A STUDY OF 2-PROPENETHIALS OBTAINED BY FLASH VACUUM PYROLYSIS OF 2-ETHENYL-1,3-DITHIOLANE 1,1-DIOXIDES

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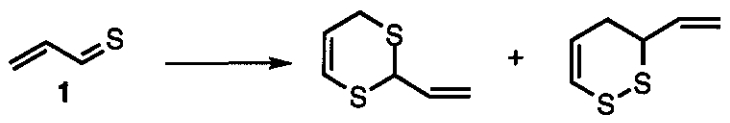
Abstract–Synthesis of substituted 2-propenethials by the flash vacuum pyrolysis of appropriately substituted 2-ethenyl-1,3-dithiolane 1,1-dioxides has been investigated. Pyrolysis of 2-propenyl-1,3-dithiolane 1,1-dioxide (**5a**) gives thiophene, 2,5-dihydrothiophene, a [4+2] dimer (**11**) and a [4+4] dimer (**12**) of 2-butenethial (**4a**). Pyrolysis of 2-(1-methylpropenyl)-1,3-dithiolane 1,1-dioxide (**5b**) gives 3-methylthiophene and a [4+4+4] trimer (**14**) of 2-methyl-2-butenethial (**4b**). Pyrolysis of 2-(2-phenylethenyl)-1,3-dithiolane 1,1-dioxide (**5c**) gives 2*H*-1-benzothiin (**15**) and a [4+2] dimer (**16**) of 3-phenyl-2-propenethial (**4c**). The dimer (**11**), 2-propenyl-4-methyl-4*H*-1,3-dithiin, can be considered as the *meta*-substituted cycloaddition product of 2-butenethial, whereas the dimer (**16**), 3-(2-phenylethenyl)-4-phenyl-3,4-dihydro-1,2-dithiin, can be considered as the *ortho*-substituted cycloaddition product of 2-phenyl-2-propenethial.

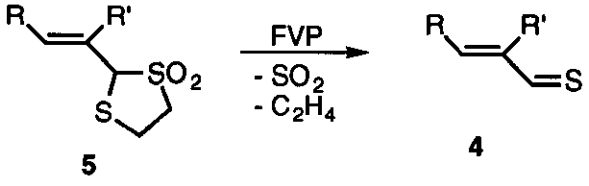
2-Propenethial (**1**, thioacrolein),[1] a reactive intermediate of the essential oil of garlic,[2] is a compound of considerable interest and has been investigated actively from theoretical,[3-5] physical,[6-8] and synthetic organic[9-15] points of view. Compound (**1**) has been synthesized in solution,[9] by photolysis[10] and by

thermolysis.[12-15] In the absence of dienophile as a trapping agent, **1**, once generated, gives two [4+2] dimers, 2-ethenyl-4*H*-1,3-dithiin (**2**) and 3-ethenyl-4*H*-1,2-dithiin (**3**).[3, 6, 14]



1 **2** **3**

Substituted 2-propenethial, on the other hand, is still rarely known. In order to study the effect of substituent on the chemistry of **1**, we aimed to prepare 2-butenethial (**4a**), 2-methyl-2-butenethial (**4b**) and 3-phenyl-2-propenethial (**4c**) by flash vacuum pyrolysis (FVP) of the corresponding 2-ethenyl-1,3-dithiolane 1,1-dioxides (**5a-c**) and to study the chemistry of **4a-c** in the absence of a trapping agent. The results of our investigation are presented herein.

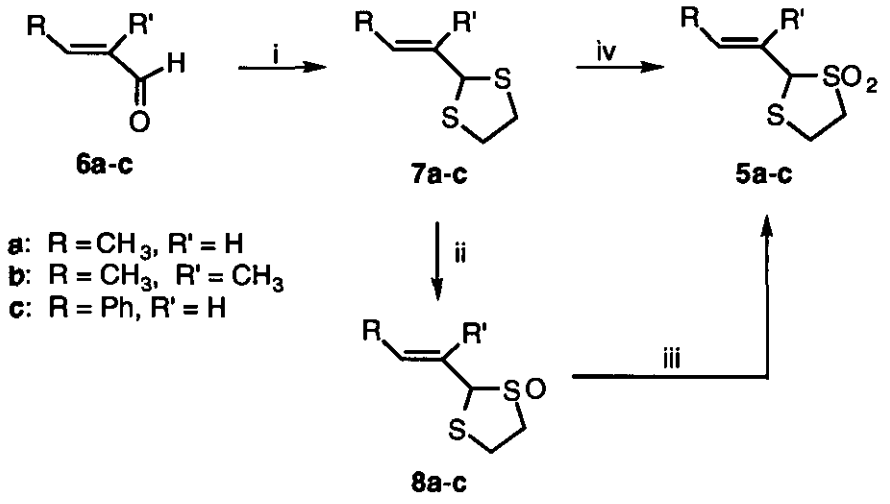


5 **4**

a: R = CH_3, R' = H
b: R = R' = CH_3
c: R = Ph, R' = H

RESULTS AND DISCUSSION

2-Ethenyl-1,3-dithiolane 1,1-dioxides (**5a-c**) were prepared (Scheme 1) by oxidation of the corresponding 2-ethenyl-1,3-dithiolanes (**7a-c**), which were obtained by condensation of appropriate conjugated aldehydes (**6a-c**) with 1,2-ethanedithiol in the presence of $Mg(ClO_4)_2$.[16] By using Method A,[17] **7a** was oxidized with 1 equiv. of $NaIO_4$ to give the sulfoxide (**8a**), which was subsequently oxidized with $KMnO_4$ in the presence of $MgSO_4$ to give the 1,1-dioxide (**5a**) in 38% overall yield. An improved procedure, Method B,[18] using OsO_4-catalyzed oxidation of dithiolane (**7a**) afforded directly the desired 1,1-dioxide (**5a**) in 62% yield. Dithiolane (**7c**) was similarly converted to its corresponding dioxide (**5c**) in 57% yield.



Scheme 1 *Reagents and conditions*: i, $HSCH_2CH_2SH$, cat. $Mg(ClO_4)_2$, $CHCl_3$, 0 °C, 2 h; **7a**, 80%; **7b**, 72%; **7c**, 91%; ii, $NaIO_4$ (1 equiv.), CH_3OH, 0 °C, 12 h; **8a**, 80%; **8b**, 78%; **8c**, 86%. iii, $KMnO_4$, $MgSO_4$, $(CH_3)_2CO$, room temperature, 5 h; **5a**, 48%; **5b**, 47%; **5c**, 42%. iv, cat. OsO_4, $(CH_3)_3NO$, THF, H_2O, room temperature, 30 h; **5a**, 62%; **5c**, 57%.

FVP of **5a** was performed as previously reported[19, 20] at temperatures 430-600 °C and *ca.* 10^{-2} torr, to give thiophene (**9**), 2,5-dihydrothiophene (**10**), a [4+2] dimer and a [4+4] dimer of **4a**, namely, 4-methyl-2-propenyl-4*H*-1,3-dithiin (**11**) and 4,8-dimethyl-1,5-dithiacycloocta-2,6-diene (**12**), respectively. A quantitative ^1H nmr analysis, using dibromomethane as the standard, indicated that **9**, **10**, **11** and **12** (26:34:20:20) were formed in 85% total yield. Compound (**11**) was separated by tlc, the ^1H nmr spectrum showed that it consisted of four diastereomers, 1'*E(Z)*,2,4-*cis(trans)*-isomers, which were inseparable by tlc or hplc. Dimer (**12**) showed a parent peak at *m/z* 172.038 attributable to a molecular formula $C_8H_{12}S_2$. The stereochemistry of **12** was not determined though the ^1H nmr spectrum showed a single isomer.

FVP of **5b** did not give a dimer of 2-methyl-2-butenethial (**4b**). Instead, FVP of **5b** gave 3-methylthiophene (**13**) and a trimer of **4b**, 3,4,7,8,11,12-hexamethyl-1,5,9-trithiacyclododeca-2,6,10-triene (**14**) in 70% yield. The trimer (**14**) ($C_{15}H_{24}S_3$) was solid; attempt of recrystallization for X-ray analysis, however, failed. The stereochemistry of **14** was unknown.

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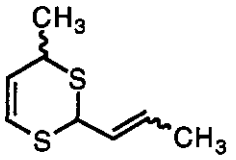

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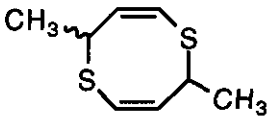

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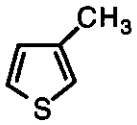
When **5c** was pyrolyzed, 2*H*-1-benzothiin (**15**) and a [4+2] dimer of 3-phenyl-2-propenethial (**4c**), namely, 3,4-dihydro-4-phenyl-3-(2-phenylethenyl)-1,2-dithiin (**16**) were obtained in a ratio of 1:1 and 85% yield. Compound (**16**) consists of *cis* and *trans* isomers in a ratio of 6:5. The *trans*-**16** isomer was isolated from the isomeric mixture by tlc using hexane as the developing solvent. A comparison of the ^{1}H nmr spectrum of *trans*-**16** with that of isomeric mixture of **16** allowed the ^{1}H nmr assignments of *cis*-**16**. The assignments of these resonances to respective protons of *cis*-**16** and *trans*-**16** are listed in Experimental part and their structures are depicted as follows. The axially orienting H-3 and H-4 in *trans*-**16** exhibited a coupling constant of 7.8 Hz larger than the value in *cis*-**16** ($J_{3,4}$ = 4.2 Hz).



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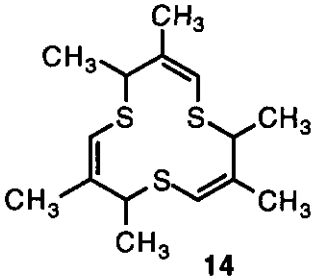

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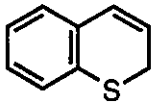

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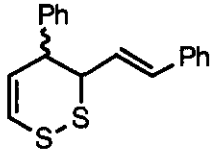

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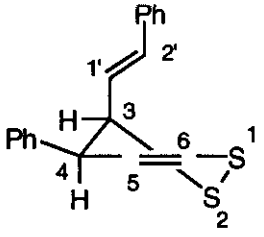
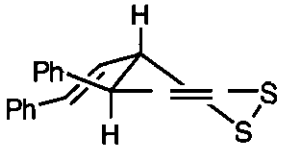


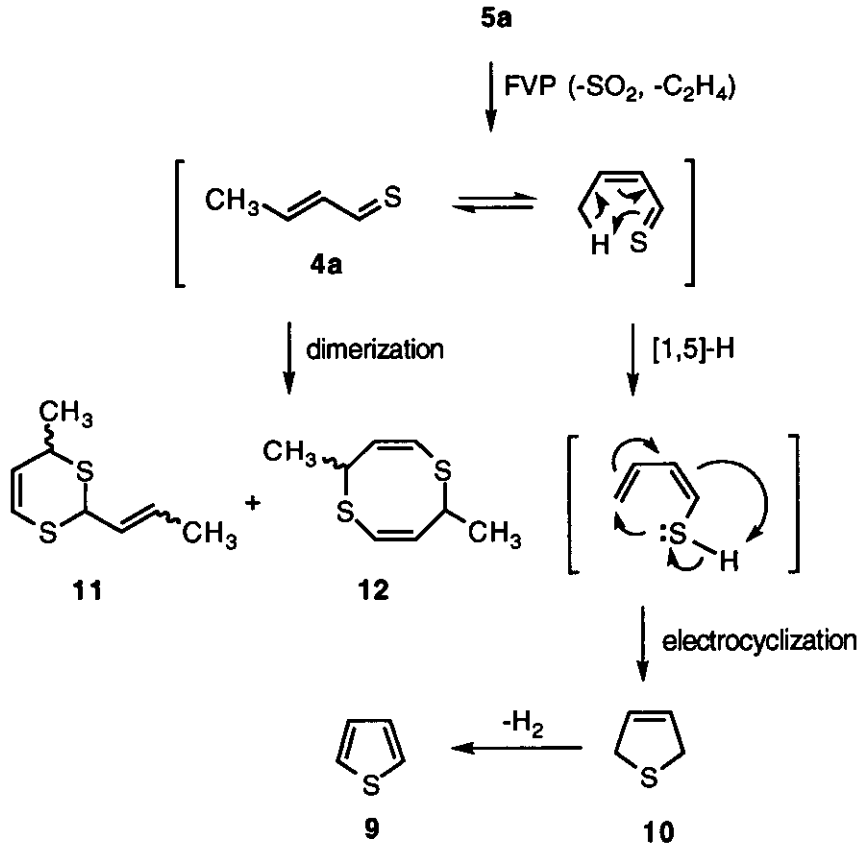
cis-**16**



trans-**16**

As shown above, the substituted 2-propenthials (**4a-c**) generated from pyrolysis of **5a-c** proceeded with different pathways. The formation of **9-12** from FVP of **5a** can be rationalized by a set of pathways involving 2-butenethial (**4a**) as the primary pyrolysis product (Scheme 2). Formation of dihydrothiophene (**10**) might involve a [1,5]-H shift of *cis*-2-butenethial, followed by an intramolecular

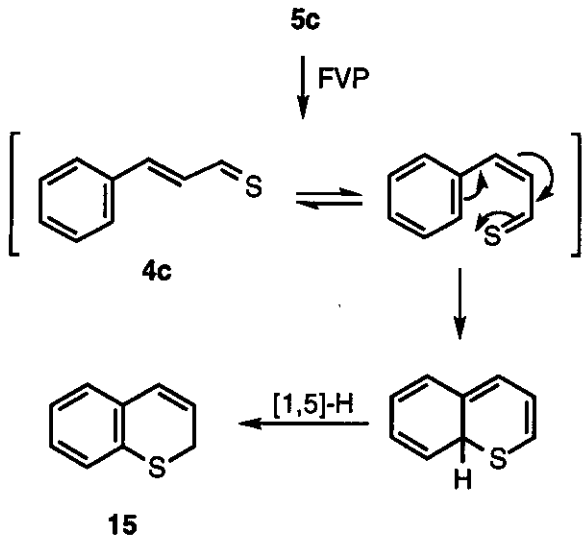
cyclization. Oxidative aromatization of **10** eventually led to thiophene (**9**). The regiochemistry of the [4+2] dimer (**11**) from **4a** is similar to that of the major [4+2] dimer (**2**) from 2-propenethial (**1**). The formation of **2** from **1** has been rationalized by the MINDO/3 method.[6] Unlike **1**, dimerization of **4a** also gave the [4+4] head-to-tail dimer (**12**). The formation of **12** from **4a** could proceed either by a concerted $[_4\pi_s + _4\pi_a]$ mechanism or by a stepwise mechanism.



Scheme 2 Pyrolysis pathways of 2-propenyl-1,3-dithiolane 1,1-dioxide

After pyrolysis of **5b**, the primary product (**4b**) underwent a [4+4+4] trimerization to give **14**. The trimerization presumably occurred in condensate, and the result was attributable to the steric hindrance of the 2-methyl group in **4b** which somewhat hampered the formation of dimer(s). The alternative regioisomer of **14** containing a disulfide bond was not formed presumably due to severe allylic strain. 3-Methylthiophene (**13**) could be derived from the rearrangement of *cis*-2-methyl-2-butenethial and the subsequent oxidative aromatization by a route similar to that shown in Scheme 2 for thiophene (**9**).

FVP of **5c** gave **16** as the [4+2] dimer of the primary pyrolysis product (**4c**). This regioselectivity is different from that observed in the [4+2] dimerization of **4a**, giving **11.** The reason for different regioselectivities is unclear. One might assume that formation of 1,2-dithiin (**16**) was enhanced by the secondary interaction between the phenyl and styryl groups of two **4c** molecules, whereas related 3,4-dihydro-4-methyl-3-propenyl-1,2-dithiin from **4a** was not formed due to the steric effect of the adjacent methyl and propenyl groups. Formation of 2*H*-1-benzothiin (**15**) could be realized by electrocyclization of **4c** followed by a [1,5]-H migration (Scheme 3).



Scheme 3 A mechanism for formation of 2*H*-1-benzothiin (**15**)

EXPERIMENTAL

Mps are uncorrected. ^{1}H Nmr spectra were recorded at 200 or 300 MHz and ^{13}C nmr spectra at 50 or 75 MHz using chlorotrimethylsilane as an internal standard (*J* values in Hz). Mass spectra were recorded at an ionizing voltage of 70 eV. Merck silica gel 60F sheets were used for analytical thin-layer chromatography. Column chromatography was performed on SiO_2 (70-230 mesh).

2-Propenyl-1,3-dithiolane 1,1-dioxide (5a): Method A: 2-Propenyl-1,3-dithiolane (**7a**) (1.46 g, 10 mmol) in cooled (0 °C) MeOH (80 ml) was added an aqueous solution (20 ml) of $NaIO_4$ (2.14 g, 10 mmol). The mixture was stirred for 12 h at 0 °C and filtered. The filtrate was concentrated *in vacuo*, and

the residue was extracted three times with EtOAc, and the extract was washed with brine. The organic phase was dried (Na_2SO_4), filtered, concentrated and the residue was chromatographed on a silica gel column by elution with EtOAc-hexane (1:1) to give 2-propenyl-1,3-dithiolane 1-oxide (**8a**) (1.30 g, 80%) containing two isomers (*trans*/*cis* = 3:1). The *cis*-isomer was liquid while the *trans*-isomer was crystal, mp 108-109 °C.[21] The isomeric mixture of **8a** (1.30 g, 8 mmol) and $MgSO_4$ (2.88 g, 24 mmol) were stirred in acetone (100 ml) at room temperature (27 °C) and an aqueous solution (50 ml) of $KMnO_4$ (1.5 g, 9.5 mmol) was added drop-by-drop. The purple color faded, the dark brown mixture was stirred for 5 h and filtered. The filtrate was concentrated and the residue was extracted three times with EtOAc. The organic phase was dried (Na_2SO_4), filtered, concentrated and the residue was chromatographed on a silica gel column by elution with EtOAc-hexane (1:1) to give the title compound (**5a**) (0.69 g, 48%) as an oily solid.

Method B: OsO_4 (100 mg) was dissolved in THF-H_2O (10 ml, v/v = 4:1) to prepare a 1% solution. The OsO_4 solution (2.5 ml) was added to a mixture of **7a** (292 mg, 2 mmol) and trimethylamine *N*-oxide (0.45 g, 4 mmol) in THF-H_2O (10 ml, v/v = 4:1). The mixture was stirred for 30 h at room temperature, THF was removed by rotary evaporation, and the residue was extracted three times with EtOAc. The combined extracts were dried (Na_2SO_4), filtered, concentrated and the residue was chromatographed on a silica gel column by elution with EtOAc-hexane (1:1) to give **5a** (222 mg, 62%). Oil; tlc (EtOAc-hexane, 1:1) R_f 0.48; υ_{max} (neat)/cm^{-1} 1659 and 1316 (SO_2); δ_H ($CDCl_3$) 6.95 (dq, *J* 15.0, 6.3, 1H), 5.43 (dd, *J* 15.0, 8.8, 8.4, 1H), 4.55 (d, *J* 8.8, 1H), 3.41-3.33 (m, 2H), 3.18-3.12 (m, 2H) and 1.81 (d, *J* 6.3, 3H); δ_C ($CDCl_3$) 136.1 (d), 119.1 (d), 62.7 (d), 50.5 (t), 22.5 (t) and 17.9 (q); *m/z* 179 (16%, M^++1), 114 (71, M^+-SO_2), 86 (89) and 85 (100) (Found: M^++1, 179.0189. $C_6H_{11}O_2S_2$ requires *M* + 1, 179.0222). *Anal.* Calcd for $C_6H_{10}O_2S_2$: C, 40.43; H, 5.65; S, 35.97. Found: C, 40.55; H, 5.72; S, 35.84.

2-(1-Methylpropenyl)-1,3-dithiolane 1,1-dioxide (5b): Compound (**5b**) was prepared from 2-(1-methylpropenyl)-1,3-dithiolane (**7b**) in 37% overall yield by a procedure similar to Method A for **5a**. Oil; Tlc (EtOAc-hexane, 1:1) R_f 0.5; υ_{max} (neat)/cm^{-1} 1649 and 1310; δ_H ($CDCl_3$) 5.83 (q, *J* 6.8, 1H), 4.57 (s, 1H), 3.39-3.25 (m, 2H), 3.21-3.09 (m, 2H), 1.88 (s, 3H) and 1.72 (d, *J* 6.8, 3H); δ_C ($CDCl_3$) 131.0 (d), 125.6 (s), 69.2 (d), 51.4 (t), 22.9 (t), 14.2 (q) and 14.1 (q); *m/z* 193 (100%, M^++1), 192 (0.5, M^+), 176 (7), 128 (20, M^+-SO_2) and 100 (60) (Found: M^+, 192.0257. $C_7H_{12}O_2S_2$ requires *M*, 192.0278). *Anal.* Calcd for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29; S, 33.35. Found: C, 43.83; H, 6.21; S, 33.25.

2-(2-Phenylethenyl)-1,3-dithiolane 1,1-dioxide (5c): Compound (**5c**) was prepared from 2-(2-phenylethenyl)-1,3-dithiolane (**7c**) by a procedure similar to that for **5a**, in 36% overall yield by using Method A or in 57% yield by using Method B. White solid, mp 93-95 °C; tlc (EtOAc-hexane, 1:1) R_f 0.6; υ_{max} (KBr)/cm^{-1} 1317 and 1113; δ_H ($CDCl_3$) 7.43-7.28 (m, 5H), 6.79 (d, *J* 15.6, 1H), 6.11 (dd, *J* 15.6, 8.9, 1H), 4.73 (d, *J* 8.9, 1H), 3.44-3.36 (m, 2H) and 3.21-3.14 (m, 2H); δ_C ($CDCl_3$) 138.6 (d), 135.1 (s), 128.8 (d), 128.6(d, 2C), 127.0 (d, 2C), 117,2 (d), 63.4 (d), 51.1 (t) and 23.0 (t); *m/z* 240 (12%, M$^+$), 176 (41, M$^+$-SO_2) and 148 (100) (Found: M$^+$, 240.0289. $C_{11}H_{12}O_2S_2$ requires *M*, 240.0278). *Anal.* Calcd for $C_{11}H_{12}O_2S_2$: C, 54.97; H, 5.03; S, 26.68. Found: C, 54.96; H, 4.93; S, 26.82.

General Pyrolysis Procedure: The furnace was maintained at temperatures in the range of 430-600 °C. A sample (200-300 mg) was placed into the sample chamber and the system was evacuated to *ca.* 10^{-2} torr. During pyrolysis, a liquid-nitrogen-cooled trap was used to collect all the pyrolysis products. Upon completion of the pyrolysis, a cold (-78 °C) solvent ($CDCl_3$ or Et_2O, 5 ml) was used to rinse the walls of the trap. The product solution was slowly warmed to room temperature, dried, filtered and concentrated. The product mixture was analyzed by nmr spectra and/or separated by tlc.

Thiophene (9): A quantative ^{1}H nmr analysis, using dibromomethane as the standard, indicated that the pyrolysis products of **5a** consisted of **9**, dihydrothiophene **10**, dimers **11** and **12** (26:34:20:20). **9**: δ_H 7.20 (m, 2H), 6.96 (m, 2H). The gc retention time of **9** was identical to that of an authentic sample.

2,5-Dihydrothiophene (10):[22] Oil; υ_{max} (neat)/cm^{-1} 3000, 1600, 1430, 1220, 870 and 680; δ_H ($CDCl_3$) 5.78 (s, 2H) and 3.68 (s, 4H); δ_C ($CDCl_3$) 127.0 (d) and 39.0 (t); GC-ms *m/z* 86 (16%, M$^+$), 85 (100), 71 (7) and 58 (13).

4-Methyl-2-propenyl-4*H*-1,3-dithiin (11): After removal of solvent, **9** and **10** *in vacuo*, the oily residue of pyrolysis mixture was subjected to tlc separation on a silica-gel plate to yield **11**. Compound (**11**) existed as a mixture of four diastereomers (36:33:17:14) by analysis of its ^{1}H nmr spectrum; tlc (hexane) R_f 0.4; ν_{max} (neat)/cm^{-1} 2964, 1694, 1601 and 1447; δ_H ($CDCl_3$) 6.32-6.26 (m, H-6), 6.00-5.92 (m, H-1'), 5.82-5.58 (m, H-2'), 5.26 (d, *J* 9.6, H-2)/5.01 (d, *J* 9.6)/4.98 (d, *J* 7.8)/4.66 (d, *J* 7.8), 3.80-3.50 (m, H-4), 1.78-1.76 (m, vinyl CH_3) and 1.48-1.44 (m, 4-CH_3); δ_C ($CDCl_3$) 131.8 (d), 130.2 (d), 128.6 (d), 127.4 (d), 126.5 (d), 126.2 (d), 124.2 (d), 123.6 (d), 122.9 (d), 121.4 (d), 47.8 (d), 41.9 (d), 36.7 (d), 33.6 (d), 33.1 (d), 23.2 (q), 22.7 (q), 20.0 (q), 17.6 (q) and 13.2 (q); *m/z* 172 (13%, M$^+$), 139 (40), 117 (7), 86 (56) and 85 (100) (Found: M$^+$,172.0366. $C_8H_{12}S_2$ requires *M*,172.0381).

4,8-Dimethyl-1,5-dithia-2,6-cyclooctadiene (12): Oil; tlc (EtOAc-hexane, 5:95) R_f 0.5; υ_{max} (neat)/cm^{-1} 3000, 2900, 1610, 1400 and 680; δ_H ($CDCl_3$) 5.79 (d, *J* 14.7, H-2, H-6), 5.62 (dd, *J* 14.7, 9.6, H-3, H-7), 3.50 (m, H-4, H-8) and 1.29 (d, *J* 9.6, 4-Me, 8-Me); δ_C ($CDCl_3$) 139.8 (d), 123.0 (d), 46.0 (d) and 19.4 (q); *m/z* 172 (10%, M^+), 140 (12), 139 (38), 86 (52) and 85 (100) (Found: M^+, 172.0378. $C_8H_{12}S_2$ requires *M*, 172.0381).

3-Methylthiophene (13):[23] A quantitative ^{1}H nmr analysis, using dibromomethane as the standard, indicated that the pyrolysis products of **5b** consisted of 3-methylthiophene (**13**) and trimer (**14**) (6:1). Pure **13** and **14** were isolated from the mixture by tlc on a silica gel plate using a developing solution of EtOAc-hexane (5:95). **13**: Oil; ν_{max} (neat)/cm^{-1} 2900, 1410, 860 and 770; δ_H ($CDCl_3$) 7.23 (m, 1H), 6.91 (m, 2H) and 2.29 (s, 3H); GC-ms *m/z* 98 (55%, M^+), 97 (100) and 45 (30).

3,4,7,8,11,12-Hexamethyl-1,5,9-trithiacyclododeca-2,6,10-triene (14): Pale yellow solid, mp 210 ^{0}C (decomp.); ν_{max} (KBr)/cm^{-1} 2900, 1600, 940 and 680; δ_H ($CDCl_3$) 5.64 (q, *J* 1.2, H-2, H-6, H-10), 3.59 (q, *J* 7.2, H-4, H-8, H-12), 1.71 (d, *J* 1.2, 3-Me, 7-Me, 11-Me) and 1.29 (d, *J* 7.2, 4-Me, 8-Me, 12-Me); δ_C ($CDCl_3$) 143.6 (s), 119.4 (d), 51.8 (d), 18.4 (q) and 12.2 (q); *m/z* 300 (3%, M^+), 200 (15), 167 (29), 139 (23), 100 (58), 99 (86) and 85 (100) (Found: M^+, 300.1043. $C_{15}H_{24}S_3$ requires *M*, 300.1040).

2*H*-1-Benzothiin (15):[23] The pyrolysis products of **5c** were collected in Et_2O (5 ml) and concentrated. Gc and ^{1}H nmr analyses indicated that the crude product mixture consisted of 2*H*-1-benzothiin (**15**), *cis*-**16** and *trans*-**16** (50:27:23). The product (**15**) was isolated by tlc on a silica gel plate using a developing solution of EtOAc-hexane (2:98). Oil; ν_{max} (neat)/cm^{-1} 3500, 2300, 1600, 1490 and 910; δ_H ($CDCl_3$) 7.21 (m, 1H), 7.08 (m, 3H), 6.48 (d, *J* 10.2, 1H), 5.94 (m, 1H), 3.45 (dd, *J* 5.1, 1.5, 2H); δ_C ($CDCl_3$) 132.2(s), 131.7 (s), 129.0 (d), 128.1 (d), 127.9 (d), 127.1 (d), 125.6 (d), 121.7 (d) and 25.1 (t); *m/z* 148 (58%, M^+), 147, (100), 74 (11) and 69 (17) (Found: M^+, 148.0349. C_9H_8S requires *M*, 148.0347).

3,4-Dihydro-4-phenyl-3-(2-phenylethenyl)-1,2-dithiin (16): ν_{max} (neat)/cm^{-1} 3100, 1600, 1500, 1450, 750 and 700. A sample of pure *trans*-**16** was isolated by tlc on a silica-gel plate using hexane as the developing solvent. *Trans*-**16**: Oil; δ_H ($CDCl_3$) 7.28 (m, 5H), 6.63 (dd, *J* 10.5, 1.8, H-6), 6.54 (d, *J* 15.8, H-2'), 6.28 (dd, *J* 15.8, 7.8, H-1'), 6.10 (dd, *J* 10.5, 4.2, H-5), 3.84 (t, *J* 7.8, H-3), 3.78 (ddd, *J* 7.8, 4.2, 1.8, H-4); δ_C ($CDCl_3$) 142.3, 136.4, 133.2, 129.0, 128.8, 128.6, 128.5, 127.9, 127.3, 127.2, 126.5, 121.6, 49.9, 46.1; *m/z* 296 (2%, M^+), 264 (2), 263 (5), 229 (3), 215 (3), 202 (4), 185 (6), 179 (8), 147 (100), 115 (90) and 77, (59) (Found: M^+, 296.0692. $C_{18}H_{16}S_2$ requires *M*, 296.0694). *Cis*-**16**: δ_H ($CDCl_3$) 7.28 (m, 5H), 6.60 (dd, *J* 10.5, 2.4, H-6), 6.53 (d, *J* 15.6, H-2'), 6.12 (dd, *J* 10.5, 4.8, H-5), 5.83 (dd, *J* 15.6, 9.6, H-

1'), 4.07 (dd, *J* 9.6, 4.2, H-3), 3.93 (ddd, *J* 4.8, 4.2, 2.4, H-4); δ_C ($CDCl_3$) 140.1, 136.5, 133.5, 128.7, 128.3, 128.2, 128.1, 127.8, 127.2, 125.9, 120.7, 50.3, 45.1.

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