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The diastereoselectivity of the addition of tricarbonyl-(η^6-2-lithiothiophene)chromium(0) complexes on aldehydes

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Abstract

It has been shown that the reactions of tricarbonyl(η^6-2-lithiothiophene)chromium(0) with various arene carboxaldehydes yields mixtures of unequal amounts of diastereoisomers, which can be separated by flash chromatography. The structures of the products have been established by ^{1}H NMR spectroscopy and by independent synthesis. A novel synthesis of tricarbonyl(η^6-thiophene)chromium(0) (1) is described.

Key words: Chromium; Thiophene; Carbonyl; Aldehyde

1. Introduction

The chirality of tricarbonylchromium(0) complexes of benzene derivatives with two different substituents in *ortho* and *meta* positions has been well documented, and it is known that *ortho*-disubstituted tricarbonyl(η^6-benzene)chromium(0) complexes undergo several reactions with high stereoselectivity [1]. In contrast, the stereochemistry of tricarbonylchromium(0) complexes of monosubstituted heterocyclic compounds has been very little studied, the only example being the work of Davies *et al.* [2] who observed completely stereoselective reactions between tricarbonyl (η^6-2-ethylpyridine)chromium(0) and non-enolisable aldehydes.

We describe below the results of a study of the diastereoselectivity of addition of tricarbonyl (η^6-2-lithiothiophene)chromium(0) complexes to aldehydes.

2. Results and discussion

The original aim of our work was to synthesise either tricarbonyl(η^6-2-formylthiophene)chromium(0) or tricarbonyl(η^6-2-acetylthiophene)chromium(0) complexes in order to study the diastereoselectivity of additions to the carbonyl group. Unfortunately, all attempts to bring about complexation of 2-acetylthiophene by treatment with $Cr(CO)_6$ in decalin (method A) [3] or with $Cr(CO)_3(NH_3)_3$ in dioxane (method B) [4], or by ligand exchange reactions with tricarbonyl(η^6-naphthalene)chromium(0) (method C) [5], failed. Method C gave a 13% yield of the tricarbonyl[η^6-2-(2-thienyl)-1,3-dioxolane]chromium(0), but the hydrolysis of this acetal complex by HCl in ethanol [6,7] or by H_3PO_4 in ethanol [8] did not yield the expected product. Hydrolysis with HCl in benzene yielded tricarbonyl(η^6-benzene)chromium(0), *i.e.* the ligand exchange reaction took place. Hydrolysis with HCl in dioxane yielded red, more polar material, probably the desired tricarbonyl(η^6-2-formyl-thiophene)chromium(0), but this decomposed during attempted purification. Metallation of tricarbonyl(η^6-thiophene)chromium(0) (**1**) with ^{n}BuLi in THF and subsequent quenching with DMF yielded the same red material, which again decomposed during work-up.

We therefore decided to study the metallation of tricarbonyl(η^6-thiophene)chromium(0) (**1**) and subsequent quenching with benzaldehyde or other aromatic aldehydes (Scheme 1). A mixture of diastereoisomers was obtained since the tricarbonylchromium(0) complexes of monosubstituted thiophenes are chiral. In the subsequent account the diastereoisomers are denoted by **a** and **b** with the convention that the diastereoisomer **a** is that with the greater R_f value.

At the start of this project, we needed a reliable method for making tricarbonyl(η^6-thiophene)chromi-

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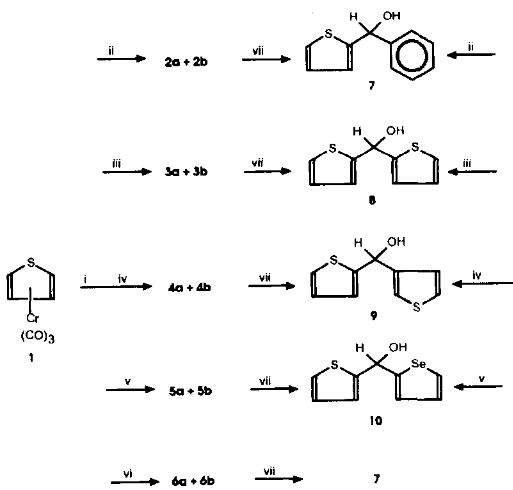


Scheme 1. Reagents and conditions: (i) BuLi, THF, −78°C; (ii) benzaldehyde; (iii) 2-thiophenecarboxaldehyde; (iv) 3-thiophenecarboxaldehyde; (v) 2-selenophenecarboxaldehyde; (vi) tricarbonyl(η^6-benzaldehyde)chromium(0); (vii) $h\nu$, O_2, EtOH; (viii) BuLi, THF, −20°C.

um(0) (**1**). This complex was made previously by direct complexation of thiophene with $Cr(CO)_6$ [6–8] but the yields were rather low (3–8%). Reasonable yields were obtained by Öfele [15], Novi [16] and Segard [17], who used as complexation agents $Cr(CO)_3(pyridine)_3$ plus BF_3 etherate or $Cr(CO)_3(CH_3CN)_3$, respectively. Both methods gave up to 70% yields. We tried three methods (see above). Method A gave variable yields in the range 10–50%, method B gave a 31% yield, while a modification of method C gave reproducible 75% yields.

Metallation of tricarbonyl(η^6-thiophene)chromium (0) (**1**) with an equivalent amount of ^{n}BuLi at −78°C took place at the α-position of thiophene ring [9]. Quenching of the tricarbonyl-(η^6-2-lithiothiophene)-chromium(0) with an excess of benzaldehyde gave a mixture of diastereoisomers **2a** + **2b** in a ratio of 72 : 28 in 53% overall yield (Table 1). This behaviour is similar to that represented by the described preferential formation of one of the diastereoisomers by complexation of *ortho* substituted α-hydroxyalkylbenzenes with $Cr(CO)_6$, which was explained in terms of the stabilising interaction of the α-OH group with the Cr atom of $Cr(CO)_3$ [10–12]. It was of interest to find out whether the ratio of 72 : 28 of the diastereoisomers **2a**/**2b** would be found also in the reactions of tricarbonyl(η^6-2-lithio-thiophene)chromium(0), prepared from complex **1**, with other aromatic aldehydes. The results listed in Table 1 show that the reaction with 2-thiophenecarboxaldehyde yielded a 73 : 27 ratio of diastereoisomers **3a** + **3b** in 66% overall yield, that with 3-thiophenecarboxaldehyde a 67 : 33 ratio of diastereoisomers **4a** + **4b** in 63% overall yield, and that with 2-selenophenecarboxaldehyde a 82 : 18 ratio of diastereoisomers **5a** + **5b** in 55% overall yield. The higher ratio in the last case could be due to the larger size of selenium than of sulphur.

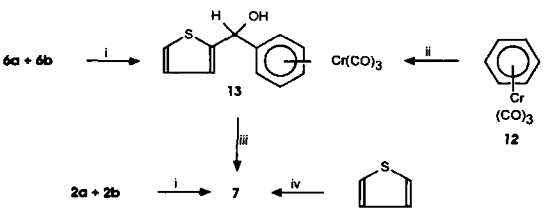
TABLE 1. Results of reactions of tricarbonyl(η^6-2-lithiothiophene)-chromium(0), prepared from complex 1, with aldehydes

Entry	Reagent	Diastereoisomers	Ratio of diastereoisomers (%)	Yield (%)
1	Benzaldehyde	**2a** + **2b**	72:28	53
2	2-Thiophenecarboxaldehyde	**3a** + **3b**	73:27	66
3	3-Thiophenecarboxaldehyde	**4a** + **4b**	67:33	63
4	2-Selenophenecarboxaldehyde	**5a** + **5b**	82:18	55
5	Tricarbonyl-(η^6-benzaldehyde)chromium(0)	**6a** + **6b**	51:49	76

The reaction of tricarbonyl(η^6-2-lithiothiophene) chromium(0) with tricarbonyl(η^6-benzaldehyde)chromium(0) yielded a 50 : 50 ratio of diastereoisomers **6a** + **6b** in 76% overall yield. We assume that the two $Cr(CO)_3$ groups in diastereoisomers **6a** and **6b** are in a mutual *trans* position. Thus, one α-OH group can interact with the Cr atom of $Cr(CO)_3$ group attached to thiophene and the other with the Cr atom attached to the benzene ring. The result of this presence of two $Cr(CO)_3$ groups is formation of equal amounts of diastereoisomers **6a** and **6b**.

Decomplexation of diastereoisomers **6a** and **6b** proceeds in two steps. Decomplexation of the thiophene moiety in benzene solution takes place readily without exposure to direct sunlight within a few days (Scheme 2). This process gives complex **13**, which was prepared independently (in 44% yield) by the reaction of tricarbonyl(η^6-benzene) chromium(0) (**12**) with ^{n}BuLi and subsequent treatment with thiophene-2-carboxaldehyde. In contrast, decomplexation of the benzene moiety of **13**, to give **7**, requires exposure to direct sunlight of an ethanolic solution.

The ratio of diastereoisomers was determined by ^{1}H NMR spectroscopy from the relative intensities of the Ar-*CH*(OH)-Ar doublets. The crude reaction mixture always contained the complex, as well as the free ligand and hexamethylenetetramine (HMTA), which



Scheme 2. Reagents and conditions: (i) O_2, EtOH; (ii) BuLi, THF, −78°C, then 2-thiophenecarboxaldehyde; (iii) $h\nu$, O_2, EtOH; (iv) BuLi, THF, −20°C, then benzaldehyde.

was present as an internal standard for determination of the yields of the complex (see Experimental section). The diastereoisomers were separated by flash chromatography on SiO_2 with benzene as eluant. The isolated diastereoisomers were rather unstable, and samples were usually contaminated with the free ligand and so it was not possible to isolate a good crystal for an X-ray diffraction study and so determine the absolute configurations of the diastereoisomers. However, it was possible to assign all the hydrogen signals of complexes, sufficiently different from those of free ligand compounds. Oxidative decomplexation of both diastereoisomers gave the same racemic ligand, which was also prepared independently by reaction of thiophene **11** with ^{n}BuLi and subsequent treatment with the appropriate aldehyde. In all cases, the decomplexation products of diastereoisomers were shown to be identical with samples of free ligands prepared independently.

3. Experimental details

All reactions involving organometallic reagents were performed in flame-dried glassware under argon, and all solvents were deoxygenated. THF was distilled from $LiAlH_4$ under argon immediately before use. Diethyl ether was dried over sodium and distilled under argon prior to use. Benzene and thiophene were distilled from sodium. n-Butyllithium (Aldrich Chemical Company, Inc.) was used as a 2.5 M solution in hexane. The commercial reagents (benzaldehyde, thiophene-3-carboxaldehyde, selenophene-2-carboxaldehyde) were purified by distillation under reduced pressure. Thiophene-2-carboxaldehyde was prepared by the published procedure [13]. Hexacarbonyl chromium(0) was sublimed before use. Tricarbonyl(η^6-naphthalene)chromium(0) [3] and tricarbonyl(η^6-benzaldehyde)chromium(0) [14] were prepared by published procedures. Flash chromatography was performed on silica gel (40–100 mm) under a positive nitrogen pressure.

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained for solutions in chloroform. ^{1}H NMR spectra were recorded with solutions in deuteriochloroform on a Tesla BS-487 spectrometer at 80 MHz, with tetramethylsilane as internal standard; J values are given in Hz; symbols used: H_{Cr}, hydrogen of aromatic ring complexed by $Cr(CO)_3$; H_S, hydrogen of thiophene, H_{Se}, hydrogen of selenophene.

3.1. *Tricarbonyl(η^6-thiophene)chromium(0) (1)*

A mixture tricarbonyl(η^6-naphthalene)chromium(0) (264 mg, 1.0 mmol), thiophene (5 ml, 62.5 mmol), and THF (0.15 ml) was heated in a sealed tube under argon at 80°C for 20 h. After evaporation of the solvent under reduced pressure, flash chromatography (SiO_2, benzene/light petroleum, 1:1) yielded tricarbonyl(η^6-thiophene)chromium(0) (**1**) (166 mg, 75%) and unchanged tricarbonyl(η^6-naphthalene)-chromium(0) (24 mg, 9%). Recrystallization from diethyl ether/light petroleum gave the title compound, **1**, as red needles, m.p. 122–123°C (decomp.) Anal. Found: C, 38.3; H, 1.7. $C_7H_4CrO_3S$ calc.: C, 38.2; H, 1.82%.

3.2. *General procedure for the lithiation of tricarbonyl (η^6-thiophene)chromium(0) (1) and subsequent quenching with aldehydes*

n-Butyllithium (0.1 ml, 0.25 mmol) was added dropwise from a syringe to a stirred solution of tricarbonyl(η^6-thiophene)-chromium(0) (**1**) (55 mg, 0.25 mmol) in THF (5 ml) cooled to −78°C. The mixture was stirred at −78°C for 30 min and the appropriate aldehyde (1.0 mmol) was then added dropwise and stirring was continued (−78°C, 30 min). The mixture was allowed to warm to 0°C, and added to ice water (50 ml) containing 0.1 ml of concentrated HCl. Extraction with benzene (70 ml) followed by drying (Na_2SO_4) of the extract and evaporation under reduced pressure left a residue which was subjected to flash chromatography under nitrogen (SiO_2, benzene). Hexamethylenetetramine (3.5 mg, 0.025 mmol; 0.5 ml of solution of 1 mmol HMTA in 20 ml $CHCl_3$) was added to each fraction as an internal standard ($\delta_H = 4.69$). After evaporation under reduced pressure, the fractions were analysed by ^{1}H NMR spectroscopy. The separated diastereoisomers were crystallized from benzene/light petroleum.

3.3. *Tricarbonyl(η^6-2-thienylphenylmethanol)chromium(0) (2a + 2b)*

Benzaldehyde (0.10 ml, 1 mmol) was added to the mixture obtained by reaction of **1** with BuLi in THF under the standard conditions. Work-up and flash chromatography gave, in addition to the decomplexed ligand **7** (6.5 mg, 14%), the diastereoisomers **2a** as red needles (23 mg, 28%), m.p. 88.5–90°C. Anal. Found: C, 51.8; H, 3.0. $C_{14}H_{10}CrO_4S$ calc.: C, 51.7; H, 3.06% ν_{max} 3606 (OH), 1967 and 1891br (CO) cm^{-1}. δ_H 7.40 (5H, m, PhH); 5.65 (1H, d, $J = 3.7$, CH); 5.51 (1H, t, $J = 3.4$, 4-H); 5.27 (2H, d, $J = 3.2$, 3-H and 5-H); 2.73 (1H, d, $J = 3.7$, OH); R_f (benzene/ethyl acetate 10:1) = 0.60, R_f(benzene) = 0.29. Diastereoisomer **2b** (9 mg, 11%), red needles, m.p. 88–89°C (decomp.). Anal. Found: C, 51.9; H, 3.1. $C_{14}H_{10}CrO_4S$ calc.: C, 51.7; H, 3.06%. ν_{max} 3607 (OH), 1968 and 1892br (CO) cm^{-1}. δ_H 7.42 (5H, m, PhH); 5.62 (1H, d, $J = 4.4$, CH); 2.49 (1H, d, $J = 4.4$, OH); 5.39 (3H, m, ThH). R_f(benzene/ethyl acetate 10:1) = 0.40, R_f(benzene) = 0.18.

*3.4. Tricarbonyl(η^6-2-thienyl-2-thienylmethanol)chromium(0) (**3a** + **3b**)*

2-Thiophenecarboxaldehyde (0.09 ml, 1 mmol) was added to the mixture obtained from of **1** and BuLi in THF under standard conditions. Work-up and flash chromatography yielded, along with the free ligand **8** (12.5 mg, 25%), the diastereoisomer **3a** as orange needles (25 mg, 30%), m.p. 85–86°C. Anal. Found: C, 43.3; H, 2.4. $C_{12}H_8CrO_4S_2$ calc.: C, 43.4; H, 2.41%. ν_{max} 1968, 1993w and 1892br (CO) cm^{-1}. δ_H 7.37 (1H, m, 5-H); 7.08–6.94 (2H, m, 3-H and 4-H); 5.89 (1H, s, CH); 5.60–5.50 (1H, m, 4-H_{Cr}); 5.43–5.24 (2H, m, 3-H_{Cr} and 5-H_{Cr}). R_f(benzene/ethyl acetate 10:1) = 0.56, R_f(benzene) = 0.29. Diastereoisomer **3b**, orange needles (9 mg, 11%), m.p. 96.5–97°C. Anal. Found: C, 43.2; H, 2.4. $C_{12}H_8CrO_4S_2$ calc.: C, 43.4; H, 2.41%. ν_{max} 1969, 1933w and 1894br (CO) cm^{-1}. δ_H 7.45–7.32 (1H, m, 5-H); 6.98 (2H, m, 3-H and 4-H); 5.93 (1H, s, CH); 5.49–5.31 (3H, m, ThH_{Cr}). R_f(benzene/ethyl acetate 10:1) = 0.42, R_f(benzene) = 0.20.

*3.5. Tricarbonyl(η^6-2-thienyl-3-thienylmethanol)chromium(0) (**4a** + **4b**)*

3-Thiophenecarboxaldehyde (0.09 ml, 1 mmol) gave, after the standard procedure and flash chromatography, the decomplexed product **9** (13 mg, 27%), the diastereoisomer **4a** as a microcrystalline orange solid (20 mg, 24%), m.p. 83–84°C. Anal. Found: C, 43.1; H, 2.3. $C_{12}H_8CrO_4S_2$ calc.: C, 43.4; H, 2.41%. ν_{max} 1968, 1934w and 1892br (CO) cm^{-1}. δ_H 7.40–7.07 (3H, m, ThH); 5.73 (1H, s, CH); 5.54 (1H, m, 4-H_{Cr}); 5.35–5.22 (2H, m, 3-H_{Cr} and 5-H_{Cr}). R_f(benzene/ethyl acetate 10:1) = 0.45, R_f(benzene) = 0.20. Diastereoisomer **4b**, orange powder (10 mg, 12%), m.p. 78–79°C (decomp.). Anal. Found: C, 43.3; H, 2.4. $C_{12}H_8CrO_4S_2$ calc.: C, 43.4; H, 2.41%. ν_{max} 1968, 1933w and 1892br (CO) cm^{-1}. δ_H 7.42–7.10 (3H, m, ThH); 5.73 (1H, s, CH); 5.36 (3H, m, ThH_{Cr}). R_f(benzene/ethyl acetate 10:1) = 0.32, R_f(benzene) = 0.14.

*3.6. Tricarbonyl(η^6-2-thienyl-selenophene-3-ylmethanol) chromium(0) (**5a** + **5b**)*

2-Selenophenecarboxaldehyde (0.1 ml, 1 mmol) gave, after the standard procedure and flash chromatography, the free ligand **10** (21 mg, 35%) and the diastereoisomer **5a** as orange needles (15 mg, 16%), m.p. 81–83°C. Anal. Found: C, 37.8; H, 2.1. $C_{12}H_8CrO_4SSe$ calc.: C, 38.0; H, 2.11%. ν_{max} 1968 and 1892br (CO) cm^{-1}. δ_H 8.07–7.98 (1H, m, 5-H), 7.37–7.18 (2H, m, 3-H and 4-H); 5.88 (1H, s, CH); 5.54 (1H, m, 4-H_{Cr}); 5.45–5.23 (2H, m, 3-H_{Cr} and 5-H_{Cr}). R_f(benzene/ethyl acetate 10 : 1) = 0.55, R_f(benzene) = 0.27. Diastereoisomer **5b**, orange powder (3 mg, 3.5%), m.p. 69–71°C. δ_H 7.96 (1H, m, 5-H); 7.26 (2H, m, 3-H and 4-H); 5.88 (1H, s, CH); 5.50–5.33 (3H, m, ThH_{Cr}). R_f(benzene/ethyl acetate 10:1) = 0.43, R_f(benzene) = 0.18.

*3.7. Bis[tricarbonyl(η^6-2-thienyl-η^6-phenylmethanol)-chromium(0)] (**6a** + **6b**)*

A solution of tricarbonyl(η^6-benzaldehyde)chromium(0) [10] (60 mg, 0.25 mmol) in THF (3 ml) was used in the standard procedure. The usual work-up and flash chromatography yielded the singly decomplexed product **13** (3 mg, 3%), the doubly decomplexed product **7** (8.5 mg, 18%) and the diastereoisomer **6a** as red needles (32 mg, 28%), m.p. 113–115°C (decomp.). Anal. Found: C, 44.3; H, 2.1. $C_{17}H_{10}Cr_2O_7S$ calc.: C, 44.2; H, 2.16%). ν_{max} 1979, 1969 and 1898br (CO) cm^{-1}. δ_H 5.54 (1H, d, $J = 3.8$, CH); 5.39 (8H, m, ThH and PhH); 2.95 (1H, d, $J = 3.9$, OH). R_f(benzene/ethyl acetate 10:1) = 0.46, R_f(benzene) = 0.22. Diastereoisomer **6b**, red needles (31 mg, 27%), m.p. 136–138°C (decomp.). Anal. Found: C, 44.1; H, 2.2. $C_{17}H_{10}Cr_2O_7S$ calc.: C, 44.2; H, 2.16%. ν_{max} 1977, 1970 and 1899br (CO) cm^{-1}. δ_H 5.70 (1H, m, PhH); 5.39 (8H, m, CH, ThH and PhH); 2.66 (1H, d, $J = 3.8$, OH). R_f(benzene/ethyl acetate 10:1) = 0.35, R_f(benzene) = 0.15.

3.8. Tricarbonyl(η^6-phenyl-2-thienylmethanol)chromium(0) (13)

BuLi (0.4 ml, 1 mmol) was added dropwise to a stirred solution of tricarbonyl(η^6-benzene)chromium(0) [4] (217 mg, 1 mmol) in THF (10 ml) cooled to −78°C. The mixture was stirred at −78°C for 1 h, 2-thiophenecarboxaldehyde (0.3 ml, 3.2 mmol) was added and stirring continued (−78°C, 30 min). The mixture was warmed to 0°C then poured on to ice-water (50 ml) containing 0.2 ml of concentrated HCl. After extraction with benzene (2 × 50 ml), the extract was dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue, which was flash chromatographed (SiO_2, benzene/light petroleum 1:1) to yield the benzene complex **13** as yellow crystals (144 mg, 44%), m.p. 113°C (from benzene/light petroleum). Anal. Found: C, 51.9; H, 3.1. $C_{14}H_{10}CrO_4S$ calc.: C, 51.5; H, 3.06%. ν_{max} 1974 and 1901br (CO) cm^{-1}. δ_H 7.30 (1H, m, 5-H); 6.99 (2H, m, 3-H and 4-H); 5.71 (2H, m, CH and PhH); 5.35 (4H, m, PhH); 2.50 (1H, s, OH). R_f(benzene/ethyl acetate 10:1) = 0.63, R_f(benzene) = 0.32.

3.9. General procedure for the lithiation of thiophene and subsequent quenching with aldehydes

Butyllithium (0.8 ml, 2 mmol) was added dropwise to a cooled (−20°C) solution of thiophene (**11**) (0.32

ml, 4 mmol) in THF (5 ml) and the mixture stirred at −20°C for 1 h, then cooled to −78°C. The appropriate aldehyde (3 mmol) was added dropwise and stirring was continued (−30°C, 1 h). The mixture was warmed to 0°C, and poured on to ice water (100 ml) containing 0.2 ml of concentrated HCl. After extraction with diethyl ether (2 × 30 ml), the organic layer was dried (Na_2SO_4) and the solvent evaporated to leave a residue, which was recrystallized from diethyl ether/light petroleum.

3.10. 2-Thienylphenylmethanol (7)

Benzaldehyde (0.29 ml, 3 mmol) was added to the mixture obtained from **11** and BuLi in THF under standard conditions. Work-up and recrystallization gave the racemic product **7** as white crystals (206 mg, 54%), m.p. 55.5°C. Anal. Found: C, 69.6; H, 5.3, S, 16.5. $C_{11}H_{10}OS$ calc.: C, 69.4; H, 5.26; S, 16.85%. ν_{max} 3614 (OH) cm^{-1}. δ_H 7.48 (5H, m, PhH); 7.30 (1H, dd, $J = 1.6$ and 4.9, 5-H); 6.98 (2H, m, 3-H and 4-H); 6.08 (1H, s, CH); 2.50 (1H, s, OH). R_f(benzene/ethyl acetate 10:1) = 0.59, R_f(benzene) = 0.28.

3.11. Bis(2-thienyl)methanol (8)

2-Thiophenecarboxaldehyde (0.28 ml, 3 mmol) gave, after the standard procedure and recrystallization, the racemic product **8** as white solid (204 mg, 52%), m.p. 53°C. Anal. Found: C, 55.3; H, 4.0. $C_9H_8OS_2$ calc.: C, 55.1; H, 4.08%. δ_H 7.29 (2 × 1-H, dd, $J = 1.7$ and 4.4, 2 × 5-H); 6.98 (2 × 2-H, m, 3-H and 4-H); 6.30 (1H, s, CH); 2.62 (1H, s, OH). R_f(benzene/ethyl acetate 10:1) = 0.64, R_f(benzene) = 0.34.

3.12. 2-Thienyl-3-thienylmethanol (9)

3-Thiophenecarboxaldehyde (0.26 ml, 3 mmol), after work-up and recrystallization, yielded white crystals of **9** (224 mg, 57%), m.p. 64–65°C. Anal. Found: C, 55.5; H, 4.1. $C_9H_8OS_2$ calc.: C, 55.1; H, 4.08%. δ_H 7.30 (3H, m, 5-H, 2′-H and 5′-H); 7.02 (3H, m, 3-H, 4-H and 4′-H); 6.12 (1H, s, CH); 2.42 (1H, s, OH). R_f(benzene/ethyl acetate 10:1) = 0.51, R_f(benzene) = 0.30.

3.13. 2-Thienyl-selenophene-2-ylmethanol (10)

2-Selenophenecarboxaldehyde (0.31 ml, 3 mmol) afforded, after the usual procedure, the product **10** as a white solid (233 mg, 48%), m.p. 62.5°C. Anal. Found: C, 44.2; H, 3.2. C_9H_8OSSe calc.: C, 44.6; H, 3.29%. δ_H 7.97 (1H, dd, $J = 2.2$ and 4.4, 5-H_{Se}); 7.28 (1H, dd, $J = 1.4$ and 5.0, 5-H_S); 7.09 (4H, m, ThH and SeH); 6.28 (1H, s, CH); 2.68 (1H, s, OH). R_f(benzene/ethyl acetate 10:1) = 0.62, R_f(benzene) = 0.29.

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