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-butene-thial (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 2H-1-benzothiin (15) and a [4+2] dimer (16) of 3-phenyl-2-propenethial (4c). The dimer (11), 2-propenyl-4-methyl-4H-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 organic9-15 points of view. Compound (1) has been synthesized in solution,9 by photolysis10 and by
thermolysis. In the absence of dienophile as a trapping agent, 1, once generated, gives two [4+2] dimers, 2-ethenyl-4H-1,3-dithiin (2) and 3-ethenyl-4H-1,2-dithiin (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.

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-ethanediol in the presence of Mg(ClO₄)₂. By using Method A, 7a was oxidized with 1 equiv. of NaIO₄ to give the sulfoxide (8a), which was subsequently oxidized with KMnO₄ in the presence of MgSO₄ to give the 1,1-dioxide (5a) in 38% overall yield. An improved procedure, Method B, using OsO₄-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$_2$CH$_2$SH, cat. Mg(ClO$_4$)$_2$, CHCl$_3$, 0 °C, 2 h; 7a, 80%; 7b, 72%; 7c, 91%;  
ii, NaIO$_4$ (1 equiv.), CH$_3$OH, 0 °C, 12 h;  
8a, 80%; 8b, 78%; 8c, 86%. iii, KMnO$_4$, MgSO$_4$, (CH$_3$)$_2$CO, room temperature, 5 h;  
5a, 48%; 5b, 47%; 5c, 42%. iv, cat. OsO$_4$, (CH$_3$)$_3$NO, THF, H$_2$O, 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-4H-1,3-dithiin (11) and 4,8-dimethyl-1,5-dithiacycloocta-2,6-diene (12), respectively. A  
quantitative $^1$H 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 $^1$H 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$_8$H$_{12}$S$_2$. The stereochemistry of 12 was not determined though the $^1$H 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$_{13}$H$_{24}$S$_3$) was solid; attempt of recrystallization for X-ray analysis,  
however, failed. The stereochemistry of 14 was unknown.
When 5c was pyrolyzed, 2H-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).

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. 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 [4πₜ + 4πₐ] mechanism or by a stepwise mechanism.

![Scheme 2](image)

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 2H-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 2H-1-benzothiin (15)](image)

**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$_2$SO$_4$), 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. 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$_2$SO$_4$), 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$_2$O (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$_2$O (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$_2$SO$_4$), 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; $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 1659 and 1316 (SO$_2$); $\delta_H$ (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); $\delta_C$ (CDCl$_3$) 136.1 (d), 119.1 (d), 62.7 (d), 50.5 (t), 22.5 (t) and 17.9 (q); $m/\zeta$ 179 (16%, M$^+$+1), 114 (71, M$^+$-SO$_2$), 86 (89) and 85 (100) (Found: M$^+$+1, 179.0189. C$_6$H$_{10}$O$_2$S$_2$ requires M $+$ 1, 179.0222). Anal. Calcd for C$_6$H$_{10}$O$_2$S$_2$: 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; $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 1649 and 1310; $\delta_H$ (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); $\delta_C$ (CDCl$_3$) 131.0 (d), 125.6 (s), 69.2 (d), 51.4 (t), 22.9 (t), 14.2 (q) and 14.1 (q); $m/\zeta$ 193 (100%, M$^+$+1), 192 (0.5, M$^+$), 176 (7), 128 (20, M$^+$-SO$_2$) and 100 (60) (Found: M$^+$, 192.0257. C$_7$H$_{12}$O$_2$S$_2$ requires M, 192.0278). Anal. Calcd for C$_7$H$_{12}$O$_2$S$_2$: 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) Rf 0.6; \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 1317 and 1113; \( \delta_{\text{H}} \) (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); \( \delta_{\text{C}} \) (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\(_2\)S\(_2\) requires \( M, 240.0278 \)). Anal. Calcd for C\(_{11}\)H\(_{12}\)O\(_2\)S\(_2\): 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\(_2\)O, 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: \( \delta_{\text{H}} \) 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):** Oil; \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \) 3000, 1600, 1430, 1220, 870 and 680; \( \delta_{\text{H}} \) (CDCl\(_3\)) 5.78 (s, 2H) and 3.68 (s, 4H); \( \delta_{\text{C}} \) (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-4H-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) \( R_f 0.4; \nu_{\text{max}} \) (neat)/cm\(^{-1} \) 2964, 1694, 1601 and 1447; \( \delta_{\text{H}} \) (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\(_3\)); \( \delta_{\text{C}} \) (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\(_8\)H\(_{12}\)S\(_2\) requires M,172.0381).
4,8-Dimethyl-1,5-dithia-2,6-cyclooctadiene (12): Oil; tlc (EtOAc-hexane; 5:95) Rf 0.5; v\textsubscript{max} (neat)/cm\textsuperscript{-1} 3000, 2900, 1610, 1400 and 680; δ\textsubscript{H} (CDCl\textsubscript{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\textsubscript{C} (CDCl\textsubscript{3}) 139.8 (d), 123.0 (d), 46.0 (d) and 19.4 (q); m/z 172 (10%, M\textsuperscript{+}), 140 (12), 139 (38), 86 (52) and 85 (100) (Found: M\textsuperscript{+}, 172.0378. C\textsubscript{8}H\textsubscript{12}S\textsubscript{2} requires M, 172.0381).

3-Methylthiophene (13): A quantitative ¹H 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; v\textsubscript{max} (neat)/cm\textsuperscript{-1} 2900, 1410, 860 and 770; δ\textsubscript{H} (CDCl\textsubscript{3}) 7.23 (m, 1H), 6.91 (m, 2H) and 2.29 (s, 3H); GC-ms m/z 300 (3%, M\textsuperscript{+}), 200 (15), 167 (29), 139 (23), 100 (58), 99 (86) and 85 (100) (Found: M\textsuperscript{+}, 300.1043. C\textsubscript{15}H\textsubscript{24}S\textsubscript{3} requires M, 300.1040).

3,4,7,8,11,12-Hexamethyl-1,5,9-trithiacyclosdocende-2,6,10-triene (14): Pale yellow solid, mp 210 °C (decomp.); v\textsubscript{max} (KBr)/cm\textsuperscript{-1} 2900, 1600, 940 and 680; δ\textsubscript{H} (CDCl\textsubscript{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\textsubscript{C} (CDCl\textsubscript{3}) 143.6 (s), 119.4 (d), 51.8 (d), 18.4 (q) and 12.2 (q); m/z 300 (3%, M\textsuperscript{+}), 200 (15), 167 (29), 139 (23), 100 (58), 99 (86) and 85 (100) (Found: M\textsuperscript{+}, 300.1043. C\textsubscript{15}H\textsubscript{24}S\textsubscript{3} requires M, 300.1040).

2H-1-Benzothiin (15): The pyrolysis products of 5c were collected in Et\textsubscript{2}O (5 ml) and concentrated. Gc and ¹H nmr analyses indicated that the crude product mixture consisted of 2H-1-benzothiin (15), cis-16 and trans-16 (50:27:23). The product (15) was isolated by tlc on a silica-gel plate using hexane as the developing solvent. Oil; v\textsubscript{max} (neat)/cm\textsuperscript{-1} 3500, 2300, 1600, 1490 and 910; δ\textsubscript{H} (CDCl\textsubscript{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\textsubscript{C} (CDCl\textsubscript{3}) 142.3, 136.4, 133.2, 129.0, 128.9, 128.6, 128.5, 127.9, 127.3, 127.2, 126.5, 121.6, 49.9, 46.1; m/z 296 (2%, M\textsuperscript{+}), 264 (2), 263 (5), 229 (3), 215 (3), 202 (4), 185 (6), 179 (8), 147 (100), 115 (90) and 77, (59) (Found: M\textsuperscript{+}, 296.0692. C\textsubscript{18}H\textsubscript{16}S\textsubscript{2} requires M, 296.0694). Cis-16: δ\textsubscript{H} (CDCl\textsubscript{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 (CDCl₃) 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.

ACKNOWLEDGMENTS

This work was supported by the National Science Council of the Republic of China, Grants NSC 82-0115-C110-0006 and NSC 82-0208-M002-031.

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Received, 7th March, 1995