy, R.W. Ransom, D. Reiss, R.S.L. Chang, C.M. Harrell, T. MacNeil, C. Tang, T. Prueksaritanont, R.M. Freidinger, D.J. Pettibone, M.G. Bock, Bioorg. Med. Chem. Lett. 15 (2005) 2385–2388.
[2] (a) A.L. Henne, C.J. Fox, J. Am. Chem. Soc. 73 (1951) 2323–2325;
(b) Y. Numata, I. Ashraful, Y. Shirai, L. Han, Chem. Commun. 47 (2011) 6159–6161;
(c) J. Hong, H. Lai, Y. Liu, C. Yuan, Y. Li, P. Liu, Q. Fang, RSC Adv. 3 (2013) 1069–1072.
[3] (a) H. Yamanaka, T. Takekawa, K. Morita, T. Ishihara, J.T. Gupton, Tetrahedron Lett. 37 (1996) 1829–1832;
(b) D. Shabashov, O. Daugulis, J. Org. Chem. 72 (2007) 7720–7725;
(c) S. Grosjean, S. Triki, J.-C. Meslin, K. Julienne, D. Deniaud, Tetrahedron 66 (2010) 9912–9924;
(d) J.K. Augustine, A. Bombrun, B. Ramappa, C. Boodappa, Tetrahedron Lett. 53 (2012) 4422–4425;
(e) J.-I. Andrés, J. Alcázar, J.M. Cid, M.D. Angelis, L. Iturrino, X. Langlois, H. Lavreysen, A.A. Trabanco, S. Celen, G. Bormans, J. Med. Chem. 55 (2012) 8685–8699.
[4] (a) T. Yokozawa, T. Nakai, N. Ishikawa, Tetrahedron Lett. 25 (1984) 3987–3990;
(b) P.V. Ramachandran, G. Parthasarathy, P.D. Gagare, Org. Lett. 12 (2010) 4474–4477.
[5] (a) T. Shimada, M. Yoshioka, T. Konno, T. Ishihara, Org. Lett. 8 (2006) 1129–1131;
(b) X. Franck, B. Seon-Meniel, B. Figadère, Angew. Chem. Int. Ed. 45 (2006) 5174–5176.
[6] T. Yokozawa, T. Nakai, N. Ishikawa, Tetrahedron Lett. 25 (1984) 3991–3994.
[7] Y. Komatsu, T. Sakamoto, T. Kitazume, J. Org. Chem. 64 (1999) 8369–8374.
[8] (a) F. Brown, W.K.R. Musgrave, J. Chem. Soc. (1953) 2087–2089;
(b) H.M. Peters, L.O. Ross, R.L. Simon, M.E. Hill, J. Chem. Eng. Data 16 (1971) 376–377;
(c) J.-P. Bouillon, C. Maliverney, R. Merényi, H.G. Viehe, J. Chem. Soc. Perkin Trans. 1 (1991) 2147–2149;
(d) T. Komata, M. Fujiwara, S. Akiba, K. Hosoi, S. Narizuka, PCT Int. Appl. WO2006046417, 2006.
(e) T. Komata, S. Akiba, K. Hosoi, K. Ogura, J. Fluorine Chem. 129 (2008) 35–39;
(f) K. Sato, T. Yuki, R. Yamaguchi, T. Hamano, A. Tarui, M. Omote, I. Kumadaki, A. Ando, J. Org. Chem. 74 (2009) 3815–3819;
(g) See also references cited in 8b–8f..
[9] 2-Bromo-3,3,3-trifluoropropene (CAS: 1514-82-5) was obtained from Tosoh F-Tech. It can be also purchased from Sigma–Aldrich, SynQuest Laboratories, and Alfa Aesar.
[10] A.L. Henne, M. Nager, J. Am. Chem. Soc. 73 (1951) 1042–1043.
[11] For examples of reactions using 2-bromo-3,3,3-trifluoropropene, see:
(a) F.G. Drakesmith, O.J. Stewart, P. Tarrant, J. Org. Chem. 33 (1967) 280–285;
(b) W.R. Dolbier Jr., C.R. Burkholder, C.A. Piedrahita, J. Fluorine Chem. 20 (1982) 637–647;
(c) T. Fuchikami, A. Yamanouchi, I. Ojima, Synthesis (1984) 766–768;
(d) B. Jiang, Y. Xu, J. Org. Chem. 56 (1991) 7336–7340;
(e) T. Yamazaki, K. Mizutani, T. Kitazume, J. Org. Chem. 60 (1995) 6046–6056;
(f) A.R. Katritzky, M. Qi, A.P. Wells, J. Fluorine Chem. 80 (1996) 145–147;
(g) B. Jiang, Q.-F. Wang, C.-G. Yang, M. Xu, Tetrahedron Lett. 42 (2001) 4083–4085;
(h) B. Jiang, F. Zhang, W. Xiong, Chem. Commun. (2003) 536–537;
(i) J. Ichikawa, H. Fukui, Y. Ishibashi, J. Org. Chem. 68 (2003) 7800–7805;
(j) J. Huang, E. Bunel, M.M. Faul, Org. Lett. 9 (2007) 4343–4346;
(k) O. Kobayashi, D. Uraguchi, T. Yamakawa, J. Fluorine Chem. 130 (2009) 591–594;
(l) T. Konno, T. Kida, A. Tani, T. Ishihara, J. Fluorine Chem. 144 (2012) 147–156;
(m) K. Hirotaki, T. Hanamoto, Org. Lett. 15 (2013) 1226–1229.
[12] (a) A.L. Henne, M. Nager, J. Am. Chem. Soc. 74 (1952) 650–652;
(b) E.K. Raunio, T.G. Frey, J. Org. Chem. 36 (1971) 345–347;
(c) F. Hong, C.-M. Hu, Chem. Commun. (1996) 57–58.
[13] The low yield was due to the volatility of the compound **8** and the reaction condition was not optimized.
[14] G.-q. Shi, X.-H. Huang, F. Hong, J. Org. Chem. 61 (1996) 3200–3204.