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Synthetic utility of 2,3,3,3-tetrafluoroprop-1-ene (HFO-1234yf)

Yuya Hiraoka [a], Tomoko Kawasaki-Takasuka [a], Yoshitomi Morizawa [b], Takashi Yamazaki [a,*]

[a] Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei 184-8588, Japan
[b] Asahi Glass Co. Ltd., Research Center, Kanagawa Ku, Yokohama 221-8755, Japan

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ABSTRACT

2,3,3,3-Tetrafluoroprop-1-ene, known as the environmentally benign fluorinated olefin recently employed for the car air-conditioning system, was proved to follow the addition–elimination sequence at its C^2 position by the reaction of a variety of alkoxides, forming CF_3-containing vinyl ethers in excellent yields.

1. Introduction

2,3,3,3-Tetrafluoroprop-1-ene **1a** (HFO-1234yf) has recently been drawing significant attention as the potent fluorinated refrigerant with the global warming potential of only 4, no ozone depleting potential, and a very short atmospheric lifetime of ca. 11 days [1]. Moreover, its similar thermophysical performance to widely used HFC-124a at present [2] allowed to launch its installation to air-conditioning systems for vehicles on markets and thus, their production in an industrial scale should open a readily available route of this interesting partially fluorinated alkene **1a** whose previous synthetic application was limited mainly to preparation of polymer materials [3]. Then, we have started our research for clarification of its reactivity from the synthetic point of view, and found out that **1a** smoothly reacted with alkoxides by the well-known addition–elimination sequence which was reported in detail in this article.

2. Results and discussion

Before starting our synthetic study, computation was performed for the representative seven compounds **1a–g** for comparison of the basic information on frontier orbital energy levels and natural charges by using the Gaussian 09W software [4] using the B3LYP/6-311 + + G** level of theory. As described in Table 1, introduction of fluorine atoms to the propene framework was found to give a significant impact. For example, trifluorination at C^3 like the case of **1a–e** allowed to significantly decrease the frontier orbital energy levels from the ones of the prototypical counterpart **1g**, which should endow clear activation of these molecules toward a variety of nucleophiles. Moreover, the vinylic fluorine atom affected the electronic circumstance around the carbon–carbon double bond on the basis of the so-called p–π repulsive interaction [5], rendering the carbon C^2 possessing this unique atom electropositive (**1a** and **f**). The same trend albeit weakly was noticed for the compound **1e** with a methoxy group at the C^2 position, while bromine in the same halogen family did not indicate such a special feature at all (see, **1c**). Combination of these two characteristic information led us to strong anticipation that anionic species would preferentially react with **1a** at the C^2 site in spite of the already reported S_N2' type reactions of appropriate nucleophiles to **1b–d** [6,7].

First of all, we have searched adequate types of nucleophiles using such representative reagents as benzyl alcohol, benzylamine, thiophenol, diethyl malonate, and phenol (Entries 1–5 in Table 2). Thus, a solution containing Nu^- species generated by simple mixing of nucleophiles (NuH) and bases (1.1 equiv to NuH) in a solvent indicated was transferred to a pressure tight reactor where 1.2 equiv of **1a** was introduced. After 0.5 h reaction at room temperature, it was found out that benzyl alcohol was the only one

* Corresponding author. Tel.: +81 42 388 7038; fax: +81 42 388 7038.
E-mail address: tyamazak@cc.tuat.ac.jp (T. Yamazaki).

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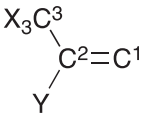
Table 1
Representative physical properties of prop-1-enes[a].

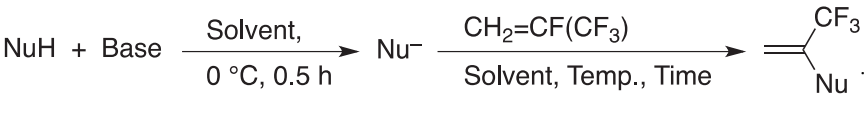


1a X=Y=F
1b X=F, Y=H
1c X=F, Y=Br
1d X=F, Y=Me_2PhSi
1e X=F Y=OMe
1f X=H Y=F
1g X=Y=H

		Energy level (eV)		Natural charge		
X	Y	HOMO	LUMO	C^1	C^2	C^3
F	F (**1a**)	−8.524	−1.324	−0.408	0.318	1.017
F	H (**1b**)	−8.661	−1.302	−0.306	−0.287	1.041
F	Br (**1c**)	−7.908	−1.613	−0.334	−0.210	1.038
F	Me_2PhSi (**1d**)	−7.266	−1.211	−0.285	−0.535	1.054
F	MeO (**1e**)	−7.333	−0.616	−0.473	0.240	1.043
H	F (**1f**)	−7.218	−0.269	−0.480	0.423	−0.639
H	H (**1g**)	−7.154	−0.128	−0.391	−0.167	−0.610

[a] Computation was carried out by the Gaussian 09W (rev. D.01) software with the B3LYP/6-311++G** level of theory. Natural charge was obtained by the NBO analysis.

Table 2
Investigation of reaction conditions.



2

Entry	NuH	(Equiv)[a]	Base	(Equiv)[a]	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	$PhCH_2OH$	(0.83)	NaH	(0.92)	THF	rt	0.5	6
2	$PhCH_2NH_2$	(0.83)	*n*-BuLi	(0.92)	THF	rt	0.5	–[c]
3	PhSH	(0.83)	NaH	(0.92)	THF	rt	0.5	–[c]
4	$CH_2(CO_2Et)_2$	(0.83)	NaH	(0.92)	THF	rt	0.5	–[c]
5	PhOH	(0.83)	NaH	(0.92)	THF	rt	0.5	–[c]
6	$PhCH_2OH$	(0.83)	NaH	(0.92)	THF	rt	3	[6]
7	$PhCH_2OH$	(0.83)	NaH	(0.92)	THF	60	2	52
8	$PhCH_2OH$	(0.83)	NaH	(0.92)	DMF	rt	2	56
9	$PhCH_2OH$	(0.83)	NaH	(0.92)	DMF	rt	Overnight	62
10	$PhCH_2OH$	(0.83)	NaH	(0.92)	DMF	60	2	59
11	$PhCH_2OH$	(0.83)	NaH	(0.92)	DMF	100	2	60
12	$PhCH_2OH$	(0.83)	NaH	(0.92)	DMSO	60	2	60
13	$PhCH_2OH$	(1.5)	NaH	(1.65)	DMF	rt	2	85
14	$PhCH_2OH$	(2)	NaH	(2.2)	DMF	rt	2	[99]
15	$PhCH_2OH$	(3)	NaH	(3.3)	DMF	rt	2	98

[a] Based on the amount of **1a** (1.0 equiv). Yields were calculated on the basis of NuH (Entries 1–12) and **1a** (Entries 13–15).
[b] Yields were determined by ^{19}F NMR using $PhCF_3$ as an internal standard, and in the brackets were shown the isolated yields. Yields were calculated on the base of the amount of NuH (Entries 1–12) or **1a** (Entries 13–15).
[c] No reaction was observed.

example which actually experienced the addition–elimination type substitution at the C^2 site of 2,3,3,3-tetrafluoroprop-1-ene **1a** in spite of a rather low yield. MeMgBr and *n*-BuLi were employed as a base instead of NaH in Entry 1, but the resultant metal alkoxides did not work properly (not shown in the Table). Although extension of the reaction period did not give any fruitful result (Entries 6 vs 1), increase of the temperature to 60 °C affected the reaction significantly to produce the desired product **2a** in 52% yield (Entry 7).

The same process under various conditions (solvents, temperature, and time)clarified that irrespective of temperature and time, constant formation of approximately 60% yield of **2a** was observed by employment of either DMF or DMSO as a solvent (Entries 8–12). For obtaining better results, quantity of a nucleophile was increased from 0.83 equiv to 3 equiv (Entries 8 and 13–15), and eventually, the condition shown in Entry 14 was proved to be the best among tested, realizing almost quantitative construction of the desired addition–elimination product **2a**.

Successful determination of the reaction conditions as above allowed us to employ a variety of alcohols for clarification of scope and limitation of the present process whose results were collected in Table 3. Like the case of benzyl alcohol, 1- and 2-phenylethanols, and 3-phenylprop-2-en-1-ol (cinnamyl alcohol) behaved in a similar manner to furnish the corresponding products in more than 80% yields in every instance. Interesting to note is the case of Entry 4 whose product **2d** with the allyl vinyl ether structure applicable for Claisen rearrangement was successfully isolated because of occurrence of this addition–elimination process only at room