Differing Reactivities and Products in the Reaction of Some *N*-Methylimidazol-2-yl, Oxazol-2-yl- and Thiazol-2-ylsilanes and -stannanes with Acid Chlorides

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Some new *N*-methylimidazoles, oxazoles and thiazoles (compounds **7-15**) with a keto-function in the 2-position have been synthesized by the reaction of heterocyclic substituted silanes and stannanes with the corresponding acid chlorides. In cases where the silylated heterocycles needed more drastic reaction conditions the use of the stannylated heterocycles was indicated. In the reaction of benzothiazol-2-yltrimethylstannane (**6**) with acetyl chloride the ester **17** and the bibenzothiazolinylidene **18** were formed. The reaction of **6** with chloromethyl methyl ether afforded the olefin **19** as the only product. Mechanisms for the above reactions are discussed.

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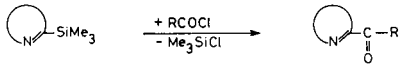
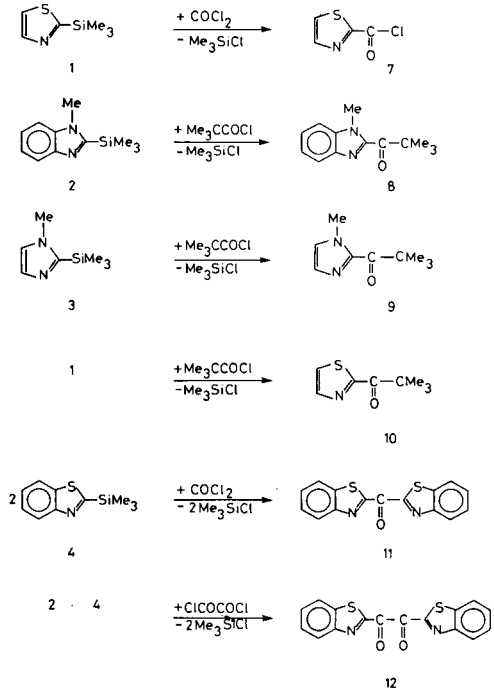
The chemistry of heterocyclic substituted silanes with the N=C—Si—unity is determined by the suprising reactivity of the silicon-carbon bond in most of these compounds. The labile nature of this silicon-heterocyclic bond has been demonstrated by an easy hydrolysis, by *trans*-silylation reactions and by reactions with acid chlorides, aldehydes, chloroformates, anhydrides and isocyanates under mild conditions. Silyl-substituted pyridines, thiazoles, *N*-methylimidazoles, *N*-methylthiazoles, pyrazines, pyrazoles and very recently also oxazoles along with their benzannelated derivatives have been investigated in the groups of Webster [1], Thames [2], Earborn [3], Birkhofer [4], Effenberger [5] and in our group [6].

The reaction of most of these heterocyclic substituted silanes with acid chlorides [2,6] provides a new synthetic method for the introduction of >C=O functions to the heterocycles according to the following scheme.



Concerning the mechanism of these exchange reactions, Pinkerton and Thames proposed a cyclic 4-member transition state [2], while we have evidence for a cyclic 5-member transition state [7], as it has been proved for the hydrolysis of silylated pyridines by Anderson, Bradney and Webster [1] and for the reaction of some stannylated thiazoles as described in this paper.

According to the work of Regel and Büchel, some of the above mentioned ketones can also be synthesized by reaction of the corresponding heterocycle with acid chlorides [8], but this procedure does not work in the case of aliphatic acid chlorides. We have extended our previous work concerning the reaction of heterocyclic substituted silanes with acid chlorides to demonstrate the general application of this synthetic route. Some new C=O—substituted heterocycles could be synthesized according to the following equations:



In the reaction with phosgene the product obtained depends on the stoichiometrie of the reactants; a 1:1 ratio leads to ketones of type **7**, a 2:1-ratio to twice heterocyclic substituted ketones of type **11**. The reactions with pivaloyl chloride leading to the ketones **8, 9, 10** demonstrate that even in the case of bulky reactants product formation can be achieved. Finally the reaction with oxalyl chloride shows, that also heterocyclic substituted diketones like **12** can be synthesized.

Tin-carbon bonds are generally more reactive than the corresponding silicon-carbon bonds. In cases where the silylated heterocycles need more drastic conditions in the reaction with acid chlorides or even do not react, the use of the corresponding stannylated heterocycles [9] was indicated. As an example we therefore synthesized the new

Table 1

Data for the Synthesis of the Compounds **7-15**

Compound	Acylsilanes, -stannanes	g	mmoles	Solvent	ml	Acid Chloride	g	mmole	Reaction Time hours	(°C)	Method of isolation 50° (Hv)	Yield g	%
7	**1**	4.72	30.0	10.0		Cl_2CO (a)	3.48	35.0	15	(0)	sublimed	2.95	68
									1	(20)			
8	**2**	4.49	22.0	—		Me_3CCOCl	3.01	25.0	12	(100)	distilled	3.19	57
9	**3**	3.39	22.0	—		Me_3CCOCl	3.01	25.0	15	(20)	distilled	3.14	86
10	**1**	3.46	22.0	—		Me_3CCOCl	3.01	25.0	15	(20)	distilled	3.05	82
11	**4**	6.21	30.0	10.0		Cl_2CO (a)	1.74	17.5	15	(0)	crystallized	3.29	74
									1	(20)	from acetone		
12	**4**	4.14	20.0	10.0		$Cl_2(CO)_2$	1.52	12.0	15	(0)	crystallized	2.53	78
									1	(20)	from DMSO/-acetone		
13	**5**	3.00	10.6	10.0		PhCOCl	1.55	11.0	15	(20)	sublimed 50° (HV)	2.01	85
14	**6**	6.49	22.0	—		Me_3CCOCl	3.01	25.0	15	(20)	distilled	3.28	68
15	**5**	3.00	10.6	—		Me_3CCOCl	1.33	11.0	2	(20)	crystallized from pentane	1.55	72

(a) About 1.4 *M* in dichloromethane.

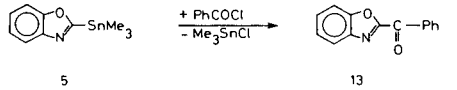
Table 2

Physical and Analytical Data of the Compounds **7-15**

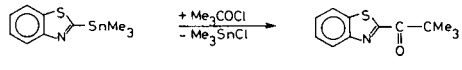
	Bp	Mp	Formula	(mol weight)	Analyses % Calcd./Found C	H	N	Molecular weight
7	—	58	C_4H_2ClNOS	(147.59)	32.55	1.37	9.49	147 (a)
					32.22	1.52	9.35	
8	144/4.8	79	$C_{13}H_{16}N_1O$	(216.28)	72.19	7.46	12.95	216 (a)
					72.24	7.53	13.26	
9	41/0.2	—	$C_9H_{14}N_2O$	(166.22)	65.03	8.49	16.85	166 (a)
					64.80	8.66	16.92	
10	41/0.2	—	$C_8H_{11}NOS$	(169.25)	56.77	6.55	8.28	169 (a)
					56.68	6.59	8.35	
11	—	183	$C_{15}H_8N_2OS_2$	(296.50)	60.76	2.72	9.49	289 (b)
					60.48	3.01	9.33	
12		245 dec	$C_{16}H_8N_2O_2S_2$	(324.39)	59.24	2.49	8.64	310 (b)
					58.88	2.67	8.38	
13		139	$C_{14}H_9NO_2$	(233.23)	75.33	4.06	6.27	215 (b)
					75.00	4.41	6.20	
14	107/0.1	50	$C_{12}H_{13}NOS$	(219.31)	65.72	5.98	6.39	219 (a)
					65.60	6.05	6.42	
15	—	91	$C_{12}H_{13}NO_2$	(203.24)	70.92	6.45	6.89	203 (a)
					71.08	6.48	6.82	

(a) By mass spectrometry. (b) Cryoscopy in benzene.

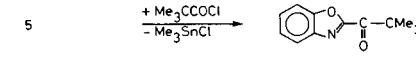
heterocyclic ketones **13, 14** and **15**, starting from the stannanes **5** and **6**. A fast reaction at room temperature according to the following equations was observed.



5 13



6 14



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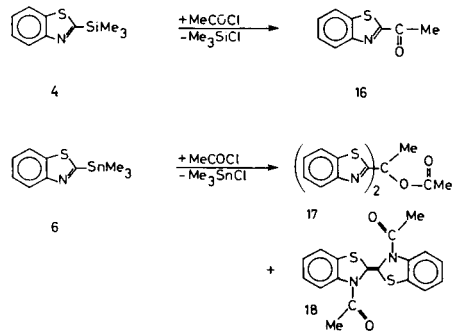
While the benzthiazol-2-yltrimethylsilane (**4**) reacts with acetyl chloride in good yields to the benzthiazol-2-ylmethyl ketone (**16**) [6a], the corresponding stannane **6** does not give the expected ketone **16**; instead of **16** the compounds **17** and **18** are the sole reaction products.

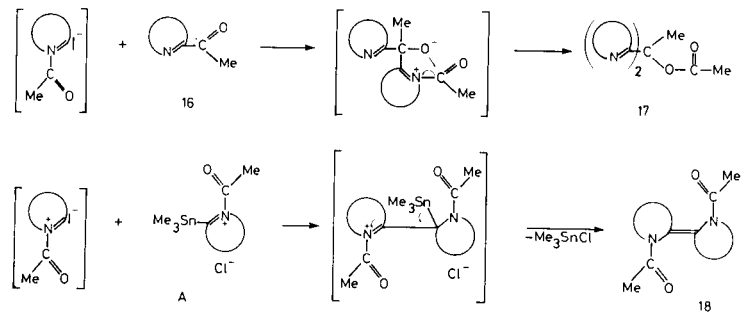
Table 3

IR and NMR Data of the Compounds **7-15**

Compound	IR (cm^{-1}) ν CO	^{1}H-NMR [ppm] δ — aromatic H	δ — R	Solvent
7	1740	7.97 [d, 1H] (a) 8.13 [d, 1H]	—	Carbon tetrachloride (TMS)
8	1675	7.17-7.43 [m, 3H] 7.70-7.95 [m, 1H]	1.53 [s, 9H, ECH_3] 4.06 [s, 3H, N—CH_3]	Dichloromethane (TMS)
9	1670	6.90 [s, 1H] 6.97 [s, 1H]	1.42 [s, 9H, C—CH_3] 3.89 [s, 3H, N—CH_3]	Dichloromethane (δ = 5.30)
10	1670	7.57 [d, 1H] (b) 7.96 [d, 1H]	1.47 [s, 9H]	Carbon tetrachloride (TMS)
11	1660	7.35-8.38 [m]	—	Carbon tetrachloride (TMS)
12	1700	7.32-8.37 [m]	—	Dichloromethane (δ = 5.30)
13	1650	7.27-7.93 [m]	—	Dichloromethane (δ = 5.30)
14	1670	7.20-8.10 [m, 4H]	1.55 [s, 9H]	Dichloromethane (TMS)
15	1685	7.23-8.03 [m, 4H]	1.53 [s, 9H]	Dichloromethane (TMS)

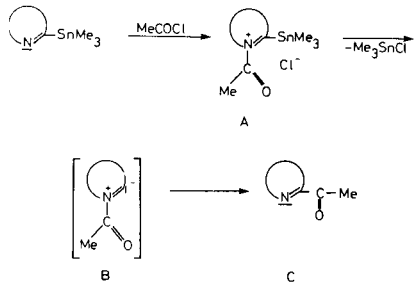
(a) J = 2.8 Hz. (b) J = 2.7 Hz.





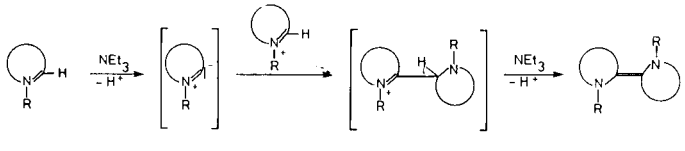
Compounds similar to **17** and **18** are known from the literature. Acylation of benzthiazole, benzoxazole and 2-phenyl-1,3,4-oxadiazole with aromatic acid chlorides leads to the desired ketones and to esters analogous to **17** [10]. Deprotonation of *N*-alkylbenzothiazolium salts yields *N,N'*-alkylated compounds of type **18**, which are of lower stability [11,12,13,14].

The formation of the products **17** and **18** can be explained, if one assumes the formation of an adduct **A** and a transient species **B**, which normally reacts to the corresponding ketone **C**.



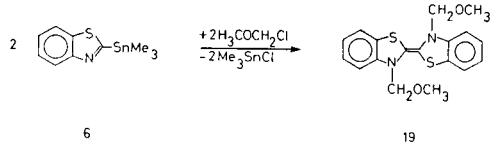
In the case of the formation of compound **17** the zwitterion **B** reacts with the already formed ketone of type **C**, in the other case **B** reacts with the adduct **A** to compound **18**.

The last reaction sequence corresponds to the dimerisation of heterocyclic ylides as formulated by Hünig and Quast [12].



For the existence of *N*-Acylium salts of type **A** we have found good evidence in the mentioned reaction of the silane **4** with phosgene. In pentane as solvent we could isolate an ionic, rather unstable intermediate which corresponds in its structure to the postulated salt **A** [7].

If in the intermediate type of **A** the acyl group is substituted by an alkyl group, then no migration to the carbon atom should take place. This could be demonstrated in the reaction of the stannane **6** with chloromethyl-methylether, where the bibenzthiazolinylidene **19** is the only reaction product.



The compounds **18** and **19** can be handled in air at room temperature for a longer time. Their trans-structure has been postulated in analogy to known compounds of this type [11-14].

EXPERIMENTAL

Synthesis of the Acylazoles **7-15** (Table 1, 2 and 3).

General Procedure.

The silanes or stannanes were combined with the stoichiometric amounts of the corresponding acid chloride in methylene chloride or without a solvent. After reaction according to the time in Table 1 all volatile components were evaporated *in vacuo*. From the residues the desired compounds **7-15** were isolated by sublimation, distillation or crystallization.

Synthesis of **17** and **18**.

To a stirred solution of 5.96 g (20.0 mmoles) **6** in 25 ml carbon tetrachloride a solution of 1.42 ml (20.0 mmoles) of acetylchloride in 25 ml of carbon tetrachloride was added dropwise at 0°. After warming to room temperature, two thirds of the solvent was evaporated. After addition of 25 ml of acetone/pentane (1:1) and further stirring for 1 hour a colourless precipitate of compound **17** was filtered and recrystallized from acetone. In the remaining solution the yellow coloured compound **18** precipitated during one day in an analytically pure form.

Compound **17**.

This compound had mp 175-176°, yield, 1.73 g (24%); ^{1}H-nmr (dichloromethane): δ-CH_3 2.32 [s, 3H], δ-C(O)CH_3 2.63 [s, 3H], δ-aromat-H 7.1-8.0 [m, 8H]; ir: ν CO 1755, 1745 cm^{-1}.

Anal. Calcd. fo $C_{16}H_{14}N_2O_2S_2$ (354.42): C, 60.96; H, 3.95; N, 7.90. Found: C, 60.61; H, 4.31; N, 7.70; Mol. weight: 354 (MS).

Compound **18**.

This compound had mp 138-139° dec, yield, 1.35 g (19%); ^{1}H-nmr (dichloromethane): δ-CH_3 2.52 [s, 6H] δ-aromat-H 6.9-7.8 [m, 8H]; ir ν CO 1680 cm^{-1}.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$ (354.42): C, 60.96; H, 3.95; N, 7.90. Found: C, 60.82; H, 3.97; N, 7.89; Mol. weight: 354 (MS).

Synthesis of **19**.

To a stirred solution of 7.76 g (26.0 mmoles) of **6** in 20 ml of dichloromethane/20 ml of petroleum ether (50-70°), 2.18 g (27.0 mmoles) of chloromethyl methyl ether was added dropwise at 0°. During a 15 hour reaction at room temperature the mixture turns deep red. Twenty ml of the solvent was evaporated. On cooling the yellow compound **19** could be obtained which was recrystallized from acetone.

Compound **19**.

This compound had mp 164°, yield, 1.80 g (39%); ^{1}H-nmr (deuteriochloroform): (TMS) δ-CH_3 3.42 [s, 6H], δ-CH_2 4.95 [s, 4H], δ-aromat-H 6.7-7.3 [m, 8H].

Anal. Calcd. for $C_{18}H_{16}N_2O_2S_2$ (358.48): C, 60.31; H, 5.06; N, 7.81. Found: C, 59.94; H, 5.32; N, 7.82; Mol. weight: 358 (MS).

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