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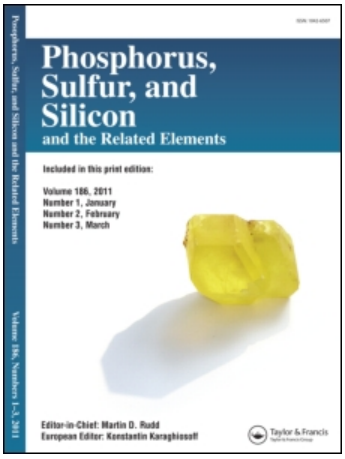

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SYNTHESIS AND BASE-CATALYZED PROTODESILYLATION OF 5-(SILYLMETHYLTHIO)-3(2H)-PYRIDAZINONE DERIVATIVES

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SYNTHESIS AND BASE-CATALYZED PROTODESILYLATION OF 5-(SILYLMETHYLTHIO)-3(2H)-PYRIDAZINONE DERIVATIVES

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A series of 2-tert-butyl-4-chloro-5-(silylmethylthio)-3(2H)-pyridazinone derivatives **1** was synthesized. Their structures were confirmed by ^{1}HNMR, IR, MS and elemental analysis. Under mild conditions, base-catalyzed protodesilylation of **1** occurred extremely easily. Substituent effects on this reaction were discussed.

Keywords: Organosilicon compound; synthesis; 3(2H)-pyridazinone derivative; protodesilylation

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INTRODUCTION

2-tert-butyl-4-chloro-5-alkylthio-3(2H)-pyridazinone derivatives possess excellent pesticidal activity[1]. In order to search for novel lead compounds with insecticidal and acaricidal activity, we synthesized a series of silicon-containing 3(2H)-pyridazinone derivatives **1** with bioisosterism in mind. Their structures were confirmed by ^{1}HNMR, IR, MS spectra and elemental analysis. The synthetic methods of **1** and their MS spectra were also discussed.

As known, protodesilylation at an sp^3 carbon atom has a considerable significance in organic synthesis, especially as a method to remove the protecting groups or to introduce deuterium. Recently this type of reaction has been carried out mainly by fluoride ion catalysis[2]. KF, CsF or n-Bu_4NF (TBAF) may be used as fluoride ion sources. t-BuOK[3] is also an effective catalyst for the protodesilylation

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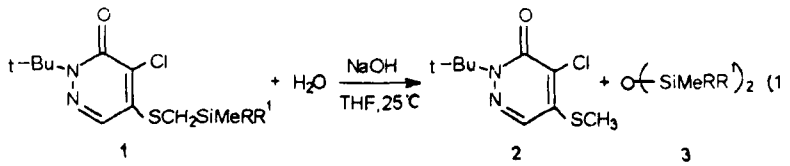
with the cleavage of sp^3 hybridized carbon-silicon bond. During the course of the study concerned with pesticidal activity of **1**, we occasionally found that protodesilylation of **1** proceeds smoothly in the presence of catalytic amount of sodium hydroxide at room temperature (25 °C) giving **2** and **3** in high yields (eq. 1).



When H_2O was replaced with D_2O, the deuterated product **2** was obtained. To the best of our knowledge, this is a first example of such a reaction. In this paper substituent effect on this reaction is discussed.

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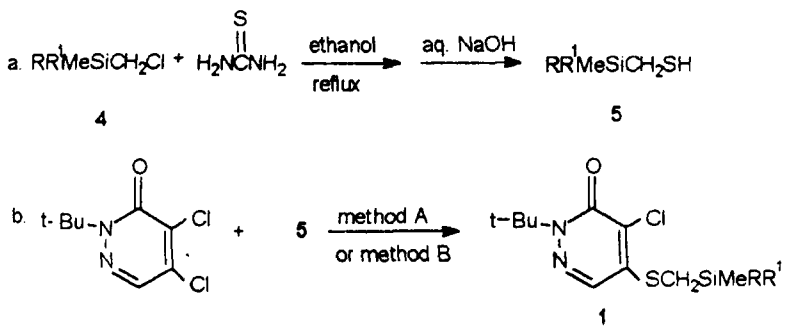
Results and Discussion

Synthesis The synthetic pathway for compound **1** is shown in Scheme 1. As the chlorine atom of chloromethylsilane **4** was difficult to be substituted. The attempt to synthesize **1** by treatment of 2-tert-butyl-4-chloro-5-mercapto-3(2H)-



method A: aqueous NaOH as HCl acceptor and CH_2Cl_2 as solvent.

method B: anhydrous K_2CO_3 as HCl acceptor and absolute ethanol as solvent.

1	*R*	*R'*	*1*	*R*	*R'*	*1*	*R*	*R'*
a	C_6H_5	CH_3	f	m-$CH_3C_6H_4$	CH_3	k	C_6H_5	C_6H_5
b	p-ClC_6H_4	CH_3	g	p-$CH_3OC_6H_4$	CH_3	l	CH_3	CH_3
c	m-ClC_6H_4	CH_3	h	p-$PhOC_6H_4$	CH_3	m	C_2H_5	CH_3
d	p-FC_6H_4	CH_3	i	2-thienyl	CH_3	n	C_2H_5	C_2H_5
e	p-$CH_3C_6H_4$	CH_3	j	2-furyl	CH_3	o	$C_4H_{9\text{-}n}$	$C_4H_{9\text{-}n}$

SCHEME 1 The synthetic pathway for preparation of **1**.

pyridazinone with **4** in the presence of inorganic or organic base was unsuccessful. **4** was converted into silylmethanethiol **5** by its reaction with thiourea. **5** reacted with 2-tert-butyl-4,5-dichloro-3(2H)-pyridazinone to give the desired product **1** in satisfactory yields (Table I,II). When R or R^1 is aryl group in **5**, method A for preparation of **1** was preferred. When R, R^1 is alkyl, method B was more suitable.

MS spectroscopy Main MS data of representative compounds **1** were listed in Table III. All recorded compound **1** produced a molecular ion peak. The base peak ion is always RR^1MeSi^+ when R equals aryl group in **1**. But it is R^1MeSi^+H resulting from β-elimination of the fragment RR^1MeSi^+ when R is ethyl or butyl (Compound **1**m, **1**o in Table III). There is a m/e (Ar + 14) ion peak in MS spectrum of **1** (R=Aryl). This ion peak suggests there is a rearrangement breakdown pattern. When R is aryl group in **1**, fragment ion $RR^1MeSiCH_2^+$ (A) probably tends to rearrange into $(RCH_2)R^1MeSi^+$ (B) which in turn undergoes a cleavage of Si-C bond to produce m/e (Ar + 14) ion RCH_2^+ (Scheme 2). According to the rational calculations by Stang and coworkers[4] it is deduced that there is a substantial driving force for the above rearrangement.

Protodesilyation Ten compounds **1** were selected for protodesilylation and results are summarized in Table IV. Data listed in Table IV show that substituent R on silicon atom plays an important role for the reaction. The electron-withdrawing R groups facilitate the protodesilylation. For example, protodesily-

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TABLE I Data for compound 1

1	*state*	*m.p.(°C) or* n_D^{25}	*yield (%)*	*elemental analysis found (Calc.)*		
				C%	*H%*	*N%*
a	white crystal	88–89	58.5	56.07(55.64)	6.31(6.32)	7.59(7.63)
b	white crystal	94–95	74.8	50.64(50.86)	5.56(5.52)	7.44(6.98)
c	white crystal	90–92	59.9	51.13(50.86)	5.45(5.52)	7.06(6.98)
d	white crystal	114–115	78.0	52.88(53.04)	6.01(5.76)	7.16(7.28)
e	white crystal	116–118	90.8	56.65(56.74)	6.59(6.61)	7.41(7.35)
f	white crystal	86–87	31.5	56.96(56.74)	6.71(6.61)	7.38(7.35)
g	white crystal	130–131	70.0	54.45(54.46)	6.36(6.35)	6.95(7.06)
h	colorless viscous oil		87.1	60.23(60.17)	5.91(5.93)	6.07(6.10)
i	colorless crystal	119–120	64.3	48.71(48.30)	5.74(5.67)	7.50(7.51)
j	colorless crystal	115–116	70.0	50.42(50.47)	5.92(5.93)	7.83(7.85)
k	white solid	99–101	56.0	61.37(61.59)	6.12(5.87)	6.85(6.53)
l	white solid	48–50	45.9	47.20(47.27)	6.91(6.94)	9.30(9.19)
m	yellow oil	1.5518	62.7	48.69(48.96)	7.38(7.27)	8.46(8.78)
n	colorless oil	1.5508	55.3	50.53(50.50)	7.69(7.57)	8.86(8.41)
o	colorless oil	1.5358	72.0	55.68(55.57)	8.43(8.55)	7.21(7.20)

TABLE II IR and ^{1}HNMR data of compounds **1**

IR (cm^{-1})			
C—O	$\delta^{S}_{Si\text{-}CH3}$	$\gamma_{Si\text{-}CH3}$	^1HNMR δ(ppm)
35(s)	1246(s)	808(s)	0.47(s, 6H, $SiCH_3$), 1.63(s, 9H, C_4H_9-t), 2.39(s, 2H, SCH_2), 7.34–7.66(m, 5H, C_6H_5), 7.66(s, 1H, CH)
33(s)	1247(m)	802(s)	0.48(s, 6H, $SiCH_3$), 1.63(s, 9H, C_4H_9-t), 2.36(s, 2H, SCH_2), 7.37–7.50(dd, 4H, C_6H_4), 7.66(s, 1H, CH)
33(s)	1251(m)	811(s)	0.48(s, 6H, $SiCH_3$), 1.60(s, 9H, C_4H_9-t), 2.36(s, 2H, SCH_2), 7.32–7.52(m, 4H, C_6H_4), 7.68(s, 1H, CH)
33(s)	1255(s)	805(s)	0.46(s, 6H, $SiCH_3$), 1.60(s, 9H, C_4H_9-t), 2.36(s, 2H, SCH_2), 7.07, 7.48–7.51 (m, 4H, C_6H_4), 7.64(s, 1H, CH)
33(s)	1247(s)	807(s)	0.46(s, 6H, $SiCH_3$), 1.64(s, 9H, C_4H_9-t), 2.38(d, 5H, SCH_2, CH_3), 7.16–7.52 (dd, 4H, C_6H_4), 7.70(s, 1H, CH)
37(s)	1247(s)	815(s)	0.42(s, 6H, $SiCH_3$), 1.58(s, 9H, C_4H_9-t), 2.32(d, 5H, SCH_2, CH_3), 7.20–7.40(m, 4H, C_6H_4), 7.70(s, 1H, CH)
29(s)	1244(s)	809(s)	0.40(s, 6H, $SiCH_3$), 1.56(s, 9H, C_4H_9-t), 2.30(s, 2H, SCH_2), 3.76(s, 3H, CH_3O), 6.88, 7.43(dd, 4H, C_6H_4), 7.62(s,
30(s)	1245(s)	815(s)	0.48(s, 6H, $SiCH_3$), 1.63(s, 9H, C_4H_9-t), 2.39(s, 2H, SCH_2), 7.00–7.53(m, 9H, C_6H_5, C_6H_4), 7.69(s, 1H, CH)
35(s)	1248(s)	817(s)	0.53(s, 6H, $SiCH_3$), 1.63(s, 9H, C_4H_9-t), 2.43(s, 2H, SCH_2), 7.24(m), 7.41(d), 7.67(d, 3H, C_4H_3S), 7.70(s, 1H, CH)
37(s)	1250(s)	815(s)	0.46(s, 6H, $SiCH_3$), 1.62(s, 9H, C_4H_9-t), 2.42(s, 2H, SCH_2), 6.41(m), 6.77(d), 7.60(d, 3H, C_4H_3O), 7.67(s, 1H, CH)
38(s)	1253(m)	801(s)	0.74(s, 6H, $SiCH_3$), 1.60(s, 9H, C_4H_9-t), 2.70(s, 2H, SCH_2), 7.36–7.68(m, 10H, C_6H_5), 7.72(s, 1H, CH)
35(s)	1243(m)	845(s)	0.19(s, 9H, $SiCH_3$), 1.62(s, 9H, C_4H_9-t), 2.19(s, 2H, SCH_2), 7.70(s, 1H, CH)
33(s)	1234(m)	828(s)	0.17(s, 6H, $SiCH_3$), 0.90(q, 2H, CH_2), 0.97(t, 3H, CH_3), 1.63(s, 9H, C_4H_9-t), 2.20(s, 2H, SCH_2), 7.72(s, 1H, CH)
37(s)	1248(s)	795(s)	0.13(s, 3H, $SiCH_3$), 0.67(q), 0.98(t, 10H, 2 × C_2H_5), 1.62(s, 9H, C_4H_9-t), 2.20(s, 2H, SCH_2), 7.73(s, 1H, CH)
35(s)	1250(m)	799(s)	0.15(s, 3H, $SiCH_3$), 0.67–0.72, 0.86–0.92, 1.29–1.36(m, 18H, C_4H_9-n), 1.63(s, 9H, C_4H_9-t), 2.19(s, 2H, SCH_2), 7.73(s, 1H, CH)

TABLE III Mass spectra data of representative compounds **1***

M^+	*base ion*	$RR'MeSiCH_2^+$ *m/e*	*rearrangement ion m/e*	*other fragment ion m/e*
366(16)	$PhMe_2Si^+$	149(4)	91(8)	311(14), 310(7), 232(19),
400(3)	$p\text{-}ClC_6H_4Me_2Si^+$	183(8)	125(7)	345(18), 344(4), 232(33),
396(1)	$p\text{-}CH_3C_6H_4Me_2Si^+$	179(4)	121(12)	197(39), 135(12), 341(2),
458(1)	$p\text{-}PhOC_6H_4Me_2Si^+$	241(3)	183(4)	403(3), 402(2), 197(38),
372(1)	$C_4H_3SMe_2Si^+$	155(6)	97(13)	317(10), 316(3), 337(21),
356(1)	$C_4H_3OMe_2Si^+$	139(8)	81(4)	301(10), 321(55), 232(20),
304(3)	Me_3Si^+	87(3)		249(8), 248(4), 57(36), 45
318(35)	Me_2Si^+H	101(3)		263(54), 262(25), 87(78),
388(43)	$BuMeSi^+H$	171(0.5)		333(43), 332(26), 157(39),

ntheses is relative intensity of fragment ion.

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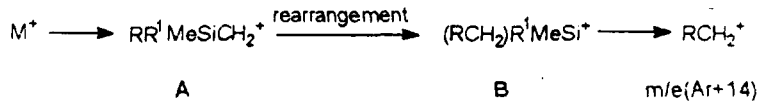

SCHEME 2 A rearrangement breakdown pattern of **1** (R = aryl).

lations of compounds **1a–d, i–j** were complete within 12 minutes to give product **2** in 80%–95% yields. For other compounds with relatively weak electron-withdrawing R, e.g. **1e–f**, substantially longer reaction times were required.

On the other hand, the presence of 3(2H)-pyridaznon-5-yl group on sulfur atom also plays a critical role in the occurence of this protodesilylation. After compound **6**, which is analogous with compound **1a**, had been stirred continuously for 60 h under the same reaction conditions as compound **1a**, no reaction occurred and **6** was recovered completely unchanged (eq. 2). This result presumably attributes to the weaker electron-withdrawing ability of phenyl group compared to that of 3(2H)-pyridazinon-5-yl group for the strong electron-withdrawing group benefits sulfur atom stabilizing the carbanion intermediate from the cleavage of carbon-silicon bond. Theoretical calculations about net charge for sulfur atoms in compounds **1a** and **6** by CNDO/2 method are also in agreement with the above conclusion. The value of net charge on sulfur atom in compound **1a** is positive 0.0006081, whereas that in compound **6** is negative 0.014999.

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EXPERIMENTAL

All temperatures were uncorrected. Melting points were determined with Yanaco MP-500 apparatus. IR spectra were recorded on Shimadzu IR- 435 spectrophotometer as thin films or KBr tablet. ^{1}HNMR spectra were measured on a JEOL-

TABLE IV Protodesilylation of compounds **1** catalyzed by NaOH**

1	*Reaction time (min.)*	*Yield of 2 (%)*	*1*	*Reaction time (min.)*	*Yield of 2 (%)*
a	10	95	f	50	87
b	6	95	g	80	84
c	8	90	i	11	80
d	11	92	j	12	82
e	40	88	l	12	94

Reaction conditions: NaOH/1** molar ratio 1:10; THF-H_2O(10:1,v/v) as solvent: Reaction temperature 25 °C.

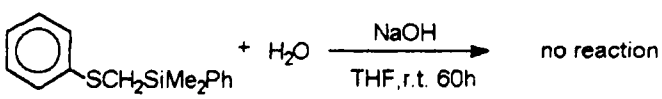
FX-90Q and a Bruker AC-200 instruments using TMS as an internal standard and $CDCl_3$ as solvent. Mass spectra were recorded on an HP-5988A instrument at 70ev. Elemental analyses were determined on an MT-3 elemental analyzer.

1. Silylmethanethiol 5

Silylmethanethiols **5** were prepared from chloromethylsilanes **4**, which were prepared from the reaction of $ClCH_2SiCl_2CH_3$ or $ClCH_2(CH_3)_2SiCl$ with organometallic reagents, as previously described in the literature[5]. The crude products **5** were purified by distillation at reduced pressure or column chromatography on silica gel using petroleum ether-CH_2Cl_2(10:1 v/v) as an eluant (Table V).

2. 2-tert-Butyl-4-chloro-5-silylmethylthio-pyridazinone 1 (Typical procedure)

Method A Sodium hydroxide 0.23 g (5mmol) was dissolved in 5 ml of water, and thereto were added 10 ml of dichloromethane, 1.1 g (5mmol) of 2-tert-butyl-4, 5-dichloro-3(2H)-pyridazinone and 0.05 g triethylbenzylammonium chloride. The resulting solution was incorporated with 0.91 g (5mmol) of



6 (2)

Table V Data of silylmethanethiols 5

5	*State*	*b.p.(°C/mm)*	n_D^{25}	*yield(%)*
a	Colorless liquid	79-81/6	1.5432	76.2
b	Colorless liquid	94-98/0.4	1.5573	60.0
c	Colorless liquid	104-105/1	1.5576	69.4
d	Colorless liquid	96-97/9	1.5270	67.5
e	Colorless liquid	110-112/9	1.5406	79.1
f	Colorless liquid	104-108/9	1.5400	81.6
g	Colorless liquid	108-110/1	1.5488	61.3
h	Colorless liquid		1.5758	85.2
i	Colorless liquid	91-92/6	1.5528	76.6
j	Colorless liquid	60-61/6	1.5094	66.9
k	Colorless liquid	134-138/0.3	1.6050	53.0
l	Colorless liquid	118-120/760	1.4564	62.2
m	Colorless liquid	46-48/27	1.4586	55.2
n	Colorless liquid	92-94/80	1.4772	77.7
o	Colorless liquid	84-88/6	1.4632	52.0

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dimethylphenylsilyl-methanethiol **5a** and then stirred at room temperature for 2 h. After completion of the reaction, the organic layer was separated, washed with water and dried over anhydrous sodium sulfate. After filtration, solvent was distilled off under reduced pressure and the resulting oily residue was incorporated with 10 ml of petroleum ether (90–120 °C) to give 1.1 g of compound **1a**, m.p. 88 °C.

Compounds **1**b-l were prepared by a similar procedure (Table I).

Method B To a solution of 1.1 g (5mmol) of 2-tert-butyl-4, 5- dichloro-3(2H)-pyridazinone in 20 ml of absolute ethanol were added 0.74 g (5mmol) of **5**n and 0.83g (6mmol) of anhydrous potassium carbonate. The resulting mixture was stirred at room temperature for 2 h and refluxed for 4 h. After removal of ethanol, the residue was dissolved in 20 ml of ether, washed and dried over anhydrous sodium sulfate. Removal of the solvent gave a crude product which was purified by column chromatography on silica gel (10–40 μ) with ether/petroleum ether (1 : 10 v/v) as the eluent to give 0.92 g of **1**n as a colorless oil, n_D^{25} 1.5508.

By method B compounds **1**l, m, o were also synthesized (Table I)

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3. Protodesilylation of 1 (Typical procedure)

To a solution of compound **1** (0.25 mmol) in 10 ml of THF, 1.0 ml of 0.1% NaOH aqueous solution (0.025 mmol) was added with stirring at 25 °C. The reaction mixture was stirred continuously and monitored by TLC until the reaction was complete. The desired products **2** and **3** were isolated by silica gel column chromatography in high yields using petroleum ether-CH_2Cl_2 (10 : 1) as an eluent.

Acknowledgements

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