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Direct Oxidative Cyclization of 1,2-Bis(benzothiophene-2-yl)ethylenes as a Replacement of Photocyclization in the Synthesis of Thiaheterohelicenes

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Photocyclization of *cis*-stilbenes **1** followed by in situ iodine oxidation is a crucial step in the synthesis of helicenes[1,2] and heterohelicenes.[3] This reaction is problematic because it normally requires very dilute solutions, typically in toluene, and, more importantly, the product acts as a filter for the incoming radiation. Using the photolysis reaction we tried to photolyze bis-ethylenes **2** in order to synthesize thiahelicenes[4] such as 6,7,9,10,-12,13-hexamethyl-5,8,11,14-tetrathia[9]helicene (**3a**), 1,2,3,4,6,7,9,10,11,12-decamethyl-5,8-dithia[5]helicene (**3b**), and 1,2,3,4,6,7,9,10,12,13,15,16,17,18-tetradecamethyl-5,8,11,14-tetrathia[9]helicene (**3c**) (Scheme 1). We found low quantum yields, and additionally it was not possible to obtain measurable amounts of compound **3c** after photolysis of compound **2c**.

Results

We have found that oxidative cyclization proceeds readily and in fair yields to give the thiahelicenes **3a**, **3b**, and **3c**. The reaction can be performed electrochemically or chemically. Our preliminary investigation of the oxidation of bis-ethylenes **2a**, **2b**, and **2c** by cyclic voltammetry using a platinum disc electrode (Figure 1) strongly indicated[5] the formation of the desired product by comparison with an authentic sample of **3a.**[4] Quantitative oxidation (3 F) of 10^{-4} mol of mixtures of *cis* and *trans* isomers of bis-ethylenes **2a**, **2b**, and **2c** followed by reduction(1 F) and purification gave isolated yields of compounds **3a**,**b**,**c** of the order of 20−50%.

We followed the reaction by reverse phase HPLC and found that both the *cis* and *trans* isomers of the bis-ethylenes **2a**, **2b**, and **2c** disappeared as the product formed. The HPLC analysis of the reaction strongly indicated that crude yields of the order of 100% are formed for **3a** and **3b** and 80% for **3c**, but some material is lost during the purification procedure.

We have also found that oxidation with anhydrous $FeCl_3$ in dry CH_2Cl_2 offers an attractive alternative to the electrochemical preparation of **3a** and **3b** (but not **3c**) due to a simpler workup procedure. Typically 10^{-4} mol of the ethylene was dissolved in 50 mL of CH_2Cl_2 and treated, under stirring, with a 4-fold molar excess of anhydrous $FeCl_3$. The solution was then washed several times with water containing sodium dithionite. After workup compounds **3a** and **3b**, but not compound **3c**, were obtained. The yields of the various processes are collected in Table 1.

Scheme 1

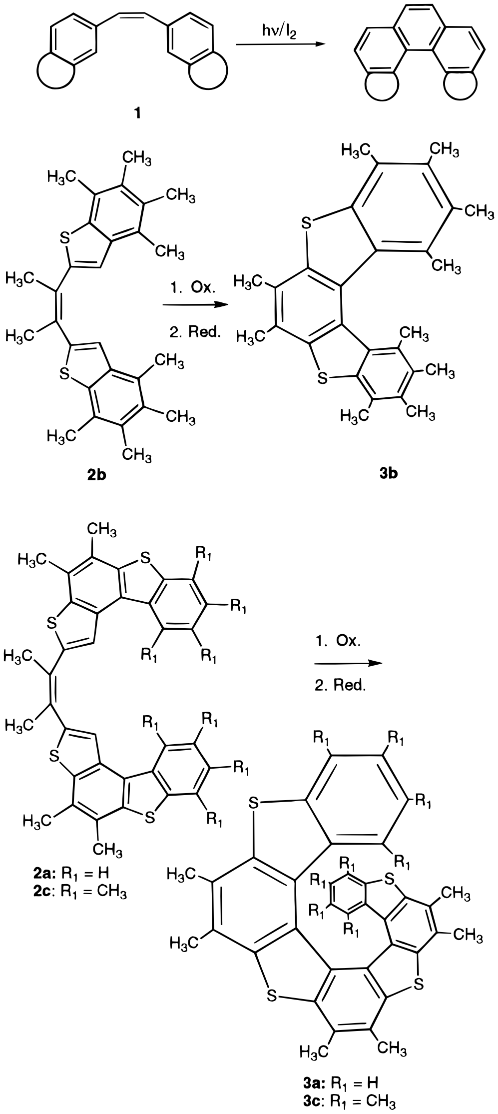

Table 1. Synthesis of Heterohelicenes

precursor[a]	product	isol. yield[b]	HPLC yield[b]	isol. yield[c]	HPLC yield[c]
2a	3a	50	100	60	90
2b	3b	50	100	65	85
2c	3c	20	85	0	0

[a] Reactions performed on a 10^{-4} molar scale. [b] Electrochemical oxidation. Isolated yields of photochemical preparation[4] are 58, 56, and 0% for compounds **3a**, **3b**, and **3c** respectively. [c] Iron chloride oxidation.

Discussion

In the literature, analogous chemical[6] and electrochemical[7] preparations of diphenylphenanthrene from tetraphenylethylene have been described. The direct oxidation method has to our knowledge not been utilized to replace the photocyclization in the synthesis of helicenes or heterohelicenes. However, oxidative coupling has been a widely used method in the preparation of condensed aromatics.[8]

The mechanism can be inferred from the cyclic voltammogram. In the positive scan an quasi-reversible wave

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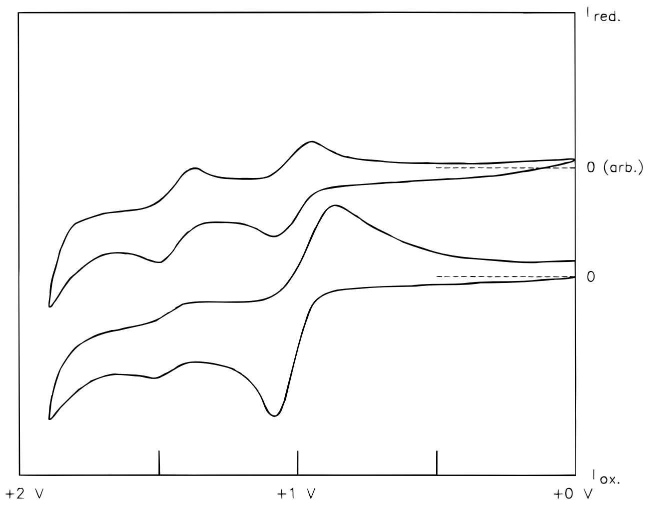

Figure 1. Cyclic voltammogram of **3a** (upper curve) and **2a** (lower curve) in CH_2Cl_2 containing nBu_4PF_6 (0.1 M). Pt vs SCE, sweep rate 200 mvVs.

around 1.1 V was observed. Upon scanning further positive, a smaller reversible wave at 1.46 V corresponding to the formation of the dication of the helicene was observed. The overall behavior resembles the behavior found for electrochemical oxidative coupling of anisoles[5] but the coupling appears to be slower. As described above the HPLC analysis of both the electrochemical and the chemical processes strongly indicated that crude yields of the order of 85−100% are formed for compounds **3a** and **3b** and 80% for compound **3c**, but some material is lost during the purification procedure.

We find it important that nearly quantitative crude yields are obtained because the cyclized product must be formed in a cisoid geometry. The results indicated that when the cation radicals of the ethylenes are formed the *trans* isomer can rearrange to yield the cyclized product. We note that strong acid (HX) was formed during the reaction by loss of protons from the cations. The acid could catalyze the isomerization.

Conclusion

We have found a convenient oxidative cyclization procedure for mixtures of *cis*- and *trans*-1,2-bis(benzothiophene-2-yl)ethylenes to give the thiahelicenes **3a, 3b**, and **3c**. Where possible, the $FeCl_3$ procedure was the simplest to perform considering that the product does not have to be separated from the supporting electrolyte.

Experimental Section

Starting materials **2a**, **2b**, and **2c** were obtained as *cis* and *trans* mixtures as described previously.[4] Analysis by HPLC on a 5 μm C18 reverse phase column using mixtures of THF and methanol as solvents indicated cis−trans ratios of 5.3:1 for **2a**, 4:1 for **2b**, and 38:1 for **2c**. The electrolysis of **2c** was monitored, and at midelectrolysis the ratio was found to approach 1:1.

Compounds 3a−c. Electrolysis. Compounds **2a**−**c** (10^{-4} mol) were dissolved or slurried in 100 mL of CH_2Cl_2 containing nBu_4NPF_6 (0.1 M) in a two-compartment cell equipped with a platinum basket electrode (2 cm^2) and a platinum rod counter-electrode. Oxidation (3 F) at currents of 10−15 mA gave solutions of the cation radicals of compounds **3a**−**c**. The solution was poured into 20 mL of water containing 5 g of $Na_2S_2O_4$ and the mixture stirred for 10 min. The phases were separated, and the organic phase was dried over $MgSO_4$. Then 100 mL of heptane was added, and the volume was reduced to 75 mL. The precipitated nBu_4NPF_6 was removed by filtration. The solution was evaporated to dryness. The solid was taken up in 10 mL of toluene and filtered through a short column of silica 3 × 4 cm and eluted further with toluene. The toluene solution was evaporated to dryness, and the filtration procedure was repeated through neutral Al_2O_3. After evaporation, the solid was recrystallized from a small amount of toluene.

Yields are given in Table 1.

Compound **3a** and compound **3b** were identified by comparison with authentic samples.[4]

Selected data for 3c: mp > 300 °C dec; ^{1}H NMR (250 MHz) ($CDCl_3$) $\delta = 2.86$ (6H, s), 2.75 (6H, s), 2.51 (6H, s), 2.46 (6H, s), 2.21(6H, s), 1.50 (6H, s), 0.49 (6H, s); reversible one-electron oxidation potentials $E_1 = +0.86$ V, $E_2 = +1.29$ V vs SCE in CH_2Cl_2 containing nBu_4NPF_6 (0.1 M).

Compounds 3a and 3b. $FeCl_3$ Oxidation. Ethylene **2a** or **2b** (10^{-4} mol) was dissolved in 50 mL of CH_2Cl_2 and treated, under stirring, with a 4-fold molar excess of anhydrous $FeCl_3$ for 2 h. The solution was then washed several times with water containing sodium dithionite (5 g/100 mL). After drying over $MgSO_4$ and filtration through a short silica gel column, the solution was evaporated in vacuo. The resulting solids were recrystallized from toluene to give **3a** or **3b**, which were identified by comparison with authentic samples.[4]

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