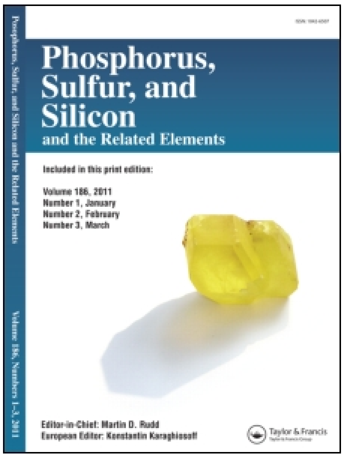

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SYNTHESIS OF MIXED OLIGOMERIC HETEROARYLENES CONTAINING FURAN, THIOPHENE, AND SELENOPHENE RINGS; THEIR UV SPECTRA AND OXIDATION POTENTIALS

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SYNTHESIS OF MIXED OLIGOMERIC HETEROARYLENES CONTAINING FURAN, THIOPHENE, AND SELENOPHENE RINGS; THEIR UV SPECTRA AND OXIDATION POTENTIALS

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Mixed oligomeric five-membered heteroarylenes **3a–f** and **4a–e** have been prepared by cross-coupling reaction of the Grignard reagents **2** derived of the appropriately substituted thiophenes 1 with either the 2-bromoheteroarylenes or the 2,5-dibromoheteroarylenes derived of furan, thiophene, and/or selenophene respectively. The UV spectra and oxidation potential of compounds **3a–f** and **4a–e** are discussed on the basis of co-planarity.

Key words: Conducting polymers; oligomeric heteroarylenes; UV spectra; oxidation potentials.

INTRODUCTION

Electrically conducting organic polymers have received considerable attention due to their potential for application in many areas.[1] Much work has been devoted to the synthesis of new organic conducting or semi-conducting materials, and it was shown that their conductivity and ionization potentials are strongly dependent on both structure and topography.[2,3] Recently[4,5] we reported on the preparation and polymerization of some oligomeric five-membered heteroarylenes containing furan and thiophene rings. Also, some of the electrical and spectral properties of these species were reported.[4–6]

There is rather scant information on the synthesis of mixed oligomeric five-membered heteroarylenes.[7–10] To obtain such mixed oligomers some of the earlier authors used coupling reactions *via* Cu-organics,[7,9] or they prepared the desired compounds by transforming substituents of monosubstituted thiophenes or furans into an additional ring.[8,10] Only recently a transition metal catalyst coupling reaction was used to synthesize such oligomers.[5,6,11] In our synthetic efforts we used only $NiCl_2(dppp)$ ($dppp = Ph_2PCH_2CH_2CH_2PPh_2$) catalyzed coupling reaction between a Grignard compound and bromosubstituted heteroarylenes. This catalyst was introduced by Kumada *et al.*[12] for the coupling of aryl

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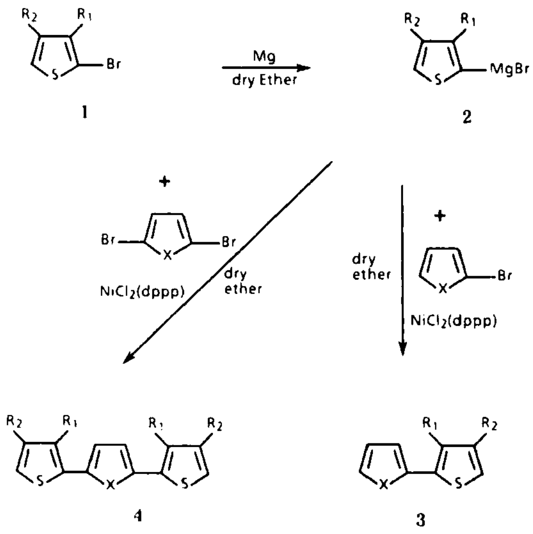
moieties. More recently this method was used by us[13] and others[14,15,16] for the preparation of oligomeric 3-substituted alkyl- and arylthiophenes.

Our interest in using oligomeric five-membered heteroarylenes for polymerization is based on the assumption that such units would lead to more uniform polymers with better electrochemical properties.[4] In addition, we were interested to learn how mixed oligomeric five-membered heteroarylenes would influence the electrochemical and spectral behavior of such oligomeric species and further our ultimate goal towards the synthesis of organic conducting materials with superior properties.

RESULTS AND DISCUSSION

Furan, thiophene, and selenophene were chosen as heteroarylenes. The desired mixed novel oligomers were obtained by a $NiCl_2$(dppp) promoted coupling reaction between a Grignard reagent derived from either 2-bromothiophene, 2-bromo-3-methylthiophene, or 2-bromo-4-methylthiophene with either 2-bromo-, 2,5-dibromofuran or the corresponding 2-bromo- and 2,5-dibromoselenophenes (Scheme I). In all of these coupling reactions the yields were adequate to high except in reactions involving 2-bromo-4-methylthiophene. This was probably due to homocoupling of the Grignard reagent derived of this compound. The results are compiled in Table I.

Scheme 1

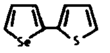
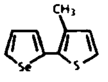
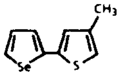
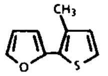
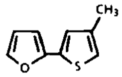
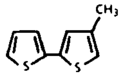
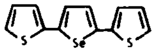
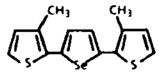
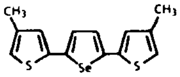
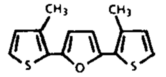
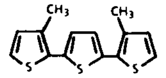


4a, $R_1 = R_2 = H$, $X = Se$
4b, $R_1 = CH_3$, $R_2 = H$, $X = Se$
4c, $R_1 = H$, $R_2 = CH_3$, $X = Se$
4d, $R_1 = CH_3$, $R_2 = H$, $X = O$
4e, $R_1 = CH_3$, $R_2 = H$, $X = S$

3a, $R_1 = R_2 = H$, $X = Se$
3b, $R_1 = CH_3$, $R_2 = H$, $X = Se$
3c, $R_1 = H$, $R_2 = CH_3$, $X = Se$
3d, $R_1 = CH_3$, $R_2 = H$, $X = O$
3e, $R_1 = H$, $R_2 = CH_3$, $X = O$
3f, $R_1 = H$, $R_2 = CH_3$, $X = S$

TABLE 1

Experimental Condition, Elemental Analyses and ^{1}H NMR Spectra for Compounds 3a–f and 4a–e

Comp. No.	Structure Formula	M.P/B.P. (°C)	^{1}H NMR (ppm) CDCl$_3$	Microanalyses (Calc./Found)% C	H	Experimental Conditions	Yield (%)
3a		38 - 40	7.8 - 7.9 (dd, 1^{1}H, ortho H in selenophene ring), 6.8 - 7.4 (m, 5^{1}H, for both thiophene and selenophene ring	45.09* 46.09	2.83 3.78	Coupling at 0°C, stirred for 3 h in cold ice bath	84.5
3b		oil	7.9 - 8.1 (1^{1}H, dd, ortho proton in selenophene ring), 7.2 - 7.4 (m, 2H, meta proton in selenophene ring) 7.0 - 7.2 (d, 1^{1}H, ortho proton in thiophene ring); 6.8 - 6.9 (d, 1^{1}H, meta proton 2.3 - 2.5 (–s, 3H, $\underline{CH}_3$)	47.58 47.93	3.55 3.67	Coupling at 0°C, stirred for 3 h at r.t.	85.2
3c		oil	7.85 (d, 1H, ortho to Se), 7.25 (s, 2H, meta proton in Se ring), 6.8 and 6.95 (2 singlets, 2H thiophene), 2.25 (s, 3H, $\underline{CH}_3$)	47.58 47.74	3.55 3.47	Coupling at 0°C, 3 h in cooled ice bath and left overnight at r.t.	25
3d		oil	7.4 (S, 1^{1}H, ortho to O), 7.15 and 6.85 (2d, 2^{1}H ortho and meta proton in thiophene ring), 6.45 (broad signal for 2^{1}H meta to O). 2.4 (s, 3^{1}H, $\underline{CH}_3$)	65.82 65.62	4.91 5.07	Coupling at r.t. stirred for 15 h at r.t.	65.7
3e		oil	7.4 (S, 1^{1}H, ortho to O), 6.95 (s, 1^{1}H, ortho to S) 6.75 (S, 1H, meta to S) 6.42 (s, 2H, meta to O)	65.82 65.17	4.91 4.76	Coupling at r.t., left overnight at reflux. (Ether)	10.4
3f		oil	6.60 - 7.25 (m, 5H, aromatic), 7.25 (s, 3H, CH$_3$)	59.96 60.08	4.47 4.44	Coupling at r.t., left 20 h at reflux (Ether-THF)	11
4a		134-136	6.90 - 7.35 (m, aromatic protons)	48.81 49.07	2.73 2.72	Coupling at r.t., r.t. for 2 h, reflux 1 h	67.8
4b		88-90	7.25 (S, 2^{1}H, m-protons in selenophene ring), 7.15 (d, 2H, o-proton in thiophene ring), 6.90 (d, 2^{1}H, m-proton in thiophene ring) 2.4 (s, 6^{1}H, 2$\underline{CH}_3$)	52.01 51.98	3.74 3.69	Coupling at r.t., r.t. for 2 h, reflux 1 h	77.4
4c		81-83	7.18 (s, 2^{1}H, m-proton in the selenophene ring), 6.95 (s, 2^{1}H o-protons in thiophene rings) 6.80 (s, 2^{1}H, m-protons in thiophene rings) 2.25 (s, 6H, 2$\underline{CH}_3$)	52.01 51.86	3.74 3.76	Coupling at r.t. and left for 20 h at r.t.	5.2
4d		105-106	7.15 (d, 2H, o-protons in the thiophene rings), 7.85 (d, 2H m-protons in the thiophene rings) 6.50 (s, 2^{1}H, m-protons in the furan ring). 2.4 (s, 6^{1}H, 2$\underline{CH}_3$)	64.61 64.56	4.65 4.78	Coupling at 0°C, 2 h at 0°C and 1 h at r.t.	69.0
4e		53-55	7.10 (m, 4^{1}H, m-protons to S) 6.85 (d, 2H, ortho proton) 2.40 (s, 6H, 2$\underline{CH}_3$)	60.83 60.99	4.37 4.25	Coupling at r.t. and left overnight	57.9

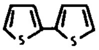
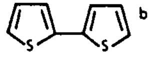
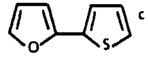
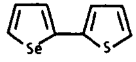
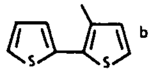
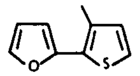
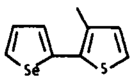
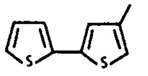
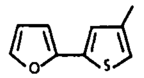
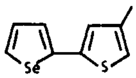
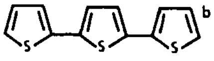
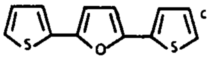
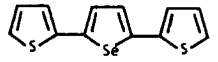
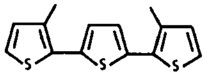
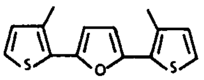
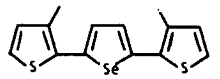
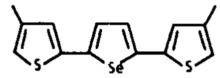
* Compound 3a contains traces of the homocoupling product  detected by GC-MS.

Table 2: UV spectra and oxidation potential for thiophene oligomers.[a]

Thiophene-Thiophene		Furan-Thiophene		Selenophene-Thiophene	
λ_{max}	E_{ox}	λ_{max}	E_{ox}	λ_{max}	E_{ox}
	[b]		[c]		
302	1.28	268	1.6	311	1.5
	[b]				
299	1.22	285	1.43	308	1.45
					
310	1.67	306	---	316	1.55
	[b]		[c]		
355	1.05	315	1.0	363	1.14
					
343	1.8	349	1.6	352	1.43
					
				370	1.53

a) E_{ox} values are reported in reference to Ag/AgCl electrode as the potential of the peak oxidation current of the cyclic voltammograms (scan rate 50 mVs^{-1}). The solvent was acetonitrile with $[(n\text{-}C_4H_9)_4]^{\oplus}BF_4^{\ominus}$ as the supporting electrolyte. The concentration of the oligomer was 50 mmol. J. R. Jezak, H. B. Mark, Jr., *J. Phys. Chem.* **74**, 1627 (1970); R. J. Waltman and J. Bargon, *J. Electroanal. Chem.* **194**, 4 (1985); A. Amer, A. Burkhardt, A. Nkansah, R. Shabana, A. Galal, H. B. Mark, Jr., and H. Zimmer, *Phosphorus and Sulfur*, submitted.

b) See ref. 4.

c) A. Carpita, R. Rossi, C. A. Veracini, Tetrahedron, 41, 1919 (1985).

The UV spectroscopic data and the oxidation potentials of the monomeric oligomers are listed in Table II. For purpose of comparison a number of earlier described oligomers are also included in Table II.

Inspection of these data reveals the following trends: A methyl substitution in the 3- or 3′-position in both the thiophene–thiophene and thiophene–selenophene dimers causes a hypsochromic shift of λ_{max} of the UV spectra. A methyl substitution in the 4- or 4′-position in the analogous dimers, however, gives rise to a bathochromic shift of the long wavelength absorption peak. This behavior can be rationalized by impeding of coplanarity in the 3- and 3′-substituted specimen comparing with the 4-, and 4′-isomers. A similar trend also was observed with positions of the long wavelength absorptions of the UV spectra and with the values of the oxidation potentials of the trimers. When comparing the unsubstituted species 2,2′:5′2″-terthiophene with 3,3″-dimethyl-2,2′:5′,2″-terthiophene the E_{ox} value increases from 1.05 V to 1.8 V and the λ_{max} of the UV spectrum decreases from 355 nm to 343 nm. In the S–Se–S series the corresponding parameters show the same trend, thus, the λ_{max} of the long wavelength absorption decreases from 363 nm of the unsubstituted to 352 nm of the

3,3''-dimethyl substituted compound, whereas, as expected the oxidation potentials for the same two compounds increase from 1.14 V to 1.43 V. Such a trend, however, does not exist for furan containing dimers and trimers. The reason for this observation is at this point not clear.

In summary then, this investigation may allow certain conclusions to be drawn, namely, that substitution in the 3- and 3''-positions of the heteroarylene rings of the oligomer reduces the conjugation while substitution in the 4- and 4''-position does not impede coplanarity of the rings in both thiophene–thiophene and thiophene-selenophene ologomers. Also, it seems to be a general fact that, when comparing isomeric unsubstituted oligomeric five-membered S- and Se-heteroarylenes the isomer with a UV absorption at the longest wavelength always has the lowest oxidation potential, while with substituted ones, the correlation between λ_{max} and E_{ox} is still difficult to predict. The spectral properties and the oxidation potentials of the furan containing oligomers do not agree with the ones exhibited by the S–Se, and S–S analogs. A satisfactory explanation for this behavior cannot be given at the present time.

EXPERIMENTAL

Melting points were determined with a Mel Temp apparatus and are uncorrected, as are the boiling points. UV Spectra were run in $CHCl_3$ on the Perkin–Elmer Lambda 5, UV/VIS spectrophotometer. ^1H NMR spectra were recorded at 80 MHz on an IBM, FTQ NMR spectrometer. Chemical shifts are expressed in δ(ppm) relative to tetramethylsilane as internal standard and $CDCl_3$ as a solvent. Elemental analyses were performed at M–H–W Laboratories, Phoenix, Arizona. All reactions were performed under N_2. Silica gel 60 (Merck) was used for column chromatography and petroleum ether (b.p. 37–59°C) was used as an eluent. The reported yields refer to pure isolated materials.

Starting materials. The following halides were prepared according to methods reported earlier: 2-bromo-3-methylthiophene,[17] 2-bromo-4-methylthiophene,[18] 2-bromofuran,[19] 2,5-dibromofuran,[19] 2-bromo-selenophene,[20] and 2,5-dibromoselenophene.[20] 2,5-Dibromothiophene is commercially available and was used without further purification.

General procedure for the coupling reaction. Under a blanket of nitrogen were added slowly 25 mmole of the appropiate 2-bromothiophene in 15 ml anhydrous diethyl ether to a suspension of 0.61 g (25 mmole) of magnesium turnings in 15 ml of anhydrous diethyl ether. After the complete disappearance of the magnesium, the reaction mixture was transferred with a syringe to a three necked flask fitted with reflux condenser containing a mixture of 20 mmole of the 2-bromoheteroarylene (or 10 mmole of the appropriate 2,5-dibromoheteroarylene) and 100 mg of $NiCl_2$(dppp) in 50–100 ml anhydrous diethyl ether. The reaction mixture was then treated as outlined in Table I. To terminate the reaction the mixture was poured into a mixture of crushed ice and diluted HCl (2 N). The organic layer was separated and the aqueous phase extracted twice with ether. The combined organic layers were dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure the residue was purified by chromatography on a silica gel column using petroleum ether (37–59°C) as the eluent.

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