determining step, and, therefore, the TS III mechanism is ruled out.

Korzhova *et al.* found no correlationship between the reactivities of amines and their basicities for the reaction of activated acetylenes with various aliphatic secondary amines.[6a] Instead, the steric factors of amines were found to determine the reactivity. Therefore, the steric hindrance has been suggested to be important in the present type of reactions. This is consistent with the preliminary results in this study, *i.e.* sterically less hindered bases such as NH_3, RNH_2 and HO^- attack only the carbonyl carbon of **1** while the secondary amines attack only the sterically less hindered acetylenic carbon of **1**. Generally, large steric effect has been observed when the degree of bond formation at the transition state has advanced significantly.[10] Thus, the reaction, in which steric hindrance plays an important role like the present system, would proceed without significant bond formation at the rate-determining step in order to avoid steric hindrance. This would explain the small β_{nuc} value obtained in this system. Therefore, it is proposed that the addition of secondary amines to **1** proceeds *via* a stepwise mechanism with a transition state similar to TS II. The absences of primary isotope effect and general acid/base catalysis are clearly consistent with this proposed mechanism.

Acknowledgement. The financial support by the Korea Science and Engineering Foundation and the Post Graduate Research Fellowship of Center for Molecular Structure-Reactivity, Inha Univ. (K. H. Kim) are gratefully acknowledged.

References

1. (a) W. E. Truce and L. M. Markley, *J. Org. Chem.*, **35**, 3275 (1970); (b) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).
2. V. A. Breus, S. A. Neklyudov, B. N. Solomonov, and A. I. Konovalove, *Zh. Org. Khim.*, **19**, 1613 (1983).
3. (a) B. Singaram, M. V. Rangaishenvi, H. C. Brown, C. T. Goralski, D. L. Hasha, *J. Org. Chem.*, **56**, 1543 (1991); (b) R. H. Mueller and M. E. Thompson, *Tetrahedron Lett.*, **21**, 1093 (1980).
4. B. Singaram, C. T. Goralski, and G. B. Fisher, *J. Org. Chem.*, **56**, 5691 (1991).
5. (a) J. A. Marshall and D. A. Flynn, *J. Org. Chem.*, **44**, 1391 (1979); (b) P. A. Wender and M. A. Eissenstat, *J. Am. Chem. Soc.*, **100**, 292 (1978).
6. (a) N. V. Korzhove, V. S. Pisareva, S. P. Korshunov, and L. L. Kucherenko, *Zh. Org. Khim.*, **10**, 2542 (1972); (b) N. V. Korzhova, V. S. Pisareva, and S. P. Korshunov, *Zh. Org. Khim.*, **11**, 1030 (1975).
7. B. Giese and R. Huisgen, *Tetrahedron Lett.*, **20**, 1889 (1967).
8. (a) E. Buncel, I. H. Um, and S. Hoz, *J. Am. Chem. Soc.*, **111**, 971 (1989); (b) N. B. Chapman and J. Shorter Eds., *Advances in Linear Free Energy Relationships*, Plenum, London, 1972; (c) C. F. Bernasconi Ed., *Techniques of Organic Chemistry*, Vol. 6, 4th ed., Wiley, New York, 1986.
9. E. Buncel, S. S. Shaik, I. H. Um, and S. Wolfe, *J. Am. Chem. Soc.*, **110**, 1275 (1988).
10. A. F. Popov, I. F. Perepichka, and L. I. Kostenko, *J. Chem. Soc., Perkin Trans. 2*, 395 (1989).
11. F. M. Menger and J. H. Smith, *J. Am. Chem. Soc.*, **94**, 3824 (1972).
12. P. Sykes Ed., *A Guidebook to Mechanism in Organic Chemistry*, 6th ed., John Wiley & Sons, Inc., New York, 1986.
13. W. P. Jencks and F. Regenstein in *Handbook of Biochemistry. Selected data for Molecular Biology*, H. A. Sober ed., The Chemical Rubber Co., OH, 1968.

A Novel Procedure for the Synthesis of α,β-Disubstituted β-Fluorovinyl and β-Trifluoromethylvinyl Sulfides[1]

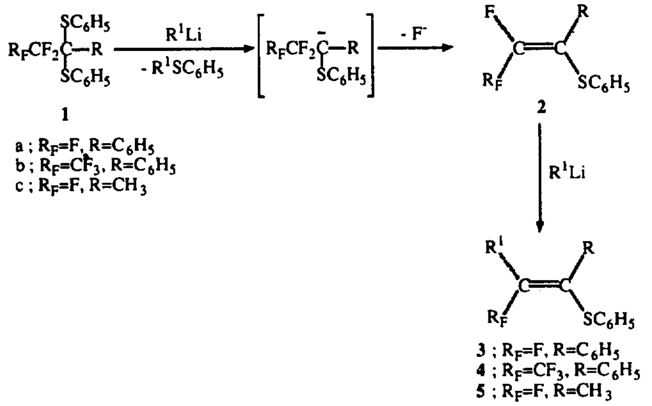
In Howa Jeong*, Yong Ki Min†, Young Sup Kim†, Kwang Yun Cho†, and Keun Jae Kim‡

Department of Chemistry, Yonsei University, Kangwondo 222-701
†Korea Research Institute of Chemical Technology, Taejon 305-606
‡Department of Chemistry, Hannam University, Taejon 300-791

Received November 6, 1992

Recently, considerable effort has been paid to the development of fluorine-containing synthetic building blocks[2,3] because of their potential to give new synthetic routes to a variety of fluoroorganic compounds, some of which exhibit unique biololgical properties in the areas of agrochemicals and pharmaceuticals.[4,5] Of particular interests in this conjunction are fluorinated vinyl sulfides which are possible synthons of vinyl fluorides and α-fluorinated ketones.[6,7] Although the synthesis and transformations of nonfluorinated vinyl sulfides have been well established,[8] there are only limited reports on the synthesis of fluorinated vinyl sulfides and most of these methods[9-11] refer to the synthesis of vinyl sulfides which do not contain an alkyl or aryl substituent at olefin carbon atoms. On the other hand, a couple of examples[12,13] has been reported on the preparation of alkyl or aryl substituted vinyl sulfides, but these methods lack generality or efficiency.

As part of our continuing studies on the chemistry and utilities of perfluoroalkylated dithioketals **1**,[14,15] we have found that **1a** and **1b** were smoothly reacted with organolithium compounds, such as alkyllithium, phenyllithium, vinyllithium and lithium alkyl or aryl acetylide, to afford α,β-disubstituted β-fluorovinyl and β-trifluoromethylvinyl sulfides **3** and **4**, but reaction of **1c** with *n*-BuLi at -78℃ resulted in the formation of β,β-difluorovinyl sulfide **2**. From the isolation of alkyl, aryl, vinyl, and acetyl phenyl sulfides in quantitative yield, reaction pathway seems likely that the initial reactions of **1** with organolithium compounds *via* attack of sulfur atom by nucleophiles provide carbanion bearing perfluoroalkyl group, which quickly undergo β-defluorination[9] to give β,β-perfluorinated vinyl sulfides **2**. The intermediate **2** is so reactive that they quickly undergo addition-elimination reaction[16] with organolithium compounds presented in solution as soon as they were formed. In this communication, we wish to describe a general prepararion of β-fluorovinyl and β-trifluoromethylvinyl sulfides **3**, **4**, and **5**.



Initially, we attempted to isolate β,β-difluorovinyl and β-fluoro-β-trifluoromethylvinyl sulfides **2a** and **2b** from the reactions of **1a** and **1b** with 1 eq. *n*-BuLi at −78℃, followed by slow warming to ambient temperature, because **2a** and **2b** can be widely utilized in addition-elimination reaction with various types of nucleophiles. However, (E) and (Z) isomeric mixtrues of **3d** and **4d** were obtained at the employed reaction condition and almost half of starting material was recovered in each case. Performance of these reactions at −78℃ for 1 hour, followed by quenching with ether solution saturated with HCl, also resulted in the formation of **3d** and **4d**. This result implies that compounds **2a** and **2b** are so reactive that they quickly undergo addition-elimination reaction with *n*-BuLi as soon as they were formed. Therefore, the use of 2 eq. *n*-BuLi in these reactions is necessary not only to complete the reaction, but also to provide **3d** and **4d** in high yields. Similarly, reactions of **1a** and **1b** with bulky alkyllithiums also provided the corresponding β-fluorovinyl sulfides **3e**, **3f**, and **4e** in moderate to high yields except for the reaction of **1b** with *t*-BuLi in which no reaction occurred. Reactions of **1a** and **1b** with vinyllithium, which is generated from the reaction of vinyltin and *n*-BuLi,[17] also afforded the corresponding (E) and (Z) isomeric mixture of vinyl sulfides **3h** and **4h** in moderate yields. When **1a** and **1b** were reacted with phenyllithium at −78℃, followed by slow warming to ambient temperature, corresponding (E) and (Z) isomeric mixture of vinyl sulfides **3g** and **4g** were obtained in excellent yields. Interestingly, product **3g** was further reacted with phenyllithium at room temperature to give triphenyl substituted vinyl sulfide **6**, which is very important framework in the synthesis of mammary tumor inhibitor,[18] in 72% yield. This further reaction opened a nice route to triphenyl substituted vinyl sulfide **6** directly from the reaction of **1a** with 3 eq. phenyllithium.

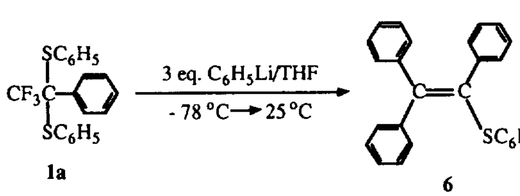
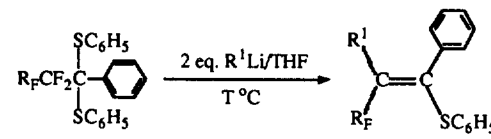


Table 1. Preparation of α-Phenyl β-Substituted β-Fluorovinyl and β-Trifluoromethylvinyl Sulfides **3** and **4**



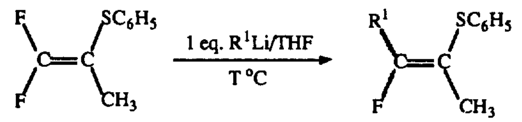
Product	R_F	R^1	T (℃)	Yield (%)[a,b,c]	Z/E[d]
3d	F	*n*-C_4H_9	−78→15	71	82/18
3e	F	*s*-C_4H_9	−78→15	89	58/42
3f	F	*t*-C_4H_9	−78→15	79	52/48
3g	F	C_6H_5	−78→15	94	79/21
3h	F	$H_2C=CH$	−78→15	51	80/20
3i	F	$C_6H_{13}C\equiv C$	0→15	93	86/14
3j	F	$C_6H_5C\equiv C$	0→15	96	80/20
4d	CF_3	n-C_4H_9	−78→15	80	87/13
4e	CF_3	s-C_4H_9	−78→15	62	82/18
4f	CF_3	t-C_4H_9	−78→15	NR[e]	−
4g	CF_3	C_6H_5	−78→15	87	83/17
4h	CF_3	$H_2C=CH$	−78→15	48	85/15
4i	CF_3	$C_6H_{13}C\equiv C$	0→15	89	90/10
4j	CF_3	$C_6H_5C\equiv C$	0→15	92	90/10

[a] Isolated yield. [b] All products are (E) and (Z) isomeric mixtures. [c] All products were isolated by column chromatography or MPLC. [d] Ratio was determined by ¹H-NMR and ¹⁹F-NMR spectrum. [e] No reaction.

Since the reaction of **1a** and **1b** with lithium alkyl or aryl acetylide is much more sluggish than that with other lithium compounds, the higher reaction temperature is required. Therefore, treatment of **1a** and **1b** with lithium hexyl and phenyl acetylide at 0℃, followed by warming to ambient temperature, gave the corresponding (E) and (Z) isomeric mixture of vinyl sulfides **3i**, **3j**, **4i**, and **4j** in excellent yields. This reaction provides very nice method for the preparation of fluorinated and trifluoromethylated enynes which would be useful as building blocks to fluorinated multifunctional molecules.[19-21] All products are (E) and (Z) isomeric mixtures which can be observed by ^1H and ^{19}F-NMR. Assignment of isomers for products was based on chemical shifts for vinyl fluorine in ^{19}F-NMR and allylic protons in ^1H-NMR. Generally, vinyl fluorine of (E) isomer comes at a higher value of chemical shift than that of (Z) isomer.[10] Allylic protons which are arranged to the same side of phenylthio group (E-isomer) are more deshielded than those of Z-isomer.[13] The results of reactions of **1a** and **1b** with organolithium compounds were summarized in Table 1.

In contrast, reaction of **1c** with 1 eq. *n*-BuLi at −78℃ for 1 hour, followed by quenching with ether solution saturated with HCl, afforded β,β-difluorovinyl sulfide **2c** in 85% yield. This result indicates that α-methyl substituted β,β-difluorovinyl sulfide **2c** is not further reacted with *n*-BuLi at the employed reaction condition. Similar result has been reported in the previous literature,[10] in which α-pentyl-β,β-difluorovinyl sulfide was prepared from the reaction of α-trifluoromethylvinyl sulfide with *n*-BuLi at −70℃. Treatment

Table 2. Preparation of α-Methyl β-Substituted β-Fluorovinyl Sulfides **5**



2c **5**

Product	R^1	T (℃)	Yield (%)[a,b,c]	Z/E[d]
5d	n-C_4H_9	−78→15	83	60/40
5e	s-C_4H_9	−78→15	60	64/36
5f	t-C_4H_9	−78→15	NR[e]	−
5g	C_6H_5	−78→15	80	66/34
5h	$H_2C=CH$	−78→15	53	63/37
5i	$C_6H_{13}C\equiv C$	0→15	81	67/33
5j	$C_6H_5C\equiv C$	0→15	80	68/32

[a] Isolated yield. [b] All products are (E) and (Z) isomeric mixtures. [c] All products were isolated by column chromatography. [d] Ratio was determined by ^{1}H-NMR and ^{19}F-NMR spectrum. [e] No reaction.

of **2c** with alkyllithium, vinyllithium, phenyllithium, and lithium alkyl or aryl acetylide at −78℃, followed by slow warming to ambient temperature, resulted in the formation of corresponding vinyl sulfides **5** in moderate to high yields. However, reaction of **2c** with t-BuLi did not occur even at room temperature. The results of these reactions are summarized in Table 2. In particular, compound **2c** can be utilized in the addition-elimination reaction[16] with various types of nitrogen and oxygen nucleophiles which cna not be reacted with compound **1c**. Although reactions of **1c** with organolithium compounds except for lithium phenyl acetylide and t-BuLi provided the corresponding vinyl sulfides **5**, the use of intermediate **2** in these reactions resulted in the clean formation and easy isolation of **5**.

In a typical procedure, a 250 m*l* two-neck flask equipped with a septum, a magnetic stir bar and a nitrogen tee connected to a source of argon, was charged with 1,1-bis(phenylthio)-2,2,2-trifluoroethylbenzene (3.76 g, 10.0 mmol) and 50 m*l* dry THF. The reaction mixture was cooled to −78℃ by using dry-ice/isopropanol slush and phenyllitium (1.8 M solution, 11.2 m*l*, 20.2 mmol) was added dropwise at −78℃, followed by slow warming to ambient temperature. The reaction mixture was quenched with water (50 m*l*) and extracted with ether (50 m*l*×2). After the ether layer was dried with anhydrous $MgSO_4$, column chromatography (hexane) provided 2.87 g (94% yield) of 1,2-diphenyl-2-fluorovinyl phenyl sulfide **3g**: m.p. 53℃; ^{1}H-NMR ($CDCl_3$) δ 7.83-7.50 (m, 5H), 7.41-7.07 (m, 10H); ^{19}F-NMR (CCl_4, external standard CF_3COOH) δ −6.67 (s, 1F), −10.57 (s, 1F); IR (KBr) 3050 (w), 1616 (m, C=C), 1577 (m, aromatic C=C), 1473 (m, aromatic C=C), 1438 (m, aromatic C=C), 1215 (m, C-F), 1064 (m), 1022 (m), 929 (m), 736 (s, =C-H OOP), 690 (s, =C-H OOP) cm^{-1}; MS, m/e (relative intensity) 306 (M^+, 100), 196 (43), 185 (25), 121 (32).

Acknowledgement. The authors thank the Ministry of Science and Technology and the Maeji Academy Institute at the Yonsei University for financial support, and professor S. K. Choi (KAIST) for recording the ^{19}F-NMR spectra.

References

1. Presented in part at the 13th International Symposium on Fluorine Chemistry, Bochum, Germany, September 2-6, 1991; For abstract, *J. Fluorine Chem.*, **54**, 123 (1991).
2. B. Jiang and Y. Xu, *J. Org. Chem.*, **56**, 7336 (1991) and references cited therein.
3. F. Jin, B. Jiang, and Y. Xu, *Tetrahedron Lett.*, **33**, 1221 (1992).
4. R. Filler and Y. Kobayashi, *Biomedicinal Aspects of Fluorine Chemistry*, Kodansha Tokyo, 1982.
5. J. T. Welch, *Tetrahedron*, **43**, 3123 (1987).
6. J. Mann, *Chem. Soc. Rev.*, **13**, 381 (1987).
7. E. Block, "*Reactions in Organosulfur Compounds*", Academic, New York, 1976.
8. B. M. Trost and A. C. Lavoie, *J. Am. Chem. Soc.*, **105**, 5075 (1983).
9. T. Nakai, K. Tanaka, and N. Ishikawa, *Chem. Lett.*, 1263 (1976).
10. A. E. Feiring, *J. Org. Chem.*, **45**, 1962 (1980).
11. S. Piettre, Ch. De Cock, R. Merenyi, and H. G. Viehe, *Tetrahedron*, **43**, 4309 (1987).
12. T. Fuchigami, Y. Nakagawa, and T. Nonaka, *Tetrahedron Lett.*, **27**, 3869 (1986).
13. L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc. Perkin Trans. I*, 1691 (1990).
14. I. H. Jeong, Y. K. Min, Y. S. Kim, K. Y. Cho, and K. J. Kim, *Bull. Korean Chem. Soc.*, **12**, 355 (1991).
15. I. H. Jeong, *Bull. Korean Chem. Soc.*, **13**, 468 (1992).
16. R. Sauvetre and J. Normant, *Tetrahedron*, **31**, 897 (1975).
17. D. Seyferth and L. G. Vaugham, *J. Am. Chem. Soc.*, **86**, 883 (1964).
18. M. R. Schneider, *J. Med. Chem.*, **29**, 1494 (1986).
19. F. Camps, G. Fabrias, and A. Guerrero, *Tetrahedron*, **42**, 3623 (1986).
20. S. Eddarir, C. Francesch, H. Mestdagh, and C. Rolando, *Tetrahedron Lett.*, **31**, 4449 (1990).
21. Z. Y. Yang and D. J. Burton, *Tetrahedron Lett.*, **31**, 1369 (1990).

Separation of Fullerene with Poly-p-Phenylene

Sung Ho Kim*, Jong Shin Yoo†, Jee Hyun Hahn‡, and Il Cheol Jeon#

Department of Chemistry, Seonam University, Namwon 590-170

†*School of Public Health, Harvard University, Boston, MA 02115, USA*

‡*Lab. of Organic Chemistry, OCI Research Center, Inchon 403-020*

#*Department of Chemistry, Jeonbuk National University, Jeonju 560-756*

Received November 9, 1992

Because of its various chemical reactivity and applicability,

*To whom correspondence should be addressed.