

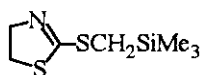
**PREPARATION OF NEW THIOCARBANION SPECIES BEARING
THIAZOLINYL AND BENZOTHAZOLYL GROUPS AND REACTIONS
WITH CARBONYL COMPOUNDS**

Shinya Kohra,^a Hiroshi Ueda,^b and Yoshinori Tominaga^{b*}

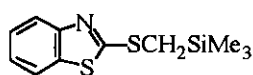
^aFaculty of Liberal Arts, ^bFaculty of Pharmaceutical Sciences, Nagasaki University,
1-14 Bunkyo-machi, Nagasaki 852, Japan

Abstract-----2-Trimethylsilylmethylthiothiazoline (1) reacted with aromatic aldehydes in the presence of cesium fluoride or tris(dimethylamino)sulfur(trimethylsilyl)difluoride (TASF) to give 2-heteroarylthioethanol (4) or thiiran (5) derivatives in good yields. The reactions of 2-trimethylsilylmethylthiobenzothiazole (2) with aromatic aldehydes are also discussed.

The α -thiocarbanions¹ are readily prepared by the fluoride ion-promoted desilylation of trimethylsilylmethyl sulfides under mild conditions and can be conveniently applied to obtain various 1,3-dipolar reagents such as thiocarbonyl ylides² and related chemical species.³ The active species generated by desilylation is very susceptible to the action of substituted groups, particularly the heterocyclic substituted group, on the sulfur atom, so that it may behave as a only thio-carbanion or have 1,3-dipolar character. 2-Trimethylsilylmethylthiothiazoline (1)^{4,5} was recently shown to react with hetero dipolarophiles to give thiiran derivatives through the formal 1,3-dipolar cycloaddition reaction.^{2d} 2-Trimethylsilylmethylthiopyridine reacted with carbonyl compounds to give 2-pyridylthioethanol derivatives in the presence of cesium fluoride in good yields.⁶



1



2

We reinvestigated the reactions of **1** with aldehydes using TASF instead of cesium fluoride as the fluoride ion source to obtain the corresponding 2-heteroarythioethanol compounds. We also examined the reactions of 2-trimethylsilylmethylthiobenzothiazole (**2**)⁷ with carbonyl compounds in the presence of cesium fluoride in acetonitrile. At the start of this study,⁸ the reactions of **1** and **2** with carbonyl compounds in the presence of fluoride ions were carefully studied. The reaction of **1** with 2.0 equivalents of aromatic aldehydes (**3**) in the presence of 1.2 equivalents of cesium fluoride in acetonitrile proceeded at room temperature for 45 h to yield the corresponding thiirans (**6a-e**).⁹ The results are listed in Table 1 (Entries 1-5). When compound (**1**) reacted with **3** using an equivalent amount of TASF in THF at room temperature for 3 h, the corresponding 2-thiazolinythioethanol derivatives (**4a-d**) were obtained in good yields as shown in Table 1 (Entries 6-10).

Table 1. Reactions of 1 and 2 with Aldehydes (3) Promoted by A Fluoride Ion

$$\text{1 or 2} + \text{RCHO} \xrightarrow{\text{F}^-} \begin{matrix} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{matrix} \text{CH}_2\text{CH}_2\text{R} + \text{R} \begin{matrix} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \end{matrix} + \text{R} \text{---} \text{C} = \text{C} \text{---}$$

3
4 or 5
6
7

Entry	Heterocycle	R (3)	Conditions ^a	Yield (%)	
				4 or 5	6 7
1	1	C ₆ H ₅ (3a)	A		40 (6a)
2	1	4-MeC ₆ H ₄ (3b)	A		21 (6b)
3	1	4-MeOC ₆ H ₄ (3c)	A		38 (6c)
4	1	4-C ₆ H ₅ C ₆ H ₄ (3d)	A		75 (6d)
5	1	1-naphthyl (3e)	A		59 (6e)
6	1	3a	B	90 ^b (4a)	
7	1	3b	B	100 ^b (4b)	
8	1	3c	B	81 ^b (4c)	
9	1	3d	B	80(4d)	
10	1	4-NCC ₆ H ₄ (3f)	B	70 ^b (4e) 20 ^b (6f) 10 (7f)	
11	2	3a	A	24 (5a) 23 (6a)	
12	2	3d	A	21 (5b)	
13	2	3e	A		43 (6e)
14	2	4-O ₂ NC ₆ H ₄ (3g)	A	68 (5c)	
15	2	3a	B	39 (5a)	
16	2	3d	B	31 (5b)	
17	2	3g	B	39 (5c)	

^aConditions A: CsF (1.2 equiv.), MeCN, room temperature, 45 h;

B: TASF (1 equiv.), THF, room temperature, 3 h.

^bDetermined by ¹H-nmr.

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4. 2-Trimethylsilylmethylthiothiazoline (**1**) was prepared by reaction of 2-mercaptothiazoline with chloromethyltrimethylsilane in the presence of sodium hydroxide and sodium iodide in ethanol under reflux for 1 h in 66% yield. Compound (**2**) was synthesized from 2-mercaptopbenzothiazole and chloromethyltrimethylsilane in 74% yield in manner similar to the preparation of **1**.
5. **1**: bp 145°C (19 mmHg). ¹H-nmr (CDCl₃) δ 0.16 (s, 9H), 2.82 (s, 2H), 3.36 (t, *J* = 6.5 Hz, 2H), 4.23 (t, *J* = 6.5 Hz, 2H); ir (neat) ν max cm⁻¹ 2961, 1572, 1245, 964, 849; ms *m/z* (%) 205 (M⁺, 11), 190 (100), 158 (7), 133 (4), 116 (9), 73 (51).
6. S. Kohra, H. Ueda, and Y. Tominaga, *Heterocycles*, 1993, **36**, 1497.
7. **2**: bp 152°C (5 mmHg). ¹H-nmr (CDCl₃) δ 0.19 (s, 9H), 2.60 (s, 2H), 7.20-7.80 (m, 4H); ir (neat) ν max cm⁻¹ 2957, 1424, 1251, 847, 758; ms *m/z* (%) 253 (M⁺, 10), 238 (27), 158 (7), 86 (64), 84 (100), 73 (19), 47 (27).
8. Fluoride ions promoted the protodesilylation of **1** to afford 2-methylthiothiazoline in 95 % yield.
9. **6d**: ¹H-nmr (CDCl₃) δ 2.69 (dd, *J* = 1.5 and 5.5 Hz, 1H), 2.89 (dd, *J* = 1.5 and 6.6 Hz, 1H), 3.93 (dd, *J* = 2.9 and 5.7 Hz, 1H), 7.20-7.64 (m, 9H); ir (neat) ν max cm⁻¹ 1483, 839, 760, 687, 600; Ms *m/z* (%) 213 (M⁺, 14), 188 (7), 180 (100), 165 (16), 152 (17), 76 (9); HR-ms Calcd for C₁₄H₁₂S = 212.066. Found 212.066.
Compounds (**6**) were fully characterized by ¹H-nmr (90 MHz), ir, and HR-ms
10. **5b**: ¹H-nmr (CDCl₃) δ 3.71 (dd, *J* = 2.6 and 3.4 Hz, 2H), 5.10 (bs, 1H), 5.24 (dd, *J* = 5.8 and 6.9 Hz, 1H), 7.20-7.84 (m, 13H); ir (KBr) ν max cm⁻¹ 3400, 1421, 1057, 998, 747; ms *m/z* (%) 363 (M⁺, 6); HR-ms Calcd for C₂₁H₁₇S = 363.075. Found 363.076.
Compounds (**5**) and (**7**) were fully characterized by ¹H-nmr (90 MHz), ir, and HR-ms.
11. **4a**: ¹H-nmr (CDCl₃) δ 3.17-3.63 (4H, m, S-CH₂-, S-CH₂-), 4.19 (2H, t, *J* = 4.0 Hz, N-CH₂-), 5.04 (1H, t, *J* = 3.0 Hz, CH(OH)), 7.25-7.65 (5H, m, aromatic-H).
12. Protodesilylation of **2** by TBAF in THF did not occurred.
13. 2-Benzothiazolythiocarbanion cannot be generated by the lithiation of 2-methylthiothiazole with *n*-butyllithium: K. Hirai and Y. Kishida, *Heterocycles*, 1974, **2**, 185.

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