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# ORGANOSILICON COMPOUNDS

# XIV. THE CLEAVAGE OF 2-(TRIMETHYLSILYL)- AND 2-(TRIMETHYLSTANNYL)-1-METHYLPYRROLE AND -THIOPHENE WITH SOME CARBONYL-CONTAINING REAGENTS

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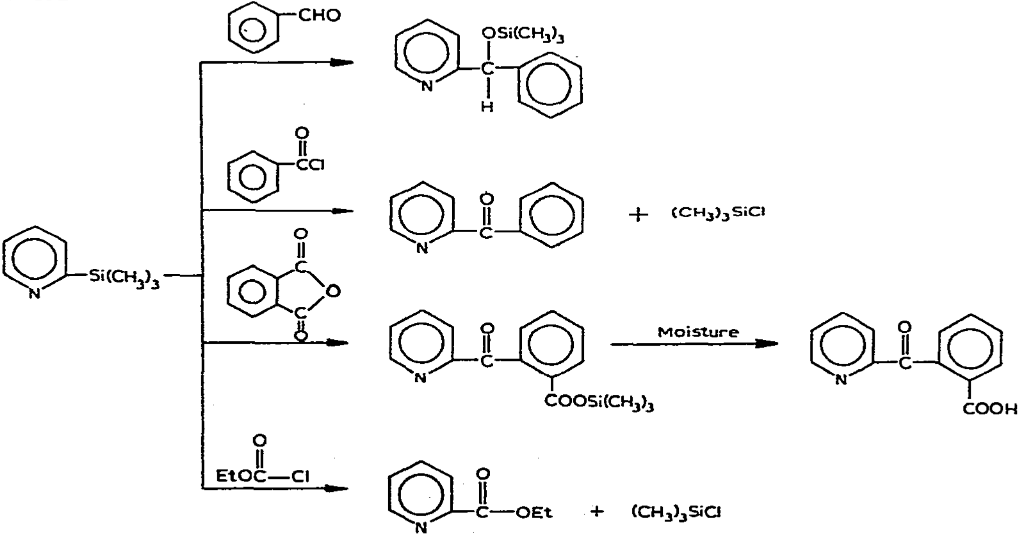
## SUMMARY

Cleavage of the metal–carbon bond of 2-(trimethylsilyl)- and 2-(trimethylstannyl)-1-methylpyrrole and -thiophene with several carbonyl-containing reagents has been effected and substantiates our previous tenet for the importance of bond polarity on reactivity

## INTRODUCTION

The silicon–carbon bond of 2-(trimethylsilyl)pyridine has recently been shown to react with certain neutral, non-protic reagents such as benzaldehyde, benzoyl

SCHEME A



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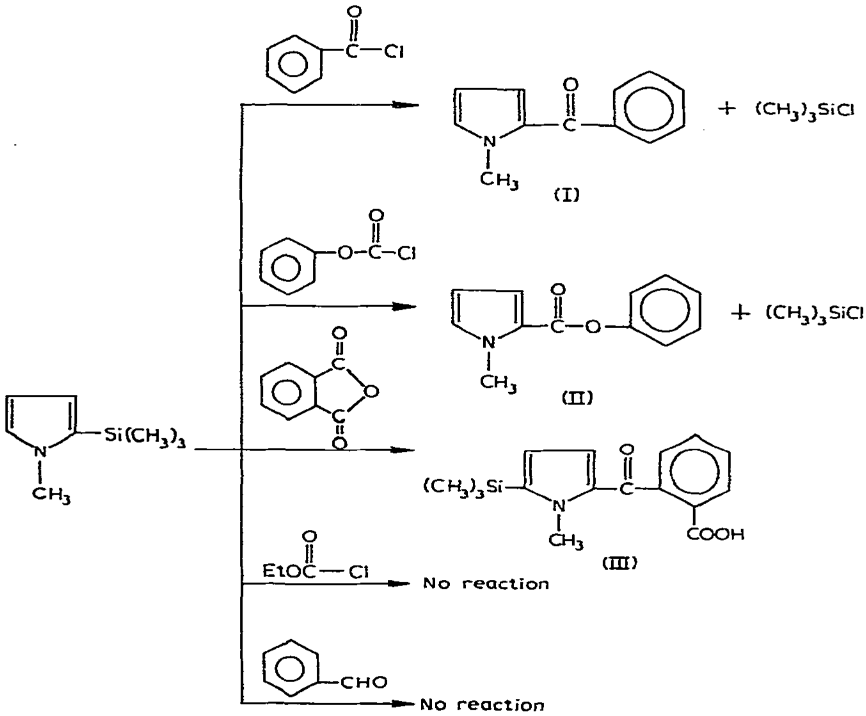
chloride, ethyl chloroformate, and phthalic anhydride (Scheme A)[1,2]. To account for this reactivity a polar silicon–carbon bond was postulated as a requirement for the formation of a cyclic four-membered transition state.

In an attempt to expand the scope of this reaction and further ascertain the importance of metal–carbon bond polarity, we have investigated the reactivity of 2-(trimethylsilyl)- and 2-(trimethylstannyl)-1-methylpyrrole and -thiophene with some carbonyl containing reagents. We have extended our investigation to include organotin compounds, as it was our tenet that the utilization of the larger, more polarizable tin atom would engender reactivity to otherwise inert substituted heterocycles.

## RESULTS AND DISCUSSION

1-Methyl-2-(trimethylsilyl)pyrrole reacted with benzoyl chloride, phenyl chloroformate, and phthalic anhydride to form phenyl 1-methyl-2-pyrrolyl ketone (I), phenyl 1-methylpyrrole-2-carboxylate (II), and 2-carboxyphenyl 1-methyl-5-(trimethylsilyl)-2-pyrrolyl ketone (III) in 72, 46, and 25% yields respectively (Scheme B).

SCHEME B

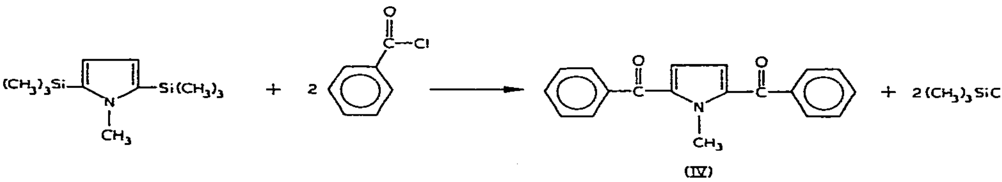


The isolation of (III) was entirely unexpected, and its structure was further verified by an unambiguous synthesis. We suspect that it arose through acylation of 1-methyl-2-(trimethylsilyl)pyrrole, since such reactions of organosilicon compounds have been been reported[3].

No reaction was detected between 1-methyl-2-(trimethylsilyl)pyrrole and benzaldehyde or with ethyl chloroformate, even after refluxing for 18 and 26 h respectively. We attributed the reactivity of phenyl chloroformate, as compared to ethyl chloroformate, to the electron withdrawal capability of the phenyl group and/or to the higher boiling point of the former, thereby permitting the attainment of higher reaction temperatures.

Analogously, 1-methyl-2,5-bis(trimethylsilyl)pyrrole reacted with benzoyl chloride to form the 2,5-diketone (IV) in 4% yield (Scheme C).

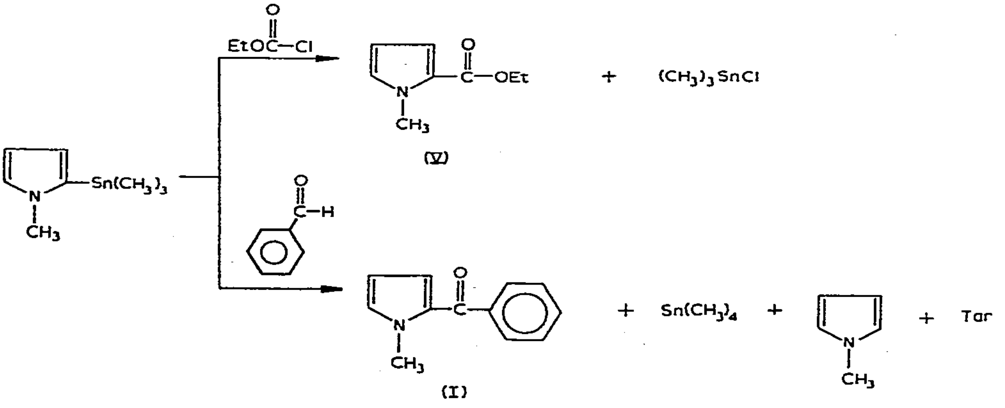
SCHEME C



It is interesting to note that, whereas 2-(trimethylsilyl)pyridine reacted with several carbonyl containing reagents in good yields and, in one case (ethyl chloroformate), exothermically, 1-methyl-2-(trimethylsilyl)pyrrole reacted correspondingly with these reagents in poor yields or not at all, and was accompanied in every case by the production of tarry materials under reaction conditions of mild reflux. We explain the lack of reactivity of 1-methyl-2-(trimethylsilyl)pyrrole with benzaldehyde as a result of the combined influence of the reduced polarity of the silicon–carbon bond, due to the positive induction of the *N*-methyl group and to electronic differences between the pyridine and 1-methylpyrrole rings, as well as the reduced polarity of benzaldehyde as compared to the chloroformate, anhydride, and acid chloride moieties.

Although the electronegativities of silicon and tin are comparable[4], the lower strength and greater polarizability[5] of bonds to tin enhance the cleavage reaction of 2-(trimethylstannyl)-substituted compounds. For instance, 1-methyl-2-(trimethylstannyl)pyrrole reacted with ethyl chloroformate and benzaldehyde to form ethyl 1-methylpyrrole-2-carboxylate (V) and the unexpected phenyl 1-methyl-2-pyrrolyl ketone (I) in yields of 28 and 57 % respectively (Scheme D). The isolation of the ketone

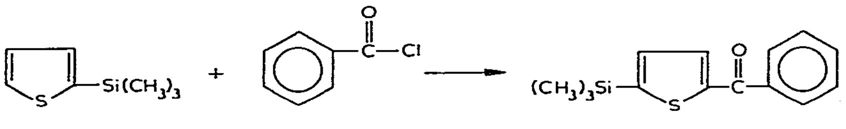
SCHEME D



may be explained by the oxidation of the stannyl ether intermediate under the reaction conditions used, although this intermediate was not isolated. The isolation of tetramethyltin and 1-methylpyrrole rather than the expected trimethyltin hydride has not been explained.

The reaction of benzoyl chloride with 2-(trimethylsilyl)thiophene provided the unexpected substituted product, phenyl 5-(trimethylsilyl)-2-thienyl ketone (VI) in 17% yield (Scheme E). However, no reaction was detected between 2-(trimethylsilyl)thiophene and benzaldehyde, phenyl chloroformate, or phthalic anhydride after reflux periods of 21, 24, and 14 h respectively.

SCHEME E

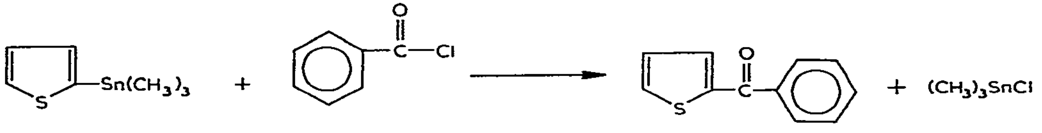


(VI)

The thiophene nucleus was not activated by multiple halogen substitution, as 2-(trimethylsilyl)trichlorothiophene failed to react with benzaldehyde[6], benzoyl chloride, and phenyl chloroformate.

However, 2-(trimethylstannyl)thiophene (VII) did indeed react with benzoyl chloride to provide a 45% yield of phenyl 2-thienyl ketone (VIII) and trimethyltin chloride (Scheme F). No reaction was detected with phthalic anhydride, and only a trace of unidentified product (containing several carbonyl stretching frequencies in the IR) was noted when benzaldehyde was used.

SCHEME F



(VII) (VIII)

The reaction of (VII) with phenyl chloroformate provided trimethyltin chloride, diphenyl carbonate, and a small quantity of material believed by spectral data to be phenyl thiophene-2-carboxylate, although the latter could not be purified for a complete identification.

Finally, more recent results in these laboratories have established the reactive nature of 1-methyl-2-(trimethylsilyl)imidazole[7], 1-methyl-2-(trimethylsilyl)benzimidazole[7], and 2-(trimethylsilyl)benzothiazole[8], each of which reacted, often exothermically, with all of the previously mentioned carbonyl reagents in yields ranging from 70–95%. Thus, the high yields and reactivity of these silicon substituted heterocycles (in contrast to those of 1-methylpyrrole and thiophene) again emphasize the necessity of a polar metal–carbon bond. Such polarity is indeed achieved in these latter three reactive heterocycles via flanking the metal–carbon bond with multiple heteroatoms.

We are continuing our efforts in the study of the reaction of silicon and tin substituted heterocycles with these and other cleavage reagents. Future efforts will be directed toward ascertaining the possible role of charge-transfer complexes in these and other similar transformations.

## EXPERIMENTAL

The NMR spectra reported herein were obtained on a Varian A-60D spectrometer at approximate concentrations of 40% by volume in $CCl_4$ unless otherwise noted and were referenced to TMS as an internal standard. The IR spectra were obtained on a Perkin–Elmer 257 grating spectrometer. Melting points are uncorrected. Yields were not optimized and in most cases were low due, in part, to non-identifiable decomposition products. All reactions were run under nitrogen in glassware previously dried at 110° for several hours.

### *Phenyl 1-methyl-2-pyrrolyl ketone (I)*

*Method a: Cleavage of 1-methyl-2-(trimethylsilyl)pyrrole with benzoyl chloride.* Benzoyl chloride (14.6 g, 0.103 mole) and 1-methyl-2-(trimethylsilyl)pyrrole[9] (15.8 g, 0.103 mole) were refluxed for 12 h at 165°. Trimethylchlorosilane was collected as the reaction progressed. Fractional distillation of the mixture afforded 13.7 g (72%) of (I), b.p. 131–133°/0.85 mm, $n_D^{25}$ 1.6148. (Found: C, 77.73; H, 6.06; N, 7.56. $C_{12}H_{11}NO$ calcd.: C, 77.81; H, 5.98; N, 7.56%.) 2,4-DNP of (I), m.p. 203–204°.

The NMR of (I) showed a multiplet at $\delta$ 7.24–8.00, a triplet at $\delta$ 6.78, a quartet at $\delta$ 6.61, a quartet at $\delta$ 6.02, and a singlet at $\delta$ 3.95 ppm representing the five phenyl protons, the 5-, 3-, and 4-pyrrole ring protons, and the *N*-methyl protons respectively and integrated as 5/1/1/1/3.

*Method b: Cleavage of 1-methyl-2-(trimethylstannyl)pyrrole with benzaldehyde.* Benzaldehyde (7.5 g, 0.0705 mole) and 1-methyl-2-(trimethylstannyl)pyrrole[10] (17.2 g, 0.0705 mole) were refluxed for 12 h at 195°, collecting the low boiling material as the reaction progressed.

Fractionation of the tarry residue afforded 7.4 g (57%) of (I), b.p. 81.5–82°/0.04 mm, 2,4-DNP m.p. 203–204°. A mixed melting point of the 2,4-DNP derivatives of (I) by methods *a* and *b* showed no depression. Both the IR (neat) and NMR spectra of (I) prepared by methods *a* and *b* were identical.

The low boiling material (7.3 g) collected during the reaction was shown by GLC on 10% Carbowax to be composed only of tetramethyltin (73%) and 1-methylpyrrole (27%) as follows. A sample of the first component was collected for analysis. The NMR showed a single line at $\delta$ 0.23 ppm. (Found: C, 26.94; H, 6.39. $C_4H_{12}Sn$ calcd.: C, 26.87; H, 6.76%.) The second component had an identical retention time as, and showed only one component when mixed with 1-methylpyrrole. In addition the NMR spectrum of this GLC separated component and an authentic sample of 1-methylpyrrole were identical.

### *Phenyl 1-methylpyrrole-2-carboxylate (II)*

Phenyl chloroformate (6.0 g, 0.039 mole) and 1-methyl-2-(trimethylsilyl)pyrrole (6.0 g, 0.039 mole) were refluxed for 34 h at 145°. Trimethylchlorosilane (1.7 g, 40%) was collected as the reaction progressed. Fractional distillation of the product yielded a crude solid material which was subsequently recrystallized from ethanol to afford 3.6 g (46%) of (II), m.p. 50–52°. (Found: C, 71.81; H, 5.38. $C_{12}H_{11}NO_2$ calcd.: C, 71.63; H, 5.51%.)

The IR of (II) showed a strong carbonyl stretch at 5.8 μ. The NMR showed a multiplet at δ 7.00–7.60 representing the five phenyl protons and the 3-pyrrole ring proton, a broad doublet at δ 6.75 representing the 5-pyrrole ring proton, a multiplet at δ 6.00–6.20 representing the 4-pyrrole ring proton, and a singlet at δ 3.90 ppm representing the three *N*-methyl protons and integrated respectively as 6/1/1/3.

### 2-*Carboxyphenyl 1-methyl-5-(trimethylsilyl)-2-pyrrolyl ketone (III)*

Phthalic anhydride (10.0 g, 0.068 mole) and 1-methyl-2-(trimethylsilyl)pyrrole (10.4 g, 0.068 mole) were heated for 14 h at 160–180°. On cooling, unreacted phthalic anhydride (6.0 g, 60%) crystallized out of the reaction solution and then was filtered and washed with warm hexane. After the hexane had been removed *in vacuo*, the unreacted 1-methyl-2-(trimethylsilyl)pyrrole (5.7 g, 55%) was distilled, and the solid residue was recrystallized from ethanol/water (50/50) to afford 5.0 g (25%) of (III), m.p. 154–156°. (Found: C, 63.94; H, 6.14. $C_{16}H_{19}NO_3Si$ calcd.: C, 63.75; H, 6.37%.)

The NMR of (III) showed a broad singlet at δ 10.33 representing the acid proton, a multiplet at δ 7.30–8.10 representing four phenyl protons, a singlet at δ 6.25 representing the two pyrrole ring protons, a singlet at δ 4.13 representing the three *N*-methyl protons, and a singlet at δ 0.34 ppm representing the trimethylsilyl protons and integrated respectively as 1/4/2/3/9.

(III) was unambiguously synthesized by treating 1-methyl-2-(trimethylsilyl)-pyrrole with a solution of n-butyllithium in hexane at room temperature, followed by adding the freshly prepared 1-methyl-2-(trimethylsilyl)-5-lithiopyrrole dropwise to an ethereal solution of phthalic anhydride at 0°. After the work-up procedure, the resultant solid was recrystallized from ethanol/water to afford 13% of (III), m.p. 154–156°. A mixed melting point of (III) and the unambiguously synthesized product showed no depression.

### 1-*Methyl-2,5-dibenzoylpyrrole (IV)*

Benzoyl chloride (12.7 g, 0.09 mole) and 1-methyl-2,5-bis(trimethylsilyl)pyrrole[9] (10.2 g, 0.045 mole) were refluxed for 11 h at 218°. Trimethylchlorosilane (6.95 g, 71%) was collected as the reaction progressed. Recrystallization of the resultant tar from heptane, after treatment with charcoal, afforded 0.5 g, (4%) of colorless plates, m.p. 135.5–137.5°. (Found: C, 78.60; H, 5.13. $C_{19}H_{15}NO_2$ calcd.: C, 78.87; H, 5.23%.) The remaining tarry material could not be further purified.

The NMR of (IV) in $CDCl_3$ showed a multiplet at δ 7.46–8.05 representing the ten phenyl protons, a singlet at δ 6.66 representing the two aromatic protons on the pyrrole ring, and a singlet at δ 4.32 ppm representing the three *N*-methyl protons and integrated respectively as 10/2/3.

### *Ethyl 1-methylpyrrole-2-carboxylate (V)*

Ethyl chloroformate (3.6 g, 0.0328 mole) and 1-methyl-2-(trimethylstannyl)-pyrrole (8.0 g, 0.0328 mole) were refluxed at 120–130° for 7 h. The crude product was purified by fractionation to give 2.4 g (67%) of recovered ethyl chloroformate, 8.1 g of a fraction which required further purification by GLC, and 1.1 g of tar. The GLC analysis on both 10% Carbowax and 30% SE-30 columns gave a 28% yield (determined by comparison of peak heights with an authentic standard*) of (V) with an

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* This standard was prepared[11] by adding ethyl chloroformate dropwise at −70° to the previously prepared 1-methyl-2-lithiopyrrole, yield 46%, b.p. 110–113°/27 mm.

identical retention time as, and showing only one peak on mixing with, the unambiguously prepared compound. Trimethyltin chloride was similarly identified by GLC and by its melting point, 35°. Lit. reports m.p. 37°.

The NMR of the GLC purified (V) showed an unsymmetrical quartet at $\delta$ 6.86, a triplet at $\delta$ 6.65, and a multiplet at $\delta$ 5.91–6.10 representing the 3-, 5-, and 4-pyrrole ring protons respectively, a quartet at $\delta$ 4.19 representing the two methylene protons, a singlet at $\delta$ 3.82 representing the three *N*-methyl protons, and a triplet at $\delta$ 1.26 ppm representing the three methyl protons of the ethyl group and integrated respectively as 1/1/1/2/3/3. This spectrum was identical with that of the unambiguously prepared standard. The IR exhibited a strong carbonyl stretch at 5.95 $\mu$.

*Phenyl 5-(trimethylsilyl)-2-thienyl ketone (VI)*

Benzoyl chloride (9.03 g, 0.064 mole) and 2-(trimethylsilyl)thiophene[3] (10.0 g, 0.064 mole) were refluxed for 28 h at 162–175°. Fractional distillation of the mixture at reduced pressure afforded a crude product which was further purified by recrystallization from hexanes at −70° to give 2.8 g (17%) of (VI), m.p. 40.5–41°. (Found: C, 64.33; H, 6.16. $C_{14}H_{16}OSSi$ calcd.: C, 64.57; H, 6.19%.) Starting materials (11.3 g) and tar were also isolated from the reaction mixture.

The NMR of (VI) showed a multiplet at $\delta$ 7.15–8.03 representing the seven aromatic protons and a singlet at $\delta$ 0.37 ppm representing the nine trimethylsilyl protons and integrated respectively as 7/9.

A 2,4-DNP was prepared, m.p. 195–197°. (Found: C, 54.71; H, 4.43; N, 12.77; Si, 6.58. $C_{20}H_{20}N_4O_4SSi$ calcd.: C, 54.53; H, 4.58; N, 12.72; Si, 6.38%.)

*2-(Trimethylstannyl)thiophene (VII)*

An anhydrous ethereal solution of 15.1 g (0.18 mole) of freshly distilled thiophene was treated dropwise at 0° with 76 ml (0.18 mole) of 2.37 *N* n-butyllithium solution in hexane. The mixture was allowed to stand with stirring at room temperature for 3 h before 35 g (0.18 mole) of trimethyltin chloride in ether was added dropwise. After a 4 h reaction period the lithium chloride was removed by filtration and the filtrate washed with very dilute acetic acid and water. After drying over anhydrous $MgSO_4$ and removal of the ether *in vacuo*, the product was distilled to afford 31.5 g (71%) of (VII), b.p. 97–99°/33 mm, $n_D^{26}$ 1.5408. (Found: C, 34.33; H, 4.69. $C_7H_{12}SSn$ calcd.: C, 34.05; H, 4.90%.)

The NMR spectrum of (VII) showed a multiplet at $\delta$ 7.04–7.69 representing the three aromatic protons and a singlet at $\delta$ 0.34 ppm representing the nine trimethylstannyl protons and integrated respectively as 3/9.

*Phenyl 2-thienyl ketone (VIII)*

Benzoyl chloride (5.8 g, 0.041 mole) and 2-(trimethylstannyl)thiophene (VII) (10.2 g, 0.041 mole) were refluxed for 6 h at 172°. Fractional distillation of the mixture afforded trimethyltin chloride (3.45 g, 42%), 3.5 g (45%) of (VIII), b.p. 78–80°/0.04 mm, and unreacted starting materials. (VIII) was subsequently recrystallized from hexanes to give a solid, m.p. 55–56°, exhibiting no depression on melting with an authentic sample of the known compound. Lit.[12] reports b.p. 143–144°/4.0 mm, m.p. 56.5–57°. The 2,4-DNP of (VIII), m.p. 220–221°, melted identically with that of the 2,4-DNP of an authentic sample of phenyl 2-thienyl ketone, and a mixed melting point showed no depression.

The NMR of (VIII) exhibited only an unassignable multiplet at $\delta$ 6.98–7.96 ppm.

### *The reaction of 2-(trimethylstannyl)thiophene with phenyl chloroformate*

Freshly distilled phenyl chloroformate (17.4 g, 0.110 mole) and 2-(trimethylstannyl)thiophene (13.6 g, 0.055 mole) were refluxed for 26.5 h at 150–186°, and 1.5 g of trimethyltin chloride was collected as the reaction progressed. Fractionation of the reaction mixture and subsequent comparison of GLC retention times and peak heights with those of authentic samples on a 30% SE-30 column resulted in a 75% recovery of phenyl chloroformate and a 48% recovery of 2-(trimethylstannyl)thiophene. In addition to a small yield of tarry material which could not be identified, 6.5 g of crude, high boiling product was isolated. This material was further purified by recrystallization from hexanes and identified as diphenyl carbonate, m.p. 79.5–80°. Lit. reports m.p. 83°. (Found: C, 73.10; H, 4.82. $C_{13}H_{10}O_3$ calcd.: C, 72.89; H, 4.71%.)

The NMR of this compound showed a singlet at $\delta$ 7.30 ppm; the IR displayed a strong absorption at 5.6 $\mu$ (KBr pellet). The yield was estimated by NMR to be 28%.

Attempts to further purify and identify the remaining component in the high boiling fraction by fractional crystallization, GLC, TLC, and vacuum sublimation were unsuccessful. Based only on spectral evidence, however, a small yield of phenyl thiophene-2-carboxylate was indicated; *i.e.*, the IR exhibited a strong absorption at 5.8 $\mu$; the NMR exhibited a multiplet at $\delta$ 7.81–8.00 and a multiplet at $\delta$ 6.99–7.69 ppm characteristic of thiophene and phenyl protons.

## ACKNOWLEDGEMENT

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