11.5, 9.8 Hz, 1H), 5.82 (m, 1H), 5.58 (d, J=16.5 Hz, 1H), 5.46 (d, J=11.5 Hz, 1H), 5.00 (d, J=16.0 Hz, 1H), 4.95 (d, J=9.6 Hz, 1H), 3.71 (s, 3H), 3.17 (d, J=10.0 Hz, 2H). **6b**: IR (neat, cm^{-1}) 3050, 3020, 2950, 1700, 1620, 1430, 1280, 1230, 1190, 1080, 965, 745; ^1H NMR (200 MHz) δ 7.50-7.42 (m, 3H), 7.37-7.11 (m, 8H), 7.07 (d, J=11.1 Hz, 1H), 6.88 (d, J=15.4 Hz, 1H), 6.45 (d, J=15.8 Hz, 1H), 6.14 (dt, J=15.8, 5.9 Hz, 1H), 3.77 (s, 3H), 3.42 (d, J=5.9 Hz, 2H). **6c**: IR (neat, cm^{-1}) 2995, 1693, 1602, 1420, 1240, 1185, 1065, 745; ^1H NMR (200 MHz) δ 7.93 (s, 1H), 7.35-7.20 (m, 10H), 3.95 (s, 2H), 3.74 (s, 3H). **6d**: IR (neat, cm^{-1}) 2900, 1700, 1245; ^1H NMR (200 MHz) δ 7.16 (d, J=11.4 Hz, 1H), 6.66 (ddd, J=16.8, 11.4, 10.0 Hz, 1H), 5.56 (dd, J=16.8, 1.2 Hz, 1H), 5.45 (dd, J=10.0, 1.2 Hz, 1H), 3.76 (s, 3H), 2.41 (t, J=7.3 Hz, 2H), 1.26 (s, 14H), 0.88 (t, J=6.2 Hz, 3H). **6e**: IR (neat, cm^{-1}) 3280, 2940, 2850, 1700, 1635, 1430; ^1H NMR (200 MHz) δ 7.17 (d, J=11.5 Hz, 1H), 6.65 (ddd, J=16.6, 11.4, 10.0 Hz, 1H), 5.58 (dd, J=16.6, 1.5 Hz, 1H), 5.45 (dd, J=10.2, 1.5 Hz, 1H), 3.73 (s, 3H), 2.40 (t, J=7.2 Hz, 2H), 2.23 (m, 2H), 1.93 (t, J=2.5 Hz, 1H), 1.90-1.35 (m, 4H). **6f**: IR (neat, cm^{-1}) 2890, 1680, 1240, 720; ^1H NMR (200 MHz) δ 7.19 (d, J=11.4 Hz, 1H), 6.65 (ddd, J=16.7, 11.4, 10.0 Hz, 1H), 5.81 (ddt, J=17.0, 10.2, 6.8 Hz, 1H), 5.58 (d, J=16.6 Hz, 1H), 5.46 (d, J=10.2 Hz, 1H), 5.02 (dt, J=17.1, 1.5 Hz, 1H), 4.96 (dt, J=9.1, 1.5 Hz, 1H), 3.77 (s, 3H), 2.52 (t, J=7.5 Hz, 2H), 2.18 (q, J=6.8 Hz, 2H).

The Nucleophilic Reaction of β,β-Difluoro-α-phenylvinyl Sulfide with Heteroatom (O, N, S) Nucleophiles

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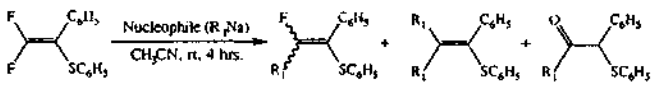
Fluoroolefins substituted by two fluorines at terminal olefinic carbon have a unique reactivity toward nucleophiles and thus can be used as a useful synthetic block for further synthesis of fluorinated or nonfluorinated compounds.[1] Although considerable efforts have included investigation of nucleophilic reaction of *gem*-difluoroolefins for last two decades, most of these reactions are related to stereochemistry of addition-elimination products,[2] proton exchange reactions of resultant carbanion in alcoholic media,[3] and study on ease of β-defluorination of resultant carbanion.[4] However, a study on the doubly nucleophilic substitution reaction of *gem*-difluoroolefins with more than two equivalents of heteroatom nucleophiles has not been reported. Only one example has been reported on the reaction of symmetrical *gem*-dichlorinated and *gem*-difluorinated ketene dithioacetals with only a bidentate sulfur nucleophile in recent years.[5] Of particular interests in connection with a study on the doubly nucleophilic substitution reaction of *gem*-difluoroolefins is β,β-difluoro-α-phenylvinyl sulfide **1**, because this sulfide **1** is a novel compound and thus reactivity of **1** toward ionic species has not been studied yet. Recently, we found that β,β-difluoro-α-phenylvinyl sulfide **1** can be easily prepared from the reaction of 2,2,2-trifluoro-1,1-bis(phenylthio)ethylbenzene with a mixture of 2 equiv. $TiCl_4$ and 4 equiv. $LiAlH_4$.[6] In this communication, we wish to describe about reactions of **1** with various types of heteroatom (N, O, S) nucleophiles.

Treatment of **1** with 1 equiv. of oxygen nucleophiles, such as alkoxides or phenoxides, in acetonitrile at room temperature for 4 hours resulted in the formation of only monosubstituted vinyl sulfides **2** *via* addition-elimination reaction in good yields. The use of sulfur nucleophile in this reaction caused to formation of disubstituted vinyl sulfide **3**, even though minor product, as well as formation of **2** along with recovery of 5% starting material **1**. The formation of **3** indicates that sulfur substituted vinyl sulfide **2g** is more reactive than oxygen substituted vinyl sulfides **2a-f** for the further reaction with nucleophile. When **1** was reacted with 2 equiv. of nucleophile under the same reaction condition, unexpected results were obtained. Therefore, the reaction of **1** with 2 equiv. of unbranched alkoxides, such as methoxide or ethoxide, afforded a mixture **2a** and **2b** and α-phenylthio substituted esters **4a** and **4b**. Complete conversion of **2a** and **2b**[7] to **4a** and **4b**[8] was achieved by the use of large excess (4 equiv.) of nucleophile. In contrast, the similar reactions of **1** with 2 equiv. of branched alkoxides, such as *i*-propoxide or *t*-butoxide, under the same reaction condition did not provide esters **4c** and **4d**, but only **2c** and **2d** were obtained in 81% and 78% isolated yields, respectively. Progress did not occur even if 4 equiv. of nucleophile was used in this reaction. However, **1** was reacted with more than 2 equiv. of nucleophiles, such as 2,2,2-trifluoroethoxide, phenoxide, or thioethoxide, to yield only disubstituted vinyl sulfides **3e**, **3f**, and **3g** in good yields. The formation of **4** was not detected in these reactions. This result is probably due to the blocking effect of 2,2,2-trifluoromethyl or phenyl group of **2** against dealkylation reaction by nucleophiles as well as activating effect of 2,2,2-trifluoromethoxy and phenoxy group on vinyl carbon atom. The reactions of **1** with several types of nucleophiles are summarized in Table 1.

From these results, it is recognized that structure of monosubstituents (R_1) of **2** affects the further reaction with another equiv. of nucleophile. The formation of **4a** and **4b** can be rationalized by the reaction of ketene(I) which might be generated *via* dealkylation of alkoxy group of **2**, followed by dehalogenation, with nucleophile. Although the isolation of ketene(I) was failed because of high reactivity of ketene in this reaction system, the corresponding alkyl ethers which are formed *via* the dealkylation reaction of **2** with alkoxides were isolated in excellent yields and then identified by ^1H NMR and mass spectroscopy. Therefore, it seems likely that dealkylation of alkoxy group of **2** is most important step to approach the products **4**. No formation of **4c** and **4d** provides a good evidence to support this speculation because *i*-propyl and *t*-butyl group are too bulky to undergo the dealkylation of alkoxy group of **2**. After products **2b** and **2c** were isolated,

Table 1. The Reactions of β,β-Difluoro-α-phenylvinyl Sulfide **1** with Heteroatom Nucleophiles

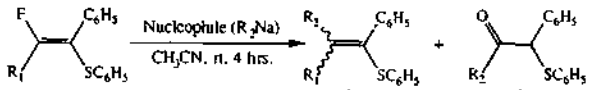


1 **2** **3** **4**

Nucleophile (R_1)	Equiv. of Nucleophile	Products (%)[a] 2[b]	3	4
CH_3O	1	**2a** (84)	**3a** (−)	**4a** (−)
CH_3O	2	**2a** (40)	**3a** (−)	**4a** (43)
CH_3O	4	**2a** (−)	**3a** (−)	**4a** (84)
CH_3CH_2O	1	**2b** (87)	**3b** (−)	**4b** (−)
CH_3CH_2O	2	**2b** (45)	**3b** (−)	**4b** (43)
CH_3CH_2O	4	**2b** (−)	**3b** (−)	**4b** (88)
$(CH_3)_2CHO$	1	**2c** (83)	**3c** (−)	**4c** (−)
$(CH_3)_2CHO$	2	**2c** (81)	**3c** (−)	**4c** (−)
$(CH_3)_2CHO$	4	**2c** (83)	**3c** (−)	**4c** (−)
$(CH_3)_3CO$	1	**2d** (76)	**3d** (−)	**4d** (−)
$(CH_3)_3CO$	2	**2d** (78)	**3d** (−)	**4d** (−)
$(CH_3)_3CO$	4	**2d** (80)	**3d** (−)	**4d** (−)
CF_3CH_2O	1	**2e** (89)	**3e** (−)	**4e** (−)
CF_3CH_2O	2	**2e** (−)	**3e** (80)	**4e** (−)
CF_3CH_2O	4	**2e** (−)	**3e** (84)	**4e** (−)
C_6H_5O	1	**2f** (84)	**3f** (−)	**4f** (−)
C_6H_5O	2	**2f** (−)	**3f** (85)	**4f** (−)
C_6H_5O	4	**2f** (−)	**3f** (88)	**4f** (−)
C_2H_5S	1	**2g** (60)	**3g** (16)	**4g** (−)
C_2H_5S	2	**2g** (−)	**3g** (83)	**4g** (−)
C_2H_5S	4	**2g** (−)	**3g** (82)	**4g** (−)

[a]Isolated yield. [b]Products are (E) and (Z) isomeric mixtures.

Table 2. The Reaction of β-Fluorinated Vinyl Sulfides **2** with Ethoxide



2 **3** **4**

Reactants 2	Nuleophile (R_2)	Equiv. of Nucleophile	Conversion of 2 (%)	products (%)[a] 3	4
2b	C_2H_5O	1	54	**3b**(−)	**4b**(90)
2c	C_2H_5O	1	0[b]	—	—
2f	C_2H_5O	1	100	**3h**(96)[c]	**4b**(−)

[a]Isolated yield. [b]No reaction occured. [c]Product is (E) and (Z) isomeric mixture.

reactions of these products with 1 equiv. of ethoxides were carried out to confirm the reactivity of **2b** and **2c** toward ethoxide. The results are summarized in Table 2.

As shown in Table 2, the treatment of **2** with 1 equiv. of ethoxide provided the same results as those obtained from the reactions of **1** with 2 equiv. of alkoxides. For example, reaction of **2b** with 1 equiv. of ethoxide in acetonitrile at room temperature for 4 hours resulted in the formation of

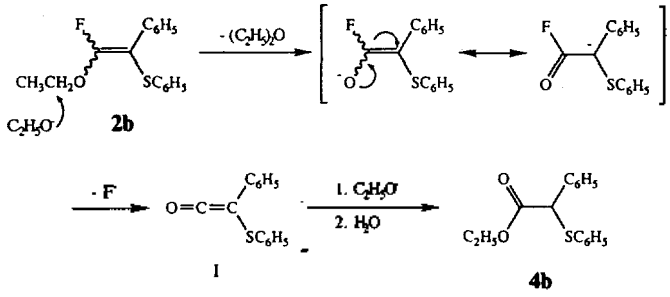
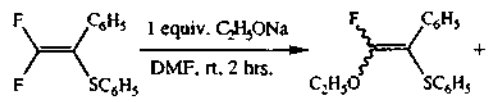


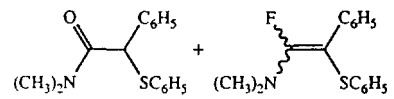
Figure 1. A Plausible Mechanism for the Formation of Product **4**.

product **4b** along with unreacted starting material **2b**. In contrast, reaction of **2c** with ethoxide did not occur at all and thus starting material **2c** was recovered. This result indicates that dealkylation of **2** with ethoxide is influenced by the structure of alkyl group of **2**. Therefore, a plausible mechanism for the formation of **4** can be postulated as shown in Figure 1.

An attempt to prepare the disubstituted vinyl sulfides **3a-d** was performed by the use of N,N-dimethylformamide (DMF) instead of acetonitrile as a solvent, since the enhancement of nucleophilicity of ethoxide in DMF may cause the further addition-elimination reaction of **2a-d** to give **3a-d**. When the reaction of **1** with 2 equiv. of ethoxide was carried out in DMF at room temperature for 2 hours, however, a mixture of **2b** and unexpected amide **5**[9] was obtained in 5% and 41% yield, respectively. No product **4b** was detected. The treatment of **1** with 1 equiv. of ethoxide under the same reaction condition afforded the products **2b** and **5** in better yields. The prolonged reaction time caused to make a better conversion of **2b** to **5**. No formation of dialkylamino substituted vinyl sulfide **6** excludes a possibility of existence of amide ion at the early stage of reaction because starting material **1** reacts easily with amide ion to give the product **6** which do not undergo dealkylation with anions. Therefore, it is speculated that product **2b** was formed from the reaction of **1** with ethoxide at the early stage of reaction and then product **5** was formed *via* a further reaction of **2b** with dimethylamino anion, which is generated from reaction of N,N-dimethylformamide with fluoride ion. A detailed study for the formation of **5** and synthetic utility of this reaction are now in progress.



1 **2b** (25%)



5 (73%) **6** (0%)

In a typical experiment for the formation of disubstituted vinyl sulfide **3e**, sodium hydride (2.1 mmol) and 2,2,2-trifluroethanol (2.1 mmol) in dry CH_3CN (10 m*l*) were stirred at room temperature for 1 hr. under nitrogen atmosphere.

β,β-Difluoro-α-phenylvinyl sulfide 1 (1.0 mmol) was added dropwise at room temperature and then stirred for further 4 hr. The reaction mixture was poured on water (10 ml) and extracted with ethyl acetate (10 ml×2). The ethyl acetate solution was dried and chromatographed on SiO_2 column. Elution with a mixture of hexane and ethyl acetate (20 : 1) provided **3e** in 80% yield. **3e** : colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.78-7.02 (m, 10H), 4.48 (q, J=7.3 Hz, 2H), 4.10 (q, J=7.3 Hz, 2H); MS, m/e (relative intensity) 408 (M^+, 54), 325 (48), 309 (100), 225 (10), 197 (32); IR (neat) 3050, 3000, 1630, 1450, 1290, 1170, 970, 770, 750, 700 cm^{-1}.

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7. Spectroscopic data of **2b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.75-7.10 (m, 10H), 4.25 (q, J=7.3 Hz, 2H), 1.35 (t, J=7.3 Hz, 3H); MS, m/e (relative intensity) 274 (M^+, 86), 245 (100), 217 (95), 197 (48), 121 (95), 77 (71); IR (neat) 3000, 1640, 1570, 1470, 1230, 1150, 760, 690 cm^{-1}.
8. Spectroscopic data of **4b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.50-7.15 (m, 10H), 4.90 (s, 1H), 4.10 (q, J=7.3 Hz, 2H), 1.15 (t, J=7.3 Hz, 3H); MS, m/e (relative intensity) 272 (M^+, 42), 199 (100), 135 (20), 109 (24), 91 (27), 77 (29); IR (neat) 3000, 1730, 1430, 1150, 760, 700 cm^{-1}.
9. Spectroscopic data of **5**: mp. 109-110 ℃ ; ^{1}H NMR ($CDCl_3$) δ 7.40-7.20 (m, 10H), 5.15 (s, 1H), 2.99 (s, 3H), 2.91 (s, 3H), MS, m/e (relative intensity) 271 (M^+, 15), 199 (100), 162 (8), 134 (34), 72 (17); IR (neat) 3000, 1640, 1400, 1130, 750, 710 cm^{-1}.

Diisopinocampheylchloroborane as a Highly Selective Reducing Agent for the Conversion of α,β-Unsaturated Aldehydes and Ketones to the Corresponding Allylic Alcohols

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Chiral diisopinocampheylchloroborane (^{d}Ipc$_2$BCl and ^{l}Ipc$_2$BCl)[1] has proven to be extremely efficient for the asymmetric reduction of a wide variety of ketones to obtain chiral alcohols in high ee.[2-6] Most organic functional groups, except for aldehydes, ketones[2-6] and epoxides,[7] are compatible with the reagent. Moreover, the ready availability of both the enantiomers, simple reaction conditions, easy work-up procedure, and completely recovery of the chiral auxiliary α-pinene[7] make this reagent especially attractive. The mechanism of the reduction is explained *via* a cyclic boatlike transition state.[4] This fascinating reagent attracted us to investigate its general reducing characteristics in greater detail. In the course of this investigation, we found that Ipc$_2$BCl readily reduces crotonaldehyde, an α,β-unsaturated aldehyde, to the corresponding allylic alcohol at 0° without any detectable 1,4-reduction product. Selective 1,2-reduction of α,β-unsaturated aldehydes and ketones with metal hydride reducing agents is often difficult to achieve in organic synthesis due to competing 1,2- *vs.* 1,4-attack by hydride.[8] Among the various reducing systems which have been devised for this purpose, diisobutylaluminum hydride (DIBAH),[9] lithium aluminum hydride (LAH),[10] 9-borabicyclo[3.3.1]nonane (9-BBN),[11] lithium *n*-butylborohydride,[12] and sodium borohydride in aqueous methanol containing rare earth chloride[13] are generally the most efficient and convenient.[14] However, these can by no means be adapted as a very general procedure.[11,13,15,16] Accordingly, it appeared desirable to generalize the reagent Ipc$_2$BCl as an ideal reducing agent for the selective reduction of α,β-unsaturated aldehydes and ketones to the corresponding allylic alcohols.

The reduction was carried out by the addition of 10% excess Ipc$_2$BCl in pentane to the aldehyde in pentane at 0° and to the ketone in pentane at room temperature.

Reduction of simple conjugated aldehydes, such as crotonaldehyde, 2-hexenal and cinnamaldehyde, afforded exclusively the corresponding allylic alcohols, resulting only from 1,2-reduction. Acyclic enones, such as 3-penten-2-one, benzalacetone and chalcone, were also selectively converted into the corresponding allylic alcohols in essentially quantitative yield at room temperature. Excess reagent (two equivalents) did not affect the selectivity, but accelerated the reduction rate. 2-cyclohexenone was converted to 2-cyclohexenol in quantitative yields. Even 2-cyclopentenone, known for its susceptibility to undergo conjugate reduction, was clearly converted to the desired 2-cyclopentenol in quantitative yield. Similarly, isophorone was readily reduced to 3,5,5-trimethyl-2-cyclohexen-1-ol.