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Preparation of 2,5-Bis(diarylmethylene)-2,5-dihydrothiophenes and Their Furan, Selenophene, and *N*-Methylpyrrole Analogs

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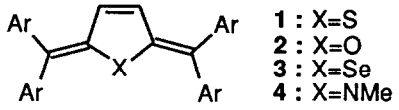
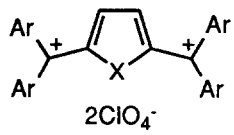
Key Words: 2,5-dimethylene-2,5-dihydrofuran; 2,5-dimethylene-2,5-dihydrothiophene; 2,5-dimethylene-2,5-dihydroselenophene; *N*-methyl-2,5-dimethylene-2,5-dihydropyrrole

Abstract: A series of 2,5-bis(diarylmethylene)-2,5-dihydrothiophenes and their furan, selenophene, and *N*-methylpyrrole analogs were synthesized in three steps either starting from 2,5-dilithiated five-membered heteroaromatics and 2 equiv of diaryl ketones or from 2,5-diaroyl five-membered heteroaromatics and 2 equiv of aryllithiums.

Recently 2,5-dimethylene-2,5-dihydrothiophenes[1] have been attracting much attention because of their amphoteric property as electron-donors[2,3] and acceptors[4,5] depending on the nature of substituents on the exocyclic double bonds. In connection with our previous investigation on the reactivity of tri-2-thienylcarbenium salts,[6] we have become interested in the reactivity of bis-carbenium salts **5**. We report here a convenient synthesis of 2,5-bis(diarylmethylene)-2,5-dihydrothiophenes **1** from the diols **9** via the salts **5**. We also report the application of this method to the preparation of furan, selenophene, and *N*-methylpyrrole analogs **2**-**4**.



1 : X=S
2 : X=O
3 : X=Se
4 : X=NMe



5 : X=S
6 : X=O
7 : X=Se
8 : X=NMe

Treatment of 2,5-dilithiothiophene (**13**)[7] with 2 equiv of di-2-thienyl ketone, benzophenone, 4,4'-dimethyl-, 4,4'-dimethoxy-, and 4,4'-dichlorobenzophenones, and fluorenone in THF affords the corresponding diols **9** in good yields. The diol **9** (Ar=2-thienyl) was also prepared by reaction of 2,5-di-2-thenoylthiophene (**16**)[8] (Ar=2-thienyl) with 2 equiv of 2-thienyllithium in THF. Slow addition of 60% perchloric acid to a well stirred solution of a diol **9** in Ac_2O at -40 °C followed by dilution of the mixture with anhydrous ether resulted in the precipitation of the crystalline salt **5**. The solvent was removed

by decantation and the salt was rinsed with anhydrous ether and dried under vacuum.[9] The structure of the salt was confirmed by reducing it with $NaBH_4$. For example, treatment of **5** (Ar=2-thienyl) with $NaBH_4$ in ethanol-ether at room temperature affords 2,5-bis(di-2-thienylmethyl)thiophene (53%) along with the dihydrothiophene (**1**) (Ar=2-thienyl) in 23% yield.[10]

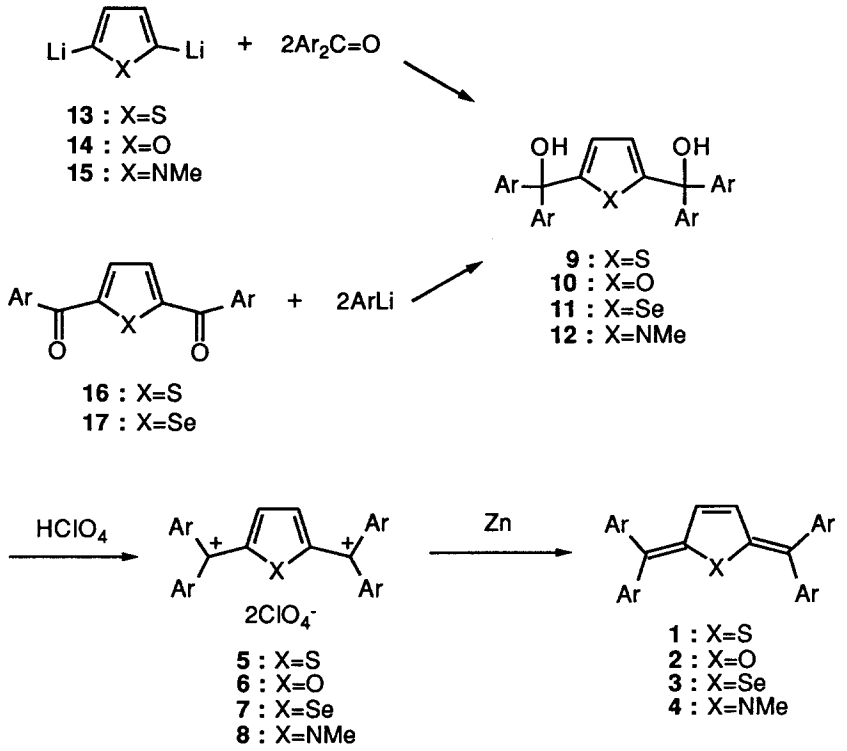
Diols **10** and **12** were also synthesized by reactions of 2,5-dilithiated furan (**14**) and *N*-methylpyrrole (**15**)[11] with diaroyl ketones, while diols **11** were obtained by reactions of 2,5-diaroylselenophenes (**17**)[12] with aryllithiums. The diols **10-12** were converted to the corresponding bis-carbenium salts **6-8** in good yields.

All of the bis-carbenium salts **5-8** thus obtained were successfully converted to the corresponding 2,5-bis(diarylmethylene)-2,5-dihydrothiophenes (**1**), furans (**2**),[13] selenophenes (**3**),[4,14] and *N*-methylpyrrole (**4**)[15] in good to reasonable yields by reduction with zinc powder in 1,2-dimethoxyethane at room temperature. The yields of compounds **1-4** are summarized in Table 1 along with their melting points and absorption maxima in UV-Vis spectra.[16, 17]

Table 1. Preparation of 2,5-Bis(diarylmethylene)-2,5- dihydrothiophenes (**1**), Furans (**2**), Selenophenes (**3**), and *N*-Methylpyrrole (**4**)

	X	Ar	Yield[a] (%)	Mp (°C)	UV-Vis (CH_3CN) λ_{max} (nm) (log ε)
1a	S	2-thienyl	79	149-150	472 (4.59), 449 (sh,4.51), 309 (4.12), 228 (4.30)
1b	S	C_6H_5	64	203-204	414 (4.32), 268 (4.03)
1c	S	4-MeC_6H_4	46	265-266	421 (4.32), 274 (4.10)
1d	S	4-$MeOC_6H_4$	86	201-202	432 (4.44), 285 (4.31)
1e	S	4-ClC_6H_4	6	238-239	424 (4.44), 276 (4.20)
1f[3]	S	Ar_2C=: 9-fluorenylidene	37	>90[b]	527 (4.04), 492 (3.87), 256 (4.37), 236 (4.43)
2a	O	C_6H_5	51	219-222	430 (sh,4.70), 417 (4.71), 271 (4.72)[c]
2b	O	4-MeC_6H_4	63	172-174	442 (4.77), 424 (4.78), 276 (4.85)[c]
2c	O	4-ClC_6H_4	51[d]	206-207	442 (sh,4.21), 426 (4.23), 278 (4.36)[c]
3a	Se	2-thienyl	71	199-200	468 (4.68), 305 (4.30), 233 (4.47)
3b	Se	C_6H_5	63	214-215	414 (4.70), 291 (sh,4.35), 266 (4.40)
4	NMe	C_6H_5	18 (26)[e]	161-162	468 (4.53), 318 (3.82), 272 (4.19)

[a] Yields based on diols. [b] The compound does not show a clear melting point. [c] In hexane. [d] The compound was directly formed on treatment of the diol with 60% perchloric acid. [e] The yield attained via the bis-tetrafluoroborate salt.



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9. Great care should be taken for the handling of perchlorate salts **5-8**, although we have not met any explosion during the present study.
10. Mechanism of the formation of **1** is uncertain. The formation of **1-3** was also observed on heating the diols **9-11** without solvent or as a by-product in the preparation of the salts **5-7**, respectively.
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16. All new compounds gave satisfactory elemental analysis results and spectroscopic data [^{1}H(400 MHz) and ^{13}C (100 MHz) NMR]. **1a**: ^{1}H NMR δ 6.87 (s, 2H), 7.04-7.08 (m, 6H), 7.24 (d, *J*=3.6 Hz, 2H), 7.36-7.38 (m, 4H); ^{13}C NMR δ 118.7 (s), 126.6 (d), 126.8 (d), 126.9 (d), 127.4 (d), 128.6 (d), 129.0 (d), 133.6 (d), 142.1 (s), 143.2 (s), 144.7 (s). **1b**: ^{1}H NMR δ 6.82 (s, 2H), 7.20-7.38 (m, 20H); ^{13}C NMR δ 127.2 (d), 127.4 (d), 128.2 (d), 128.3 (d), 129.6 (d), 130.5 (d), 131.8 (s), 133.7 (d), 141.7 (s), 142.2 (s), 142.4 (s). **1c**: ^{1}H NMR δ 2.32 (s, 6H), 2.35 (s, 6H), 6.79 (s, 2H), 7.08-7.14 (m, 12H), 7.26 (d, *J*=8.1 Hz, 4H); ^{13}C NMR δ 21.2 (q), 21.3 (q), 128.8 (d), 129.0 (d), 129.6 (d), 130.4 (d), 131.4 (s), 133.4 (d), 136.9 (s), 137.1 (s), 139.1 (s), 139.6 (s), 141.7 (s). **1d**: ^{1}H NMR δ 3.79 (s, 6H), 3.81 (s, 6H), 6.77 (s, 2H), 6.83 (d, *J*=8.6 Hz, 4H), 6.86 (d, *J*=8.6 Hz, 4H), 7.13 (br d, *J*=6.5 Hz, 4H), 7.30 (br d, *J*=7.6 Hz, 4H). **1e**: ^{1}H NMR δ 6.81 (s, 2H), 7.14 (d, *J*=6.6 Hz, 4H), 7.25-7.33 (m, 12H); ^{13}C NMR δ 128.7 (d), 128.8 (d), 129.9 (s), 131.0 (d), 131.7 (d), 133.6 (s), 133.9 (d), 139.5 (s), 140.0 (s), 142.9 (s). **2a**: ^{1}H NMR δ 6.58 (s, 2H), 7.18-7.39 (m, 16H), 7.55-7.58 (m, 4H); ^{13}C NMR δ 116.2 (s), 126.7 (d), 127.2 (d), 127.4 (d), 127.8 (d), 128.3 (d), 129.8 (d), 131.2 (d), 138. 5 (s), 139.9 (s), 155.6 (s). **2b**: ^{1}H NMR δ 2.35 (s, 6H), 2.36 (s, 6H), 6.50 (s, 2H), 7.09 (d, *J*=8.2 Hz, 4H), 7.14 (d, *J*=8.4 Hz, 4H), 7.17 (d, *J*=8.4 Hz, 4H), 7.48 (d, *J*=8.2 Hz, 4H); ^{13}C NMR δ 21.2 (q), 21.3 (q), 115.6 (s), 127.0 (d), 128.5 (d), 129.0 (d), 129.6 (d), 131.1 (d), 135.9 (s), 136.3 (s), 136.7 (s), 137.2 (s), 155.3 (s). **2c**: ^{1}H NMR δ 6.56 (s, 2H), 7.20 (d, *J*=8.4 Hz, 4H), 7.26 (d, *J*=8.7 Hz, 4H), 7.36 (d, *J*=8.4 Hz, 4H), 7.44 (d, *J*=8.7 Hz, 4H); ^{13}C NMR δ 114.6 (s), 127.6 (d), 128.2 (d), 128.8 (d), 130.8 (d), 132.3 (d), 132.9 (s), 133.6 (s), 136.4 (s), 137.6 (s), 155.7 (s). **3a**: ^{1}H NMR δ 6.97 (s, 2H), 7.03-7.08 (m, 6H), 7.17 (dd, *J*=1.0, 4.0 Hz, 2H), 7.35-7.38 (m, 4H); ^{13}C NMR δ 122.7 (s), 126.5 (d), 126.7 (d), 126.8 (d), 127.4 (d), 128.5 (d), 128.8 (d), 135.2 (d), 142.1 (s), 143.4 (s), 145.9 (s). **3b**: ^{1}H NMR δ 6.85 (s, 2H), 7.21-7.37 (m, 20H); ^{13}C NMR δ 127.3 (d), 127.7 (d), 128.2 (d), 128.4 (d), 129.1 (d), 130.3 (d), 135.1 (d), 136.1 (s), 141.5 (s), 143.7 (s). **4**: ^{1}H NMR δ 2.28 (s, 3H), 6.62 (s, 2H), 7.14-7.33 (m, 20H); ^{13}C NMR δ 41.0 (q), 116.5 (s), 125.9 (d), 126.3 (d), 127.7 (d), 128.0 (d), 129.1 (d), 131.0 (d), 131.2 (d), 141.9 (s), 142.9 (s), 150.4 (s).
17. X-Ray structures of **1a**, **1b**, **2a**, **3a**, and **3b** will be reported elsewhere.

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