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Efficient Synthesis of Novel α-Aryl(alkyl)-β, β-difluorovinyl and α-Aryl(alkyl)-β-fluoro-β-perfluoroalkylvinyl Sulfides

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Abstract : Reaction of 1, 1-bis(phenylthio)perfluoroalkyl aromatics or alkanes with a mixture of 2 equiv. of $TiCl_4$ and 4 equiv. of $LiAlH_4$ in THF at reflux temperature for 3 hours afforded α-aryl(alkyl)-β, β-difluorovinyl and α-aryl (alkyl)-β-fluoro-β-perfluoroalkylvinyl sulfides in good yields.

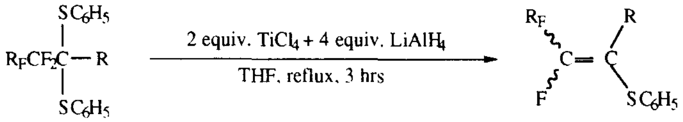
Olefins substituted by two fluorines or both fluorine and perfluoroalkyl group in a geminal manner at olefin carbon are very reactive toward nucleophiles and thus undergo nucleophilic vinylic substitution reaction via addition-elimination pathway.[1] Of particular interests in these olefins are α-aryl(alkyl)-β, β-difluorovinyl and α-aryl(alkyl)-β-fluoro-β-perfluoroalkylvinyl sulfides because these compounds are useful building block for the preparation of fluorinated and perfluoroalkylated olefins and α-fluorinated and α-perfluoroalkylated ketones which are important bioactive fluoroorganic compounds. Although several methods for the preparation of β, β-difluorovinyl sulfides have been documented,[2] most of these methods refer to the synthesis of β, β-difluorovinyl sulfides which contain a hydrogen,[2a, 2d] halogen,[2d] alkylthio[2b, 2e, 2f] or alkylseleno group[2d] at α-carbon atom. Only one example[2c] has been reported on the preparation of α-alkyl-β, β-difluorovinyl sulfides, but this method lacks generality. In this communication, we report a general and efficient method for the preparation of α-aryl(alkyl)-β, β-difluorovinyl and α-aryl(alkyl)-β-fluoro-β-perfluoroalkylvinyl sulfides.

Treatment of 1, 1-bis(phenylthio)-2, 2, 2-trifluoroethylbenzene (**1a**)[3] with a mixture of 2 equiv. of $TiCl_4$ and 4 equiv. of $LiAlH_4$ in THF at reflux temperature for 3 hours afforded only 2, 2-difluoro-1-phenylthiostyrene (**2a**) in 78% isolated yield. In this reaction, no reduced products was detected. Although reaction of **1a** with 20 equiv. of Raney Ni in acetone at reflux temperature for 2 hours also provided **2a**, yield is relatively low and reduced product, 1-phenylthio-2, 2, 2-trifluoroethylbenzene, was obtained in 10% isolated yield. Therefore, reactions of other perfluoroalkylated dithioketals with a mixture of $TiCl_4$ and $LiAlH_4$ were performed under the same condition and results are summarized in Table 1.

In a typical experiment, a mixture of titanium tetrachloride (5.0 mmol) and lithium aluminum hydride (10.0 mmol) in dry THF (50 ml) was stirred at room temperature for 1 hr. under nitrogen atmosphere and then heated to boiling. 1, 1-Bis(phenylthio)trifluoroethylbenzene (2.5 mmol) in THF (5 ml) was added under reflux and the reaction mixture was kept boiling for further 3 hrs. After cooling, the reaction mixture was poured on ice water, neutrized with conc. HCl and extracted with ether. The ether solution was dried and chromatographed on SiO_2 column. Elution with hexane provided 1-phenylthio-2, 2-difluorostyrene (**2a**) in 78% yield. **2a** : oil ; ^1H NMR ($CDCl_3$) δ 7.55-7.52 (m, 10H); ^{19}F NMR ($CDCl_3$) δ -75.57 (d, J =

12.5 Hz, 1F), -77.80 (d, J = 12.5 Hz, 1F); MS, m/e (relative intensity) 248 (M^+, 18), 121 (31), 109 (100), 77 (18); IR(neat) 3080, 1685, 1581, 1477, 1442, 1269, 1234, 760, 690 cm^{-1}.

Table 1. Preparation of Fluorinated Vinyl Sulfides **2**



1 **2**

Compound No.	R	R_F	**2**, Yield(%)[a]	Z/E[b]
1a	C_6H_5	F	78	-
1b	C_6H_5	CF_3	92	16/84
1c	C_6H_5	CF_3CF_2	87	36/64
1d	CH_3	F	78	-
1e	C_6H_{11}	F	90	-
1f	n-C_3H_7	F	77	-
1g	n-C_3H_7	CF_3	90	48/52
1g	n-C_3H_7	CF_3CF_2	86	34/66

[a] Isolated yields. [b] Z/E ratio was determined by ^{19}F NMR and ^1H NMR spectrum.

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REFERENCES

1. (a) Gimbert, Y.; Moradpour, A. *Tetrahedron Lett.* **1991**, *32*, 4897-4900. (b) Gimbert, Y. ; Moradpour, A.; Dive, G.; Dehareng, D.; Lahlil, K. *J. Org. Chem.* **1993**, *58*, 4685-4690.
2. (a) Nakai, T.; Shiraishi, S.; Ishikawa, N. *Tetrahedron Lett.* **1978**, 3101-3102. (b) Tanaka, K.; Nakai, T.; Ishikawa, N. *Chem. Lett.* **1979**, 175-178. (c) Feiring, A. E. *J. Org. Chem.* **1980**, *45*, 1962-1964. (d) Piettre, S.; De Cock, Ch.; Merenyi, R.; Viehe, H. G. *Tetrahedron* **1987**, *43*, 4309-4319. (e) Purrington, S. T.; Samaha, N. F. *J. Fluorine Chem.* **1989**, *43*, 229-234. (f) Muzard, M.; Portella, C. *J. Org. Chem.* **1993**, *58*, 29-31.
3. Jeong, I. H.; Min, Y. K.; Kim, Y. S.; Cho, K. Y.; Kim, K. J. *Bull. Korean Chem. Soc.* **1991**, *12*, 355-356.

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