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## Organosilicon Compounds II.

### Synthesis of Organosilicon Substituted Thiophene Derivatives

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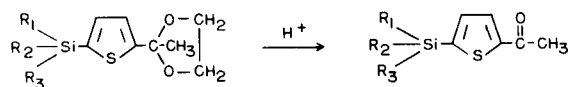
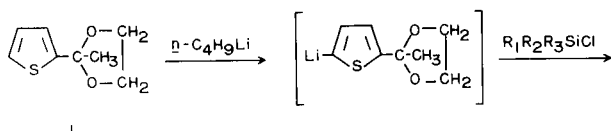
The apparent lack of silicon substituted heterocycles containing reactive functional groups, and that these, when prepared, would serve as intermediates for other research interests, has prompted us to extend our initial investigation (1). Our previous work employed the 1,3-dioxolane moiety as a carbonyl blocking group during butyllithium metalations. This procedure allowed the synthesis of a number of new thiophene derivatives, one of which was 2-acetyl-5-trimethylsilylthiophene (93% yield). This compound had been synthesized earlier by Benkesser and Currie (2) in 13% yield. The present

technique allows one to circumvent the usual arduous and uncertain Friedel-Crafts acylations and synthesize various 5-organosilicon substituted 2-acetylthiophenes in high yields and with minimal experimental difficulty. We have employed this procedure (Scheme A) for the production of eight new organosilicon substituted thiophene derivatives (Table I).

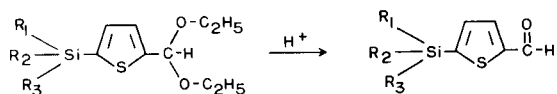
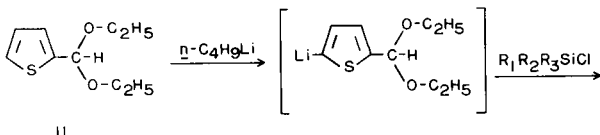
We next turned our attention to the synthesis of silicon substituted thiophene carboxaldehydes of which only one is reported in the literature (3). Thiophenecarboxaldehyde diethylacetal was metalated with *n*-butyllithium in the usual manner. Condensation of the resulting lithio salt (4) with various silylchlorides, followed by hydrolysis of the acetal moiety, gave good yields of the desired compounds (Scheme B). This technique has been employed for the synthesis of seven new organosilicon substituted thiophenes (Table I).

The structure of all products was confirmed by elemental analyses and infra-red spectral data. All organosilicon derivatives showed intense absorptions consistent with band assignments (5). That I (1) and II (4) are metalated in the five position of the thiophene nucleus has recently been confirmed.

SCHEME A



SCHEME B



#### EXPERIMENTAL

The melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. The infra-red spectra were determined with a Beckman IR-5 spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

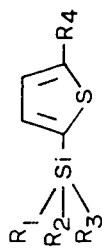
Preparation of Thiophenecarboxaldehyde Diethylacetals.

2-Thiophenecarboxaldehyde Diethylacetal (II).

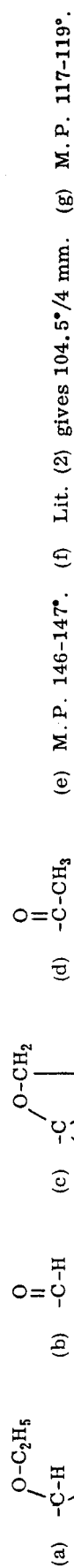
This compound was prepared according to a modification of the procedure of Van Allen (6).

2-Thiophenecarboxaldehyde (100 g., 0.895 mole) in 75 ml. of anhydrous ethyl alcohol, ethyl orthoformate (96.8 g., 1.1 moles) and ammonium nitrate (3.5 g.) were refluxed gently for 12 hours. The reaction mixture was cooled, filtered, sodium carbonate added and distilled to yield 120 g. (75%) of II boiling at 107°/23 mm.

TABLE I  
Organosilicon Substituted Thiophene Derivatives



Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Yield %	B. P. °C	Ref. Index	Formula	Calcd. %	Found %	
									C	H	Si
III	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(a)	93.5	149/23 mm.		C <sub>19</sub> H <sub>22</sub> O <sub>2</sub> SSi	55.76	8.58	55.69
IV	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	(a)	87	103/0.05 mm.	n <sub>D</sub> <sup>23</sup> = 1.4902	C <sub>15</sub> H <sub>20</sub> O <sub>2</sub> SSi	59.95	9.39	60.10
V	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(a)	55	94/0.1 mm.	n <sub>D</sub> <sup>27</sup> = 1.4823	C <sub>13</sub> H <sub>24</sub> O <sub>2</sub> SSi	57.30	8.88	57.24
VI	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(b)	65	80/0.45 mm. (h)		C <sub>8</sub> H <sub>12</sub> OSSI	52.12	6.56	52.19
VII	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	(b)	72	205/0.1 mm.		C <sub>23</sub> H <sub>18</sub> OSSI	74.54	4.89	74.37
VIII	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	(b)	49	166/1.5 mm.		C <sub>18</sub> H <sub>16</sub> OSSI	70.08	5.23	69.87
IX	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	(b)	86	132/1.6 mm.		C <sub>11</sub> H <sub>16</sub> OSSI	58.35	8.01	58.50
X	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(b)	82.5	77/0.08 mm.	n <sub>D</sub> <sup>28</sup> = 1.5350	C <sub>9</sub> H <sub>14</sub> OSSI	54.50	7.11	54.33
XI	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(c)	96	81/0.1 mm.		C <sub>11</sub> H <sub>18</sub> O <sub>2</sub> SSi	54.50	7.48	54.90
XII	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	(c)	69	(e)		C <sub>26</sub> H <sub>24</sub> O <sub>2</sub> SSi	72.83	5.65	73.03
XIII	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	(c)	74	128/1.25 mm.		C <sub>14</sub> H <sub>24</sub> O <sub>2</sub> SSi	59.11	8.50	59.30
XIV	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(c)	54	89/0.15 mm.	n <sub>D</sub> <sup>27</sup> = 1.5035	C <sub>12</sub> H <sub>20</sub> O <sub>2</sub> SSi	56.20	7.86	56.40
XV	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(d)	93	127/23 mm. (f)		C <sub>3</sub> H <sub>14</sub> OSSI	54.50	7.11	54.15
XVI	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	(d)	73	(g)		C <sub>24</sub> H <sub>20</sub> OSSI	74.99	5.24	74.76
XVII	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	(d)	67	180/1.5 mm.		C <sub>19</sub> H <sub>18</sub> OSSI	70.76	5.62	70.88
XVIII	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	(d)	58	102/0.1 mm.	n <sub>D</sub> <sup>26</sup> = 1.5290	C <sub>12</sub> H <sub>20</sub> OSSI	59.94	8.38	59.86
XIX	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(d)	85	77/0.08 mm.	n <sub>D</sub> <sup>25</sup> = 1.5268	C <sub>10</sub> H <sub>16</sub> OSSI	56.55	7.59	56.73



(h) Lit. (3) gives m. p. 33-34°.

## 2-(5-Trimethylsilyl)thiophenecarboxaldehyde Diethylacetal (III).

The preparation of III will serve as a general procedure for the preparation of 5-silyl substituted 2-thiophenecarboxaldehyde diethylacetals. All of the following procedures were carried out under nitrogen atmospheres.

To II (10 g., 0.054 mole) in 200 ml. of anhydrous ether in a flask equipped with a truebore stirrer, Fredrick condenser and a dropping funnel was added *n*-butyllithium (38.5 ml., 1.4 *N*) at ambient temperature. The solution became black during the reaction time of 1 hour after which time trimethylchlorosilane (5.87 g., 0.54 mole) was added in a dropwise manner with a concomitant color change from black to orange brown. The reaction mixture was allowed to stir and reflux gently overnight, then filtered, shaken with water and the ether layer dried over anhydrous sodium sulfate. The ethereal solution was filtered, the ether evaporated under reduced pressure and the residue distilled *in vacuo* to give III (6.5 g., 93.5%) boiling at 149-150°/23 mm.

The preparation of 2-methyl-2-[2-(5-alkyl and arylsilyl)thienyl]-1,3-dioxolanes was accomplished by the procedure described by Thames and McCleskey (1). The preparation of 2-methyl-2-(5-trimethylsilyl)thienyl]-1,3-dioxolane (XI) will serve as an example procedure. All reactions were carried out under a nitrogen atmosphere.

## 2-Methyl-2-(5-trimethylsilyl)thienyl]-1,3-dioxolane (XI).

To I (10 g., 0.058 mole) in 200 ml. of dry ether in a 250 ml. three neck flask equipped with dropping funnel, truebore stirrer, and Fredrick condenser was added 37 ml. of *n*-butyllithium (1.6 *N*) in a dropwise manner over a period of 20 minutes. This mixture was allowed to react at room temperature for 1.5 hours after which time trimethylchlorosilane (6.3 g., 0.058 mole) was added. The reaction mixture was gently refluxed overnight, the lithium chloride removed by filtration, and the ether evaporated under reduced pressure. The residue was distilled *in vacuo* to yield 8.65 g. (75.5%) of XI boiling at 81°/0.1 mm.

The general procedure for the conversion of 2-methyl-2-[2-(5-alkyl and arylsilyl)thienyl]-1,3-dioxolanes and 2-(5-alkyl and arylsilyl)thiophenecarboxaldehyde diethylacetals to the corresponding ketones and aldehydes will be exemplified by the production of 2-(5-trimethylsilyl)thiophenecarboxaldehyde (VI) from the corresponding diethylacetal.

## 2-(5-Trimethylsilyl)thiophenecarboxaldehyde (VI).

An ethereal solution of III (6.5 g., 0.025 mole) was added to 25 ml.

of 6 *N* hydrogen chloride and refluxed for 4 hours. The layers were separated and the aqueous phase extracted with two 25 ml. portions of ether. The combined ether extracts were washed with water, dilute sodium carbonate and again with water before drying over anhydrous sodium sulfate. The ether was evaporated and the residue distilled to afford 3.2 g. (65%) of VI boiling at 80°/0.45 mm.

The 2,4-dinitrophenylhydrazone derivative was prepared in the usual manner with a melting point of 233.5-235°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>SSi: C, 46.13; H, 4.42. Found: C, 46.30; H, 4.67.

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