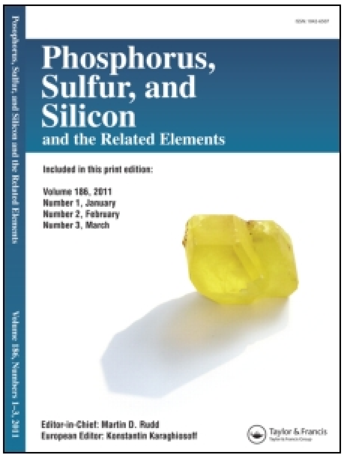

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SEPARATION OF TRIORGANOSTANNYL- AND BIS(TRIORGANOSTANNYL) BITHIOPHENE

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Separation of an organomonostannane from an organobistannane in good yields via column chromatography on neutral Alumina.

Keywords: thiophenes; stannyl compounds

The reduction of organic halides by organostannanes, first reported by VanderKerk et al.[1] has subsequently found numerous applications. The general method for the isolation of reduction products from the organotin halide byproducts. The desired separation of reduction product and organotin halide can be accomplished by conversion of the organotin halide (R_3SnX; $x = Cl, Br, I$) into the insoluble organotin fluoride[2] by simply extracting the reduction mixture, dissolved in a nonpolar solvent with a solution of potassium fluoride in water. The organotin halide is converted to an insoluble (in either the organic or aqueous phase) organotin fluoride which can be readily separated by filtration.

In connection with our studies on the palladium catalyzed cross-coupling (Stille) reaction of thiophene and 2,2′-bithiophene[3] for the construction of carbon-carbon bonds. We would like to report here the preliminary results of the general method for the isolation of an organomontin from an organobitin and the concomitantly formed organotin halide. 2,2′-Bithiophene (**1**) was prepared following the literature reports.[4,5] Stannanes 5,5′-bis(tri-n-butylstannyl)bithiophene **2** and 5-(tri-n-butylstannyl)bithi-

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ophene **3** were prepared by treatment of 2,2'-bithiophene **1** with n-BuLi at −78°C followed by trapping with tri-n-butyltin chloride. The desired separation and isolation of an organomonotin **3** from an organobitin **2**. It is very necessary to use very pure sample of organotin compound and it is important to comment about the purification. It was reported[6] that the 2,2'-bithiophene bitin was not very stable, and column chromatography on Silica gel converted about half of it to the monostannylbithiophene and starting materials. There is no reports for the separation of an organomonotin from an organobitin until now.

The crude products were dissolved in nonpolar organic solvent (hexane) and stirred for 10 h. with KF solution to convert the unreacted tributyltin chloride into their corresponding tributyltin fluoride and then isolated by filtration. Evaporated the solvent to give the combined crude product which was loaded on neutral Alumina and the columns were eluted with hexane to remove the unwanted tin compounds. Subsequent elution with polar solvent mixture (hexane/EtOAc, 100:1) isolated 5,5'-bis(tri-n-butystannyl)2,2'-bithiophene (**2**) as a clear yellow oil in 67% yield and 5-(tri-n-butystannyl)2,2'-bithiophene **3** as a colorless oil in 26% yield. The structure of products (**2**) and (**3**) were monitored by TLC and GC at $R_f = 0.9$ for bitin and $R_f =$ o. 7 for monotin.

SCHEME 1

The ^1H NMR (500 MHz, $CDCl_3$) spectrum of 5,5'-bis(tri-n-butystannyl) 2,2'-bithiophene **2** exhibited two doublet signals at δ 7.34 and δ 7.10 for four hydrogen proton at positions [(4 and 4') and (3 and 3')] respectively at the same coupling constant J = 3.3 Hz. 5-(Tri-n-butystannyl)2,2'-bithiophene **3** exhibited also three signals doublet for doublet at δ 7.29, δ 7.003 and δ 7.02 for three hydrogen proton at position 5', 4' and 3' respectively with different coupling constant (J = 1.2 and 4.8 Hz), (J = 1.29 and 3.26 Hz), and (J = 3.28 and 4.8 Hz) respectively. It shown to us two doublet signals at δ 7.16 and δ 7.05 for two hydrogen proton at positions (3 and 4) with the same coupling constant J = 3.26 Hz.

Another piece of evidence to support our assignments for the structures **2** and **3** was obtained from the MM2 calculations[7] for the minimum and total steric energy, as illustrated in figure 1. It is important to point out that we have examined steric energies from 125.1285 kcal/mole to the lowest energy structure at 33.1426 kcal/mole over 141 iterations for structure **2** and steric energies from 104.6578 kcal/mole to the lowest energy structure at 27.3109 kcal/mole over 128 iterations for structure **3**. The lone pairs into sulfur of thiophene, and all Pi System were taken into consideration is because both parameters are incorporated into conjugation which was effect on the calculations, and also due to high VDW interactions, some terms were not computed during the run. Minimization terminated normally, because the gradient norm was less than the minimum gradient norm.

FIGURE 1 MM2 Calculations for compounds **2** and **3**

*Steric Energy for structure **2**;*		*Minimize Energy for structure **2***	
Stretch:	57.4565	Stretch:	1.3970
Bend:	21.5796	Bend:	13.5360
Stretch-Bend:	−1.8622	Stretch-Bend:	0.1921
Torsion:	12.9201	Torsion:	12.9779
Non-1,4 VDW:	14.7986	Non-1,4 VDW:	−10.7089
1,4 VDW:	17.6140	1,4 VDW:	13.0847
Dipole/Dipole:	2.6218	Dipole/Dipole:	2.6639
Total steric energy:	125.1285	Total of minimum energy:	33.1426

Steric Energy for structure 3;		*Minimize Energy for structure 3*;	
Stretch:	57.0906	Stretch:	0.8020
Bend:	19.1359	Bend:	10.7316
Stretch-Bend:	−2 2693	Stretch-Bend:	−0.0859
Torsion:	13.0716	Torsion:	13.0613
Non-1,4 VDW:	7.3334	Non-1,4 VDW:	−5.5206
1,4 VDW:	8.6011	1,4 VDW:	6.5994
Dipole/Dipole:	1.6946	Dipole/Dipole:	1.7232
Total steric energy:	104.6578	Total of minimum energy:	27.3109

EXPERIMENTAL SECTION

5,5′-Bis[tri-n-butylstannyl]-2,2′-bithiophene (2) and 5-[Tri-n-butylstannyl]-2,2′-bithiophene (3)

To a solution of 2,2′-bithiophene 1 (1.079 g, 6.45 mmol) in (8 mL) THF, n-BuLi (6.9 mL, 17.28 mmol, of a 2.5 M hexane solution) was added under nitrogen atmosphere at 0°C. The reaction mixture was heated at 40°C for 3 h. then cooled to RT and a solution of tributyltin chloride (5.85 g, 18 mmol) in (8 mL) THF was added. The reaction mixture was stirred at RT for 24 h. and then the solvent was evaporated. The residue was dissolved in benzene and the solution was washed twice with aqueous saturated KF and aqueous saturated NH_4Cl. The organic layer was dried by anhydrous Na_2SO_4, concentrated and then purified by flash chromatography using neutral Alumina (hexane's / EtOAc; 100:1) to give bitin **2** (500 mg, 0.67 mmol) in 67 % yield as a clear yellow oil, and monotin **3** (119 mg, 0.26 mmol) in low yield (26%) as a colorless oil.

Compound (**2**) TLC: R_f (hexane's / EtOAc; 100:1); 0.9; LRMS (EI): m/z 634 ($[M^+\text{-}(C_4H_9)_2]$, 100), 615 (100), 557 (80), 539 (40), 476 (25), 432 (22), 345 (18), 288 (18), 161 (22), 105 (15), and 44 (100).; GC: t_R = 12.036 min.; column; DB-5 6 m × 0.01 mm +1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C $min.^{-1}$ / 250 °C / 5 min..

^1H NMR ($CDCl_3$, 500 MHz): δ 7.34 (d, J = 3.3 Hz, $Ar\text{-}H_4H_{4'}$), 7.10 (d, J = 3.3 Hz, $Ar\text{-}H_3H_{3'}$), 1.63 (tt, J = 8.4 and 7.7 Hz, 12H, $ArSnCH_2C\underline{H}_2CH_2CH_3$), 1.36 (tq, J = 7.6 and 7.8 Hz, 12H,

$ArSn(CH_2)_2C\underline{H}_2CH_3$), 1.12 (t, J = 7.9 Hz, 12H, $ArSnC\underline{H}_2CH_2CH_2CH_3$), 0.98 (t, J = 7.1 Hz, 12H, $ArSn(CH_2)_3C\underline{H}_3$) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 136.1, 136.0, 124.7, 29.01, 27.29, 13.69, and 10.92 ppm.

Compound (3) TLC: R_f (hexane's / EtOAc 100:1); 0.7; LRMS (EI): m/z 456 (M+, 6), 399 (100), 343 (45), 311 (<2), 285 (77), 259 (<3), 234 (5), 177 (23), 175 (15), 166 (58), 133 (100), 89 (20), 57 (7), and 41 (50).; GC: t_R = 13.05 min.; column; DB-5 6 m × 0.o1 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C $min.^{-1}$ / 250 °C / 5 min.

^1H NMR ($CDCl_3$, 500 MHz): δ 7.29 (dd, J = 1.2 and 4.8 Hz, Ar-$H_{5'}$), 7.16 (d, J = 3.3 Hz, Ar-H_3), 7.1 (dd, J = 1.3 and 3.3 Hz, Ar-$H_{3'}$), 7.05 (d, J = 3.3 Hz, Ar-H4), 7.003 (dd, J = 3.3 and 4.8 Hz, Ar-$H_{4'}$), 1.66 (tt, J = 7.7 and 7.7 Hz, 6H, $ArSnCH_2C\underline{H}_2CH_2CH_3$), 1.36 (tq, J = 7.6 and 7.8 Hz, 6H, $ArSnCH_2CH_2C\underline{H}_2CH_3$), 1.44 (t, J = 7.5 Hz, 6H, $ArSnC\underline{H}_2CH_2CH_2CH_3$), 0.96 (t, J = 7.1 Hz, 9H, $ArSnCH_2CH_2CH_2\ C\underline{H}_3$) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 136.1, 127.76, 125.05, 124.76, 124.40, 123.82, 123.51, 29.03, 27.31, 13.70, and 10.96 ppm.

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