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SYNTHESIS OF DITHIENOTHIOPHENES, CYCLOPENTADITHIOPHENE AND SILACYCLOPENTADITHIOPHENES USING PALLADIUM-CATALYZED CYCLIZATION

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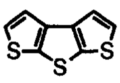
Abstract: The intramolecular cyclization of bromothiophene derivatives with hexamethylditin in the presence of tetrakis(triphenylphosphine)palladium(0) gave dithienothiophenes, cyclopentadithiophene, and silacyclopentadithiophenes in moderate to good yields. © 1997 Elsevier Science Ltd.

Dithienothiophenes (**1**, **2** and **3**) have received considerable attention, because dithienothiophenes possess three different types of π-conjugations which play an important role as a spacer and donor,[1] and because these compounds give conjugated polymers with unique features.[2] Although [3,2-b: 2',3'-d]dithienothiophene (**3**) can be easily prepared and has been employed frequently,[3] the synthetic inconvenience of [2,3-b:3',2'-d]- and [3,4-b:3',4'-d]dithienothiophenes (**1** and **2**) and related compounds (**4-6**) has prevented the use of these compounds as building blocks for organic synthesis. We report here a convenient method for the synthesis of dithienothiophenes, cyclopentadithiophene and silacyclopentadithiophenes (**1**, **2** and **4-6**).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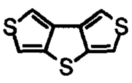
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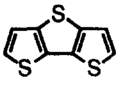
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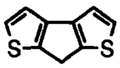
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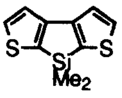
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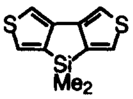
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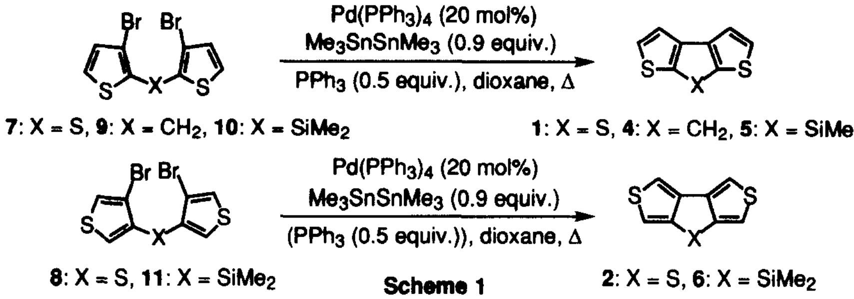
In order to develop a new and general method for the synthesis of **1**, **2** and **4-6**, we investigated transition metal-catalyzed intramolecular cyclization reactions. The new method for the preparation of these compounds is outlined in Scheme 1 and Table 1.[4] The palladium-catalyzed cyclization of **7** was carried out using 20 mol% of $Pd(PPh_3)_4$, 0.9 equiv. of hexamethylditin, and 0.5 equiv. of triphenylphosphine in dioxane at 160 °C for 24 h to produce **1** in 75% yield (Entry 3). The reaction produced **1** in 55% yield at 110 °C for 24 h, but 38% of **7** was recovered (Entry 1). The reaction required 20 mol% of $Pd(PPh_3)_4$, and a similar reaction using 15 mol% of $Pd(PPh_3)_4$ gave the product **1** in 67% yield (Entry 2). On the basis of these results, the palladium-catalyzed cyclization of **8** was carried out with $Me_3SnSnMe_3$ (0.9 equiv.) in the presence of 20 mol% of $Pd(PPh_3)_4$ to produce **2** in 78% yield (Entry 4). In the case of **9**, a similar reaction with $Me_3SnSnMe_3$ and $Pd(PPh_3)_4$ [160 °C, 24 h] gave **4** only in 20% yield, but a lower temperature and longer time [110 °C, 96 h] enhanced the cyclization (Entry 5). Interestingly, the cyclization of the silicone derivatives **10**[5] and **11**[5] proceeded smoothly under palladium-catalyzed conditions to produce the corresponding silole derivatives **5** and **6** in good yields (Entry 6 and 7).[6] In the absence of PPh_3, the reaction of **11** produced **6** in a better yield (Entry 7). The oxidative addition of the C-Br bonds in **7**-**11** to the Pd(0) complex, followed by transmetallation and reductive elimination, produces monostannylated compounds which lead to the cyclization products by palladium-catalyzed intramolecular cross-coupling reaction.



7: X = S, **9**: X = CH_2, **10**: X = $SiMe_2$ **1**: X = S, **4**: X = CH_2, **5**: X = $SiMe_2$

8: X = S, **11**: X = $SiMe_2$ **2**: X = S, **6**: X = $SiMe_2$

Scheme 1

Table 1. Palladium-catalyzed intramolecular cyclization.[a]

Entry	Compound	$Pd(PPh_3)_4$ /mol%	Temp./C	Time/h	Product	Yield/%
1[b]	**7**	15	110	24	**1**	55
2	**7**	15	160	24	**1**	67
3	**7**	20	160	24	**1**	75[c]
4	**8**	20	160	72	**2**	78[c]
5	**9**	20	110	96	**4**	50[c]
6	**10**	20	160	72	**5**	72[d]
7[b]	**11**	20	160	72	**6**	64[c]

[a] A solution of the dibromide (0.25 mmol), $Me_3SnSnMe_3$ (0.225 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and PPh_3 (0.125 mmol) in dioxane (2.5 ml) was heated in a sealed tube. The yields were determined by gas-chromatographic analysis. [b] In the absence of PPh_3. [c] Isolated yields. [d] The isolated yield is 69%.

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References and Notes

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5) The compounds **10** and **11** were prepared in 66 and 60% yields, respectively, by the reactions of 2,3- and 3,4-dibromothiophenes with Bu^nLi (1 eq.), followed by treatment with Me_2SiCl_2 (0.5 equiv.).
6) The structures of all new compounds reported here were fully characterized by spectroscopic analyses. The selected data are as follows: **5**: colorless oil, bp 84-86 °C/2.5 torr, MS (*m/z*) 222 (M^+), 208, 147; ^1H NMR (CD_2Cl_2) δ 7.50 (d, J = 4.9 Hz, 2H), 7.12 (d, J = 4.9, 2H), 0.80 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ 132.7, 132.0, 131.2, 118.5, -1.0. **6**: colorless cryst., mp 103-104 °C, MS (*m/z*) 222 (M^+), 208, 147; ^1H NMR (CD_2Cl_2) δ 7.64 (d, J = 2.4 Hz, 2H), 7.54 (d, J = 2.4, 2H), 0.41 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ 148.2, 147.8, 131.8, 116.1, -1.1.

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