

FLUORIDE ION PROMOTED AZOMETHINE YLID GENERATION FROM 1-METHYL-2-[METHYLTHIO(TRIMETHYLSILYLMETHYLIMINO)METHYLIMINO]-1,2-DIHYDROPYRIDINE, A SYNTHETIC EQUIVALENT OF AMINONITRILE YLID

Shinya Kohra*,^a and Yoshinori Tominaga^b

Faculty of Liberal Arts,^a Faculty of Pharmaceutical Sciences,^b Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan

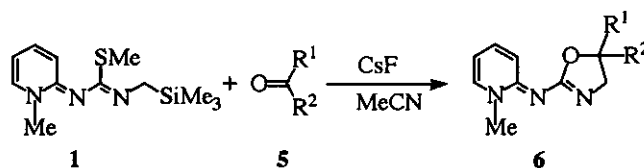
Abstract - 1-Methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine (1), prepared from 2-amino-1-methylpyridinium iodide in 3 steps, reacted with carbonyl compounds in the presence of cesium fluoride in acetonitrile to give 2-(1-methyl-1,2-dihydropyridylidene)aminooxazoline derivatives (6) via the 1,3-dipolar cycloaddition. This reaction was the first example of reaction of aminonitrile ylid with the C=O double bond.

1,3-Dipolar cycloaddition reaction is one of the most important and interesting reactions to construct five-membered ring heterocycles from a synthetic point of view.¹ Among these reactions, azomethine ylides are used for the preparation of *N*-containing five-membered heterocycles. The fluoride ion promoted desilylation of *N*-(silylmethyl)imines has been unique and valuable methodology to generate azomethine ylides.² We have reported that alkylideneazomethine ylides³ and iminoazomethine ylides⁴ can be generated by 1,3-elimination reactions of *N*-trimethylsilylmethyl-substituted ketene *N,S*-acetals and *N*-silylmethyl-substituted isothiouras promoted by fluoride ion and that [3+2] cycloadditions to a variety of dipolarophiles are achieved, giving *N*-containing 2-alkylidene- and 2-imino-heterocycles. In the extension of the studies on organosilicon compounds in

layer was washed with water (30 ml) and then brine (30 ml). After dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure. The crude product was chromatographed on an alumina (Merck, Aluminum oxide 90 active, basic) column using dichloromethane as an eluent to give 2-(1-methyl-1,2-dihydropyridylidene)amino-5-phenyloxazoline (6a) (0.180 g, 71 % yield).

This work demonstrates that 1-methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine (1), storable and easy to handle, can be viewed as a synthetic equivalent of aminonitrile ylid.

Table 1. Reaction of Organosilicon (1) and Carbonyl Compounds (5)^{a)}



Entry	5		Yield of 6 (%) ^{b)}	
	R ¹	R ²		
1	C ₆ H ₅	H	(5a)	71 (6a)
2	4-C ₆ H ₅ C ₆ H ₄	H	(5b)	73 (6b)
3	4-MeC ₆ H ₄	H	(5c)	71 (6c)
4	4-MeOC ₆ H ₄	H	(5d)	57 (6d)
5	4-ClC ₆ H ₄	H	(5e)	73 (6e)
6	2,6-Cl ₂ C ₆ H ₃	H	(5f)	77 (6f)
7	4-NCC ₆ H ₄	H	(5g)	52 (6g)
8	1-Naphthyl	H	(5h)	55 (6h)
9	2-Thienyl	H	(5i)	44 ^{c)} (6i)
10	3-Pyridyl	H	(5j)	43 (6j)
11	(E)-C ₆ H ₄ CH=CH	H	(5k)	38 ^{d)} (6k)
12	C ₆ H ₅	C ₆ H ₅ CO	(5l)	42 (6l)

a) All reactions were carried out using 1 (1.0 mmol) and 5 (1.0 mmol) in the presence of CsF (2.0 mmol) in MeCN (4 ml) at room temperature for 1 week, unless otherwise noted.

b) Yield after isolation by column chromatography

c) Cesium fluoride (4.0 mmol) was used.

d) Carbonyl compound (5) (2.0 mmol) was used.

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6. **1**: Yield 76 %; ir (neat) ν_{max} : 2950, 1640, 1600, 1550, 855 cm^{-1} ; $^1\text{H-nmr}$ (CDCl_3) δ : major isomer 0.04 (9H, s, SiMe_3), 2.34 (3H, s, SMe), 2.99 (2H, s, NCH_2Si), 3.48 (3H, s, NMe), 5.91 (1H, t, $J = 6.8$ Hz, 5-H on pyridine ring), 6.45 (1H, d, $J = 8.8$ Hz, 3-H on pyridine ring), 6.90-7.30 (2H, m, 4 and 6-H on pyridine ring); minor isomer 0.13 (9H, s, SiMe_3), 2.30 (3H, s, SMe), 3.15 (2H, s, NCH_2Si), 3.51 (3H, s, NMe), 5.91 (1H, t, $J = 6.8$ Hz, 5-H on pyridine ring), 6.45 (1H, d, $J = 8.8$ Hz, 3-H on pyridine ring), 6.90-7.30 (2H, m, 4 and 6-H on pyridine ring) (major : minor = ca. 1.6 : 1). *Anal.* Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_3\text{SSi}$: C, 53.88; H, 7.92; N, 15.71. Found; C, 53.90; H, 7.83; N, 15.69.
7. **6a**: Yield 71 %; mp 109-110 $^\circ\text{C}$ (*n*-hexane-ethyl acetate); ir (neat) ν_{max} : 3075, 2905, 2855, 1635, 1595, 1545, 1505, 1385, 1015 cm^{-1} ; $^1\text{H-nmr}$ (CDCl_3) δ : 3.70 (3H, s, NMe), 3.87 (1H, dd, $J = 13.0$ and 7.9 Hz, 4-H on oxazoline ring), 4.36 (1H, dd, $J = 13.0$ and 9.4 Hz, 4-H on oxazoline ring), 5.46 (1H, dd, $J = 9.4$ and 7.9 Hz, 5-H on oxazoline ring), 6.26 (1H, td, $J = 6.6$ and 1.3 Hz, 5'-H on pyridine ring), 7.12-7.47 (7H, m, 3'- and 4'-H on pyridine ring and phenyl-H), 8.19 (1H, dd, $J = 9.7$ and 1.3 Hz, 6'-H on pyridine ring). *Anal.* Calcd for $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$: C, 71.12; H, 5.97; N, 16.59. Found; C, 71.18; H, 6.03; N, 16.64.
Other **6** were fully characterized by $^1\text{H-nmr}$, ir, and HR-*ms* or elemental analysis.

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