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Unusual Behavior of the Anionic Species from (*E*)-1-Chloro-3,3,3-trifluoropropene (HCFC-1233t)

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Keywords: Fluorine / Rearrangement / Alcohols / Alkenes

(*E*)-1-Chloro-3,3,3-trifluoropropene was smoothly deprotonated by MeLi at the position β to the CF_3 group, and exclusive formation of propargylic alcohols was observed by addition of appropriate carbonyl compounds as long as up to 1.6 equiv. of MeLi was used, whereas more than 1.7 equiv. of this base led to selective construction of allylic alcohols.

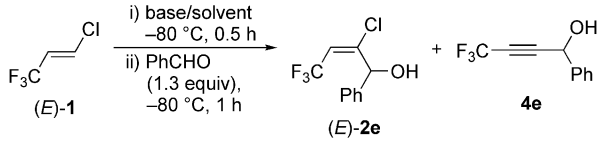
Introduction

Nonozone depleting (*E*)-1-chloro-3,3,3-trifluoropropene [(*E*)-**1**; abbreviated as HCFC-1233t], is manufactured as the convenient intermediate for the preparation of 1,1,1,3,3-pentafluoropropane (HFC-245fa) as the potent chlorofluorocarbon substitute.[1] In addition to its usage for this purpose, (*E*)-**1** is also recognized as a useful CF_3-containing building unit by installation of a structurally defined (*E*) olefin and a chlorine atom as the useful synthetic handles.[2] Moreover, consideration of the characteristic nature of the CF_3 moiety leads to the expectation that two hydrogen atoms in (*E*)-**1** are likely to be removed by treatment with an adequate base, such as the various types of RLi: H^a would be acidic enough, as the resulting anion would be inductively stabilized by the CF_3 group,[3] and abstraction of H^b would furnish vinyllithium species Int-**1** containing firm and energetically favorable intramolecular five-membered Li···F chelation (Scheme 1).[4] Then, we started to investigate the behavior of versatile substrate (*E*)-**1** towards various bases and utilization of the resultant anionic intermediates.

Results and Discussion

First of all, our attention has been focused on finding appropriate conditions for deprotonation of (*E*)-**1** and for nucleophilic attack of the resultant anion towards a representative electrophile, benzaldehyde (Table 1). Requirement of relatively higher polarity was apparent for solvents to effect smooth removal of protons: thus, hexane afforded products in very low yields irrespective of the base employed (Table 1, Entries 3, 6, and 11) but THF (Table 1, Entries 1, 4, 7, and 9) demonstrated excellent selectivity for propargylic alcohol **4e**[5] and also quite high chemical yields.[6] In contrast, Et_2O furnished a mixture of **4e** and allylic alcohol (*E*)-**2e** with the latter being preferred (Table 1, Entries 2, 5, and 10), but this was not the case when MeLi was used (Table 1, Entry 8).

Table 1. Investigation of reaction conditions.[a]



Entry	Base (equiv.)	Solvent	^{19}F NMR yield [%] (*E*)-**2e**	**4e**
1	*s*BuLi (1.2)	THF	5	59
2	*s*BuLi (1.2)	Et_2O	44	38
3	*s*BuLi (1.2)	hexane	0	0
4	BuLi (1.2)	THF	0	55
5	BuLi (1.2)	Et_2O	76	21
6	BuLi (1.2)	hexane	0	1
7	MeLi (1.2)	THF	0	52
8	MeLi (1.2)	Et_2O	0	0
9	LDA (1.2)	THF	0	55
10	LDA (1.2)	Et_2O	24	8
11	LDA (1.2)	hexane	11	7
12	*t*BuOK (1.2)	THF	0	0
13	*s*BuLi (2.2)	THF	45	55
14	BuLi (2.2)	THF	–[b]	–[b]
15	MeLi (2.2)	THF	90	5
16	LDA (2.2)	THF	75	25

[a] RLi reagents were titrated prior to use. [b] No reproducible results were obtained (constant product selectivity was not obtained and sometimes the major product was switched).

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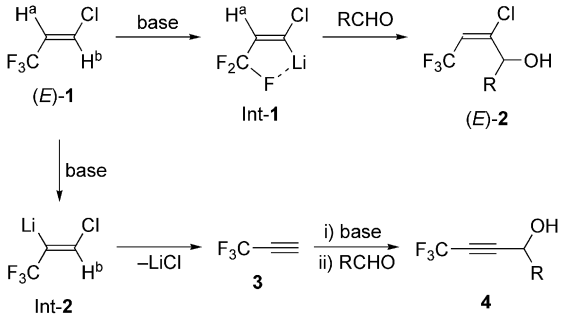
These results allowed us to propose the brief mechanism (Scheme 1). Thus, contrary to the computational results described below (see Scheme 3), a base in THF would select H^a, α to the strongly electron-withdrawing CF_3 group, and its removal would be followed by elimination of a chlorine atom to furnish 3,3,3-trifluorinated propyne **3**. Then, the second base molecule might successfully convert this intermediate into **4** by reaction of the corresponding acetylide and an appropriate carbonyl compound. In contrast, deprotonation at the β position to the CF_3 moiety seemed to compete to some extent in a less coordinating solvent like Et_2O. These experimental results suggested that Int-**2** was more energetically stable than Int-**1**, and the aggregation state of RLi species would affect the reaction course significantly.



Scheme 1. Possible routes to allylic alcohols (*E*)-**2** and propargylic alcohols **4**.

On the basis of this analysis, 2.2 equivalents of a base was employed in THF with the aim to produce **4e** in high-yield. However, a totally unexpected outcome resulted: thus, especially as shown in Entries 15 and 16 in Table 1, allylic alcohol (*E*)-**2e** was actually obtained as the major product and **4e** was formed only in low yield. *s*BuLi did not give the good (*E*)-**2e**/**4e** selectivity that we expected (Table 1Entry 13). To solve this puzzling question, (*E*)-**1** was treated with varying amounts of MeLi[7] as the model base, and it is quite intriguing to note that the chemical yields of (*E*)-**2e** and **4e** were highly dependent on the quantity of MeLi, and their selectivity clearly and drastically changed between 1.6 and 1.7 equivalents (Figure 1). A unique point was also found between 1.4 and 1.5 equivalents.

For acquiring further information about the present reaction mechanism, a couple of additional experiments were performed (Scheme 2). At first, in an attempt to spontaneously capture the anionic species initially generated from (*E*)-**1**, this substrate was subjected to a THF solution of LDA (1.2 equiv.)[8] containing PhCHO to furnish a mixture of (*E*)-**2e** and **4e** in 18 and 8% yield, respectively (conditions b). In contrast, **4e** was obtained in 55% yield as the sole product by the deprotonation sequence with LDA at –80 °C for 0.5 h, followed by the addition of PhCHO (Table 1, Entry 9; conditions a). Moreover, apparent from Figure 1, treatment of (*E*)-**1** with MeLi (1.7 equiv.) led to exclusive formation of (*E*)-**2e** (97% yield with 2% of **4e**; conditions c), whereas addition of HMPA (1 equiv.) to this

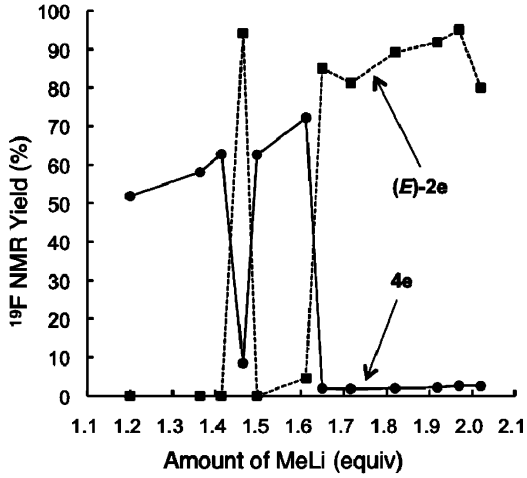
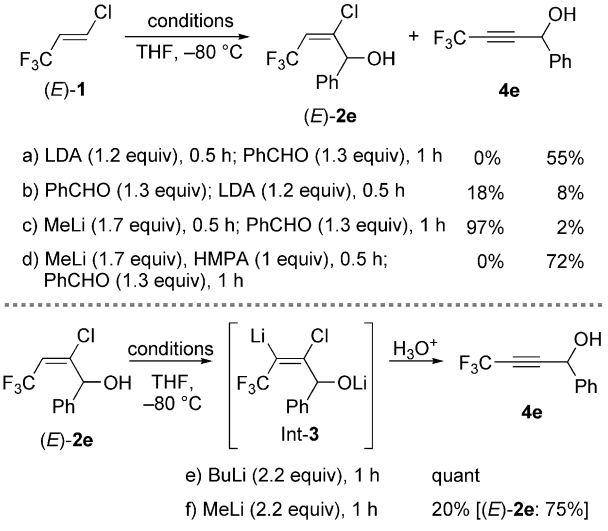


Figure 1. Relationship between the amount of MeLi employed and the product selectivity [(*E*)-**2e**: ■, **4e**: ●].

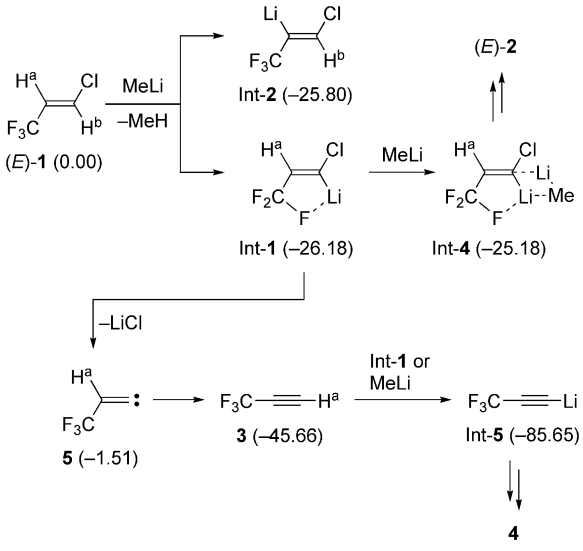
system completely altered the situation to afford **4e** selectively [72% yield without formation of (*E*)-**2e**; conditions d]. Combination of these results led to speculation that (1) production of **4e** in an excellent conversion yield by the action of LDA (1.2 equiv.) suggested the initial formation of the vinylic anion β to a CF_3 group (Int-**1** in Scheme 1), which would be then transformed into the corresponding acetylide before reaction with PhCHO and (2) the quite sharp effect of HMPA as an additive would assume an appropriate intermolecular interaction between Int-**1** and the excess amount of MeLi.



Scheme 2. Syntheses of (*E*)-**2e** and **4e** by various methods.

Additional reactions were also carried out to verify the possible production of propargylic alcohol **4e** by formal dehydrochlorination of allylic alcohol (*E*)-**2e**. In the event, smooth and quantitative conversion of (*E*)-**2e** to **4e** via Int-**3** was substantiated by 2.2 equivalents of BuLi, whereas with the same quantity of MeLi only 20% conversion to **4e** was realized along with 75% recovery of (*E*)-**2e** (conditions e and f), which led to the conclusion that (3) this was

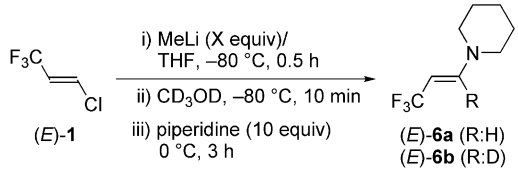
not the major route to yield **4e** as long as MeLi was employed. With these additional data in hand, we revised the mechanism to that shown in Scheme 3, which also includes the relative energy by DFT calculations[9] in parentheses. Thus, the first proton abstraction by MeLi would regioselectively occur at the β position to the CF_3 group so as to form the computationally more stable intermediate Int-**1**, which would constitute complexes like Int-**4**[10] or its oligomeric forms with an excess amount of MeLi for gaining further stabilization.[11] In contrast, because MeLi under such a situation still retained its ability as a base, it would abstract H^b from another (*E*)-**1** molecule to furnish Int-**1**, which by losing an extra stabilizing factor, would further release LiCl by the α elimination pathway when less than 1.6 equivalents of MeLi was employed.



Scheme 3. The proposed mechanism of the present reaction {in the parenthesis is shown the calculated relative energy [kcal mol^{-1}] by the B3LYP/6-311++G** level of theory with considering the effect of THF (SCIPCM)}.

Subsequent hydride migration[12] would convert carbene **5** into F_3-propyne **3**, which underwent deprotonation to give the corresponding acetylide Int-**5** by another Int-**1** molecule or MeLi itself. This interesting reaction course is already known as the Fritsch–Buttenberg–Wiechell (FBW) rearrangement.[13,14] Eventually, final intermediates Int-**4** and Int-**5** would directly correspond to products (*E*)-**2** and **4**, respectively. This scheme would at least qualitatively explain the behavior of (*E*)-**1** after lithiation: for example, addition of HMPA (1 equiv.) would be effective for decomposition of complexes like Int-**4** and liberated Int-**1** followed FBW rearrangement to give **4** (Scheme 2, conditions c vs. d). In contrast, the generation of the anionic species from (*E*)-**1** *in the presence of PhCHO* furnished a mixture of (*E*)-**2e** and **4e**, whereas the addition of PhCHO after 0.5 h mixing of (*E*)-**1** with MeLi predominantly afforded **4e** (conditions a vs. b). The fact that the former "internal trap" experiment furnished (*E*)-**2e** and **4e** in 18 and 8% yield, respectively, would be a reflection of FBW rearrangement as a relatively quick sequence.[15] As already described in Entries 2 and 5 in Table 1, different from THF, the lower Lewis basic solvent Et_2O allowed formation of (*E*)-**2e** to some extent, which would be as a result of favorable construction of complexes by interaction of Int-**1** and *s*BuLi or BuLi like the case of MeLi.

To obtain further experimental proof, we performed the deuteration reaction of the resultant possible anionic species, thus Int-**1** or **2**. Because it has already known that (*E*)-**1** readily undergoes nucleophilic attack of secondary amines by way of an addition–elimination sequence,[16,17] the in situ conversion of regenerated (*E*)-**1** to (*E*)-**6** was investigated as a result of the low boiling point of (*E*)-**1** of 21 °C (Scheme 4). At first, for confirmation of the applicability of the original method[18] with a slight modification, the anionic species from the reaction of (*E*)-**1** and 1.7 equivalents of MeLi at –80 °C was quenched with CH_3OH and addition of piperidine to this mixture afforded (*E*)-**6a** in 32% yield. Then, the same process was repeated by using the same base in amounts of 1.2 and 1.7 equivalents with CD_3OD as the deuterium source. The former conditions furnished (*E*)-**6a** in 16% yield without any sign of deuterium incorporation, but the product of the latter was found to possess 54% D only at the N-attached carbon atom. The fact that the product obtained under conditions c in Scheme 4 did not contain any deuterium seemed consistent with our proposed mechanism, because this pathway would furnish 0.6 equivalents of Int-**5** and 0.4 equivalents of (*E*)-**1** and the latter led to formation of (*E*)-**6a** and deuterated **3** from Int-**5** would be vaporized (boiling point: ca. –40 °C). The use of 1.7 equivalents of MeLi furnished a mixture of (*E*)-**6a** and **6b** in a ratio of 46:54, indicating the presence of vinyl anionic intermediates possibly like Int-**4**, which nicely compared with the result when 1.2 equivalents of MeLi was employed.

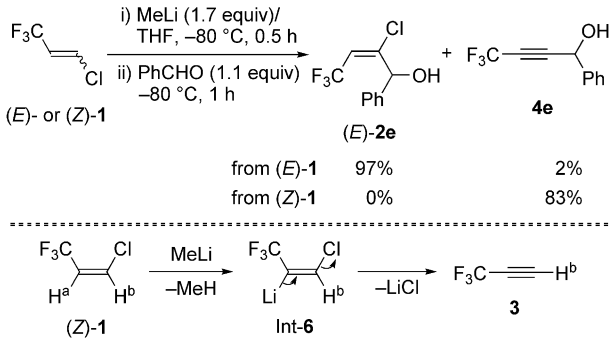


a) X=1.7; 32% yield, (*E*)-**6a** only (quenched with CH_3OH)
b) X=1.7; 13% yield, (*E*)-**6a**/(*E*)-**6b**, 46:54
c) X=1.2; 16% yield, (*E*)-**6a** only

Scheme 4. Reaction of (*E*)-**1** with piperidine under various conditions.

Another intriguing point was the fairly contrasting reactivity between stereoisomers (*E*)- and (*Z*)-**1**. Thus, treatment of (*E*)-**1** with 1.7 equivalents of MeLi followed by trapping the resultant intermediate by PhCHO predominantly furnished allylic alcohol (*E*)-**2e**, whereas exclusive formation of propargylic alcohol **4e** was realized by (*Z*)-**1** (Scheme 5). The latter would be understood as a result of selective formation of Int-**6** due to its electrostatic stability and, at the same time, impossible intramolecular Li···F chelation after deprotonation of H^b. In addition to our interpretation described above, this conclusion also stemmed

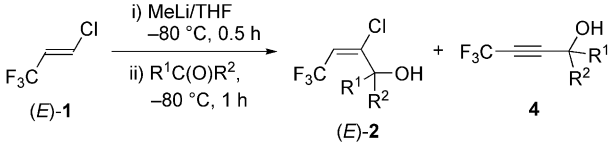
from the inherently significant rate difference of this type of elimination between stereoisomers:[19] for example, elimination of HBr from (*Z*)-2-bromo-*p*-nitrostyrene was reported to proceed 2300 times faster than the corresponding (*E*) isomer.[19a]



Scheme 5. Reaction of (*Z*)-**1** with 1.7 equivalents of MeLi and PhCHO.

The preparation of (*E*)-**2** and **4** by adding 1.7 and 1.6 equivalents of MeLi to (*E*)-**1**, respectively, enabling the selective formation of these two types of alcohols containing a variety of substituents is shown in Table 2.

Table 2. Reaction of (*E*)-**1** with a variety of carbonyl compounds in the presence of 1.6 or 1.7 equivalents. of MeLi.



Entry	R^1	R^2	Isolated yield [%] (*E*)-**2**[a]	**4**[b]
1	C_9H_{19}	H	94 (**2a**)	65 (**4a**)
2	$PhCH_2CH_2$	H	86 (**2b**)	59 (**4b**)
3	*p*-$CH_3C_6H_4$	H	88 (**2c**)	57 (**4c**)
4	*p*-$CH_3OC_6H_4$	H	85 (**2d**)	58 (**4d**)
5	Ph	H	97 (**2e**)	72 (**4e**)
6	*p*-BrC_6H_4	H	92 (**2f**)	52 (**4f**)
7	*p*-$NO_2C_6H_4$	H	84 (**2g**)	[25][c] (**4g**)
8	Ph	CH_3	57 (**2h**)	56[d] (**4h**)
9	$(CH_2)_5$		85 (**2i**)	64 (**4i**)

[a] 1.7 equiv. of MeLi was employed. [b] 1.6 equiv. of MeLi was employed. [c] Yield in square brackets represents the yield when 2.2 equiv. of MeLi and 10 equiv. of HMPA were used. [d] Reaction was carried out at –80 to –60 °C for 3 h.

Conclusions

As shown above, we have learned the interesting behavior of anionic species Int-**1** generated from (*E*)-**1**, which facilitated the formation of allylic alcohols (*E*)-**2** possibly by way of an energetically more stable complex with MeLi (MeLi > 1.7 equiv.), whereas Int-**1** itself would follow an FBW rearrangement after α-elimination of LiCl to furnish the corresponding propargylic alcohols **4** (MeLi < 1.6 equiv.). Although the mechanism has not fully been clarified, we successfully demonstrated the extraordinary convenience of the present method for the selective construction of either alcohols (*E*)-**2** or **4** just by controlling the amount of MeLi employed. Further study in this area is underway in this laboratory.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures for the preparation of allylic and propargylic alcohols (*E*)-**2** and **4**, respectively, and characterization data of the new compounds.

Acknowledgments

The generous gift of both stereoisomers of HCFC-1233 from Central Glass Co., Ltd. is gratefully acknowledged.

[1] a) T. Nakada, H. Aoyama, A. Yamamoto (Daikin Industries), PCT Int. Appl. 9724307, **1997**; b) S. Yoshikawa, R. Tamai, F. Saku, Y. Hibino (Central glass), Jpn. Kokai Tokkyo Koho, 09241188, **1997**; c) A. Lantz, B. Requieme, L. Wendlinger (Elf Atochem), Ger. Offen. 19716337, **1997**; d) M. Y. Elsheikh, B. Chen (Elf Atochem North America), Jpn. Kokai Tokkyo Koho 2000336048, **2000**; e) H.-S. Tung, R. C. Johnson, D. C. Merkel (Honeywell International), U. S. Pat. Appl. Publ. 2005020862, **2005**; f) H.-E. Yang, H.-D. Quan, M. Tamura, A. Sekiya, *J. Mol. Catal. A* **2005**, *233*, 99–104; g) H.-D. Quan, H.-E. Yang, M. Tamura, A. Sekiya, *J. Fluorine Chem.* **2007**, *128*, 190–195.

[2] a) T. Taguchi, G. Tomizawa, A. Kawara, M. Nakajima, Y. Kobayashi, *J. Fluorine Chem.* **1988**, *40*, 171–182; b) M. van der Puy, U. S. 6111139, **2000**; c) H. K. Nair, D. Nalewajek, A. Poss (Honeywell International), U. S. 6673976, **2004**; d) T. Komata, M. Fujiwara, S. Akiba, K. Hosoi, S. Narizuka (Central glass), PCT Int. Appl. 2006046417, **2006**; e) M. Fujiwara, S. Narizuka (Central glass), Jpn. Kokai Tokkyo Koho 2006083066, **2006**; f) T. Komata, K. Hosoi, S. Akiba (Central glass), PCT Int. Appl. 2007037119, **2007**; g) T. Komata, K. Hosoi, S. Akiba (Central glass), PCT Int. Appl. 2007052492, **2007**; h) T. Komata, S. Akiba, K. Hosoi, K. Ogura, *J. Fluorine Chem.* **2008**, *129*, 35–39.

[3] a) I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology*, Wiley, New York, **2009**; b) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, **2006**, pp. 10–22.

[4] a) G. Sini, A. Tessier, J. Pytkowicz, T. Brigaud, *Chem. Eur. J.* **2008**, *14*, 3363–3370; b) M. Shimizu, T. Fujimoto, X.-Y. Liu, H. Minezaki, T. Hata, T. Hiyama, *Tetrahedron* **2003**, *59*, 9811–9823; c) T. Yamazaki, T. Kitazume in *Enantiocontrolled Synthesis of Fluoro-Organic Compounds: Stereochemical Challenges and Biomedicinal Targets* (Ed.: V. A. Soloshonok), John Wiley & Sons, New York, **1999**, pp. 575–600; d) T. Yamazaki, M. Ando, T. Kitazume, T. Kubota, M. Omura, *Org. Lett.* **1999**, *1*, 905–908.

[5] a) S. Tajammal, A. E. Tipping, *J. Fluorine Chem.* **1990**, *47*, 45–57; b) T. Yamazaki, K. Mizutani, T. Kitazume, *J. Org. Chem.* **1995**, *60*, 6046–6056; c) A. R. Katritzky, M. Qi, A. P. Wells, *J. Fluorine Chem.* **1996**, *80*, 145–147; d) F.-L. Qing, W.-Z. Gao, J.-W. Ying, *J. Org. Chem.* **2000**, *65*, 2003–2006; e) A. K. Brisdon, I. R. Crossley, *Chem. Commun.* **2002**, 2420–2421; f) M. Shimizu, M. Higashi, Y. Takeda, G.-F. Jiang, M. Murai, T. Hiyama, *Synlett* **2007**, 1163–1165.

[6] Since 2 equiv. of a base is required for the formation of **4e** on the basis of the reaction mechanism shown in Scheme 1, 60% is the theoretical yield.

[7] Each point was obtained by performing the experiments 2–3 times. MeLi was titrated by a literature method. See: B. H Lipshutz in *Organometallics in Synthesis A Manual* (Ed.: M. Schlosser), John Wiley & Sons, New York, **1994**, ch. 4, pp. 283–382.

[8] Judging from Table 1, because LDA behaved basically in a similar manner to MeLi at least in THF and spontaneous reaction

was readily expected by mixing MeLi and PhCHO, we selected the former base here.

[9] Computation was carried out by Gaussian 03W using the B3LYP/6-311++G** level of theory and the solvent effect (SCIPCM) was estimated by single-point calculation. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision B.03, Gaussian, Inc., Wallingford, CT, **2004**.

[10] This is the species actually obtained by DFT optimization.

[11] Clear pictures of their structures have not been obtained yet.

[12] As a representative example of hydride migration in FBW rearrangement systems, see: T. Okuyama, S. Imamura, Y. Ishida, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 543–548. Very limited numbers of substrates with a CF_3 group were reported in related systems and no migration from $CF_3CR=C(Br)Li$ was observed; a) J.-M. Zhang, X.-M. Zhao, L. Lu, *Tetrahedron Lett.* **2007**, *48*, 1911–1913 (R = CH_2OTBS); b) H. Uno, N. Nibu, N. Misobe, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1365–1375 (R = Ph). For the similar species with zinc instead of Li, see, S. W. Hansen, T. D. Spawn, D. J. Burton, *J. Fluorine Chem.* **1987**, *35*, 415–420.

[13] a) W. A. Chalifoux, R. R. Tykwinski, *Chem. Rec.* **2006**, *6*, 169–182; b) R. Knorr, *Chem. Rev.* **2004**, *104*, 3795–3849.

[14] One of the referees pointed out the possible equilibration between Int-**1** and Int-**2** in the presence of (*E*)-**1**, whereas our experiment proved that this was not the case: To a solution of (*E*)-**1** was added MeLi (1.2 equiv.) at –80 °C and after 0.5 h, another 0.8 equiv. of MeLi was added. When 2 equiv. of MeLi was added all at once, **(*E*)-2e** was afforded in excellent selectivity by the addition of PhCHO (see Entry 15 in Table 1and Figure 1), whereas what was actually obtained was **4e** only in 68% yield.

[15] $H_2C=C$ was reported to rearrange into acetylene within a period of picoseconds. G. A. Petersson, T. G. Tensfeldt, J. A. Montgomery Jr, *J. Am. Chem. Soc.* **1992**, *114*, 6133–6138.

[16] T. Komata, M. Fujiwara, S. Akiba, K. Hosoi, S. Narizuka, WO **2006**/046417 A1.

[17] 1,2-Addition of amines to 3,3,3-trifluoropropyne was also reported. N. P. Stepanova, V. B. Lebedev, N. A. Orlova, E. S. Turbanova, A. A. Petrov, *Russ. J. Org. Chem.* **1988**, *24*, 692–699.

[18] The original procedure, mixing 4 equiv. of piperidine with (*E*)-**1** at 0 °C for 3 h, allowed the isolation of (*E*)-**6a** in 73% yield.

[19] a) S. J. Cristol, A. Begoon, W. P. Norris, P. S. Ramey, *J. Am. Chem. Soc.* **1954**, *76*, 4558–4561; b) O. M. Behr, G. Eglinton, I. A. Lardy, R. A. Raphael, *J. Chem. Soc.* **1964**, 1151–1154; c) S. Miyano, Y. Izumi, K. Fujii, Y. Ohno, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1197–1202.

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