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Pyrolytic Chemistry of Thenyl Benzoates

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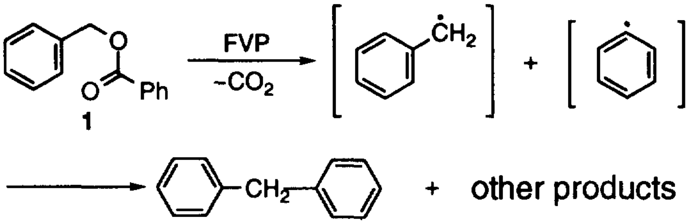
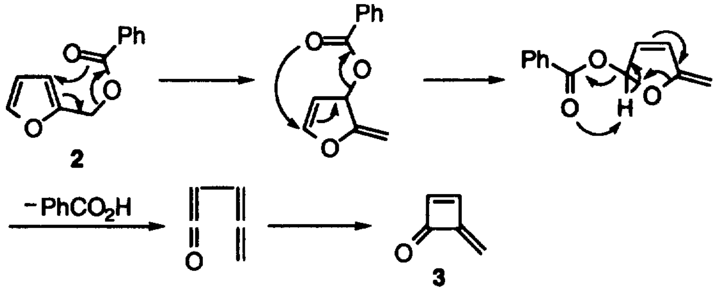
Abstract: Flash vacuum pyrolysis of 2- and 3-thenyl benzoates (**4** and **5**, respectively) at temperatures in the range 550-750 °C and ca. 10^{-2} torr gave several radical-derived products. The mechanism of formation of these pyrolysis products is proposed to involve 2-, 3-thenyl and phenyl radicals.

INTRODUCTION

We have previously reported that flash vacuum pyrolysis (FVP) of benzyl benzoate (**1**) undergoes homolytic cleavage to give benzyl and phenyl radicals.[1] A result which is contrast to that of FVP of furfuryl benzoate (**2**). Trahanovsky and Park reported that FVP of **2** produces methylenecyclobutenone (**3**). The mechanism for the formation of compound **3** involves double migrations of the benzoate group into furan ring (Scheme 1).[2,3] An explanation for such distinction between **1** and **2** is ascribed to the altered aromaticity between benzene and furan.[4] Since the aromaticity of thiophene is in between,[4] we therefore chose to study the pyrolytic chemistry of 2- and 3-thenyl benzoates (**4** and **5**, respectively), the thiophene analogues of **1**, and the results are presented herein.

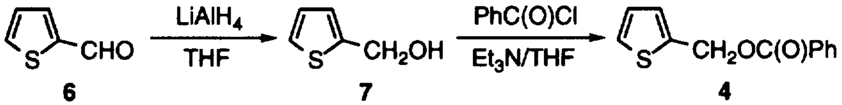




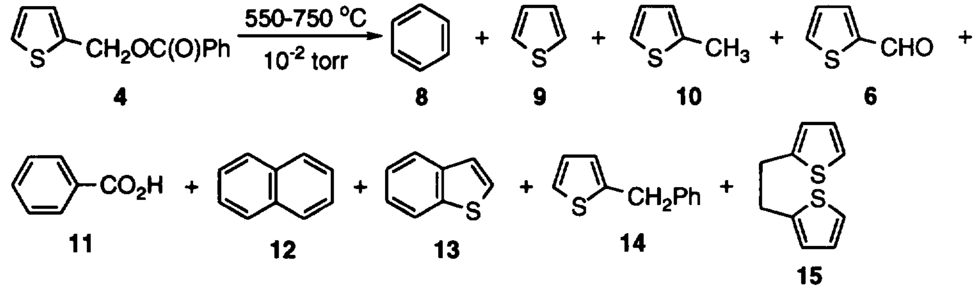
Scheme 1

RESULTS AND DISCUSSION

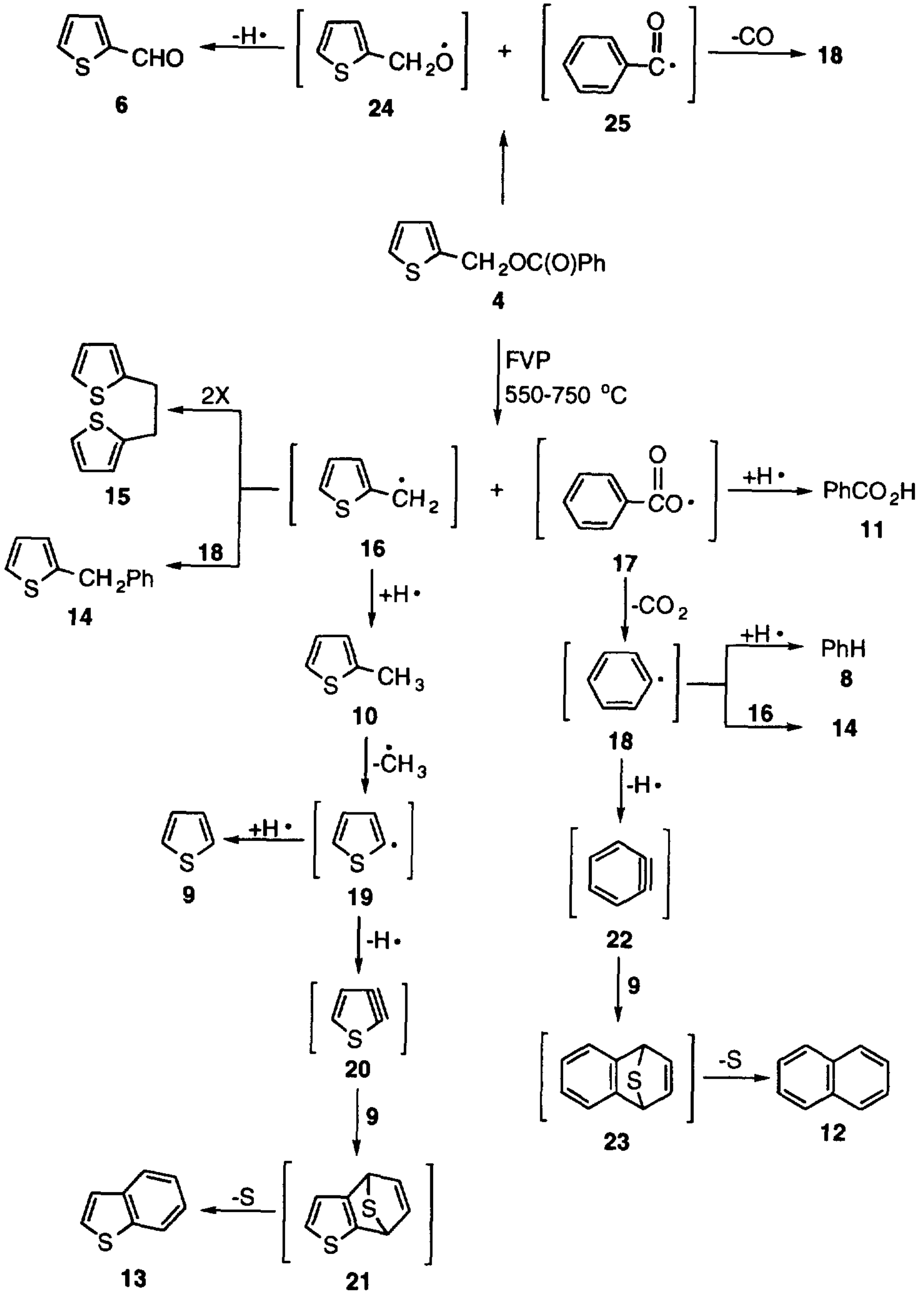
2-Thenyl benzoate (**4**), prepared by LiAlH$_4$ reduction of 2-thiophenecarbaldehyde (**6**) followed by esterification of the resulting alcohol **7** (Scheme 2), was pyrolyzed using the method previously reported[5] at temperatures in the range 550-750 °C and ca. 10^{-2} torr. NMR and GC-MS analyses of the pyrolysate separated from substantial amounts of dark-brown polymers indicated that several radical-derived products are formed, they are benzene (**8**), thiophene (**9**), 2-methylthiophene (**10**), 2-thiophenecarbaldehyde (**6**), benzoic acid (**11**), naphthalene (**12**), benzothiophene (**13**), 2-benzylthiophene (**14**)[6] and 2,2'-dithenyl (**15**). A mechanism to account for this experimental results is presented in Scheme 3 and the yields of each product generated at various temperatures are listed in Table 1.



Scheme 2



Under the pyrolysis conditions, **4** experienced a homolytic cleavage to give 2-thenyl and benzoyloxy radicals **16** and **17**. Radical **17** may further lose a CO$_2$ molecule to produce phenyl radical **18**. Abstraction of a hydrogen radical from fragments in the hot zone by radicals **16**, **17** and **18** generate 2-methylthiophene (**10**), benzoic acid (**11**) and benzene (**8**), respectively. Alternatively dimerization of radical **16** and a cross coupling of radicals **16** and **18** produce 2,2'-dithenyl (**15**) and 2-benzylthiophene (**14**),[7] respectively.

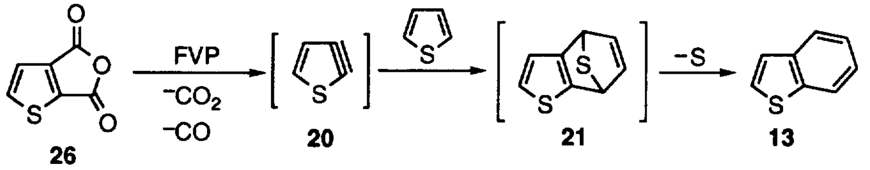

CHO
6
-H•
CH₂Ȯ
24
+
C•
25
-CO
18
CH₂OC(O)Ph
4
FVP
550-750 °C
2X
15
18
CH₂Ph
14
ĊH₂
16
+
CO•
17
+H•
PhCO₂H
11
+H•
CH₃
10
-ĊH₃
+H•
9
19
-H•
20
9
-S
13
21
-CO₂
18
+H•
PhH
8
16
14
-H•
22
9
S
23
-S
12

Scheme 3

Table 1. The Yields of the Pyrolysis Products of 2-Thenyl Benzoate (4) at Various Temperatures (and ca. 10^{-2} torr).

products / temp.(°C)	yield (%)									
	recovered **4**	**8**	**9**	**10**	**6**	**11**	**12**	**13**	**14**	**15**
550	34.4	2.0	1.0	2.3	1.2	20.2	—	—	0.2	7.2
600	12.1	6.3	4.2	3.9	2.6	38.9	—	—	0.3	21.2
650	2.4	8.7	2.6	4.0	3.2	42.3	—	—	0.3	17.8
700	—	11.9	2.0	4.8	2.2	34.7	0.4	0.4	1.2	8.4
750	—	14.6	1.2	1.6	0.8	18.9	1.6	0.9	0.7	2.6

Reinecke and Newsom had pyrolyzed thiophene-2,3-dicarboxylic acid anhydride (**26**) in the presence of thiophene to give benzothiophene (**13**) as the major product.[8] They suggested that thiophyne (**20**) should be involved in this pyrolytic reaction.



On the basis of the above result[8] and the formation of thiophene from FVP of **4**, we believe that there should be a further thermal fragmentation of 2-methylthiophene (**10**) occurred in the hot zone. Thus, **10** produced in the hot zone could lose a methyl radical to generate thiophene radical **19**. Abstraction of a hydrogen radical by **19** then gives thiophene (**9**). Additionally, radical **19** might further lose a hydrogen radical to form thiophyne (**20**) and this reactive compound could undergo a Diels-Alder reaction with thiophene to generate the intermediate **21**. Subsequent desulfurization of **21** then gives benzothiophene (**13**). Similarly, phenyl radical (**18**) can also lose a hydrogen radical to give benzyne (**22**) which undergoes the Diels-Alder reaction with thiophene followed by desulfurization of the resulting intermediate **23** gives naphthalene (**12**).

Besides radicals **16** and **18**, 2-thenyloxy and benzoyl radicals **24** and **25**, generated by homolytic cleavage of C(O)-O bond in **4**, are also included in the pyrolytic reaction of **4**. The loss of a hydrogen radical from radical **24** and a CO molecule from radical **25** leads to formation of 2-thiophenecarbaldehyde (**6**) and phenyl radical **18**, respectively.

In order to assure that thiophene (**9**) and benzothiophene (**13**) are formed from thermal reaction of 2-methylthiophene (**10**), we have pyrolyzed **10**[9] solely and obtained **9**, **13** and several other products, they are 3-methylthiophene (**27**), 2-ethylthiophene (**28**), naphthalene (**12**) and 2,2'-dithenyl (**15**). The yields of each pyrolysis product of **10** at two different temperatures are listed in Table 2.

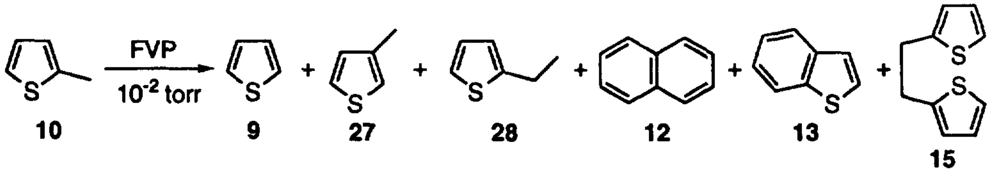
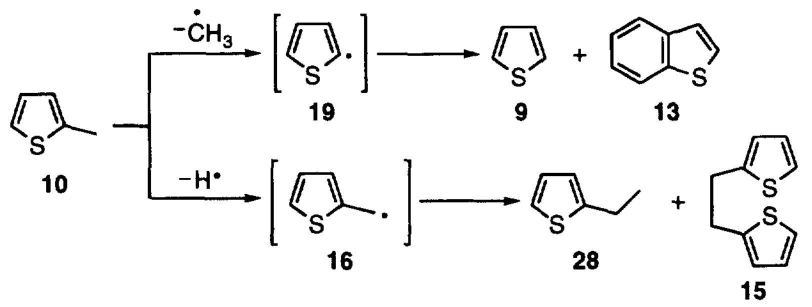


Table 2. The Yields of the Pyrolysis Products of 2-Methylthiophene (**10**) at Two Different Temperatures (and ca. 10^{-2} torr).

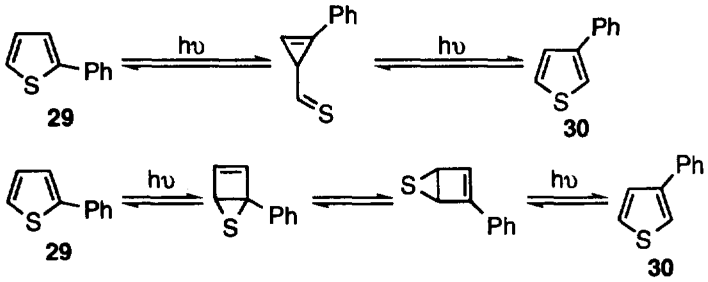
products / temp. (°C)	yield (%)						
	recovered **10**	**9**	**27**	**28**	**12**	**13**	**15**
750	73.33	1.86	4.32	1.30	—	—	1.64
900	68.26	3.15	5.62	2.10	1.80	1.52	3.10

The results showed that **10** can undergo homolytic cleavage to lose not only a methyl radical to form a thiophene radical **19** but also a hydrogen radical to produce a thenyl radical **16** (Scheme 4).



Scheme 4

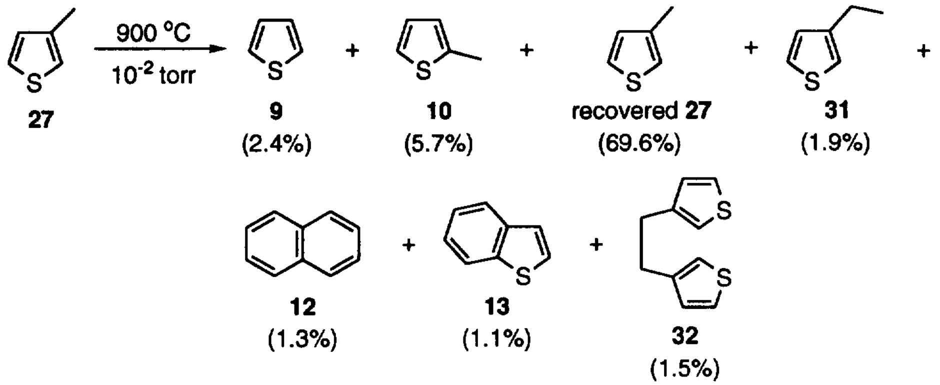
Wynberg and van Driel had reported that 2-phenylthiophene (**29**) can be converted to 3-phenyl-thiophene (**30**) by irradiation.[10] There are two mechanisms proposed for this type of rearrangement,[6,11,12] involving either cyclopropene or cyclobutene intermediate as shown in Scheme 5.



Scheme 5

We feel that similar rearrangement processes could also account for the conversion of 2-methylthiophene (**10**) to 3-methylthiophene (**27**) under the pyrolysis of **10**.

FVP of 3-methylthiophene (**27**) gives the products very much the same as those from FVP of **10**.



FVP of 3-thenyl benzoate (**5**) under the same pyrolysis conditions as **4** also give several radical-derived products, they are benzene (**8**), thiophene (**9**), 3-methylthiophene (**27**), 3-thiophenecarbaldehyde (**33**), 2-thiophenecarbaldehyde (**6**), benzoic acid (**11**), naphthalene (**12**), benzothiophene (**13**), 3-benzylthiophene (**34**)[6] and 3,3'-dithenyl (**32**). The yields of each product at various pyrolysis temperatures are listed in Table 3.

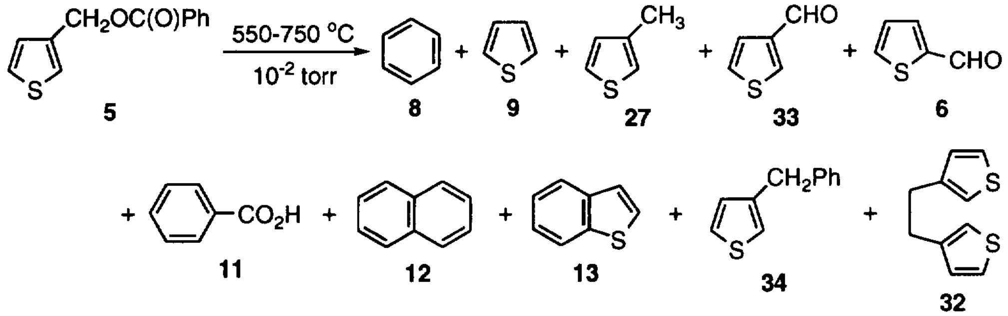


Table 3. The Yields of the Pyrolysis Products of 3-Thenyl Benzoate (**5**) at Various Temperatures (and ca. 10^{-2} torr).

products / temp.(°C)	yield (%)										
	recovered **5**	**8**	**9**	**27**	**33**	**6**	**11**	**12**	**13**	**34**	**32**
550	40.7	2.4	1.2	2.2	1.6	0.4	18.9	—	—	0.2	6.2
600	10.7	5.8	3.2	4.0	3.2	1.6	36.3	—	—	0.3	18.8
650	2.0	8.2	2.4	3.2	4.6	2.4	44.7	—	—	0.4	14.3
700	—	11.6	1.8	2.4	2.8	1.4	38.2	0.3	0.3	1.0	6.2
750	—	13.8	1.3	2.2	1.4	1.0	22.2	2.0	2.4	0.4	2.5

Similar to the pyrolytic reaction of **4**, **5** experienced homolytic cleavages and all the products but aldehyde **6** can be explained clearly in the same way as for those pyrolysis products of **4**. 2-Thiophenecarbaldehyde (**6**) could be produced from the thermal rearrangement of 3-thiophenecarbaldehyde (**33**) in the similar ways as the reactions shown in Scheme 5.

EXPERIMENTAL SECTION

Infrared spectra were recorded with a Shimadzu IR-408 spectrophotometer. ^1H and ^{13}C NMR spectra were measured with a Varian VXR-300 NMR spectrometer, with tetramethylsilane as the internal standard. GC-MS analyses were performed on a Hewlett-Packard (HP) 5890 II GC equipped with a 30 m x 0.25 mm (i. d.) capillary column (DB-5) and with a HP-5971 mass spectral detector. Mass spectra were recorded with a VG QUATTRO 5022 spectrometer. Elemental analyses were within 0.4% of the theoretical values.

2-Thenyl Benzoate (4)

To a slurry of $LiAlH_4$ (3.39 g, 89.21 mmol) in dry THF (50 mL) at 0 °C was slowly added a solution of 2-thiophenecarbaldehyde (**6**) (10.00 g, 89.28 mmol) in dry THF (50 mL). The mixture was stirred at 0 °C for 2 h and a standard workup[13] gave 2-thenyl alcohol (**7**) (9.60 g, 84.21 mmol, 94% yield): IR (neat, cm^{-1}) 3300 (*br*), 2930, 2870, 1430, 1210, 1160, 1010, 855, 830, 695; ^1H NMR ($CDCl_3$) δ 7.26-7.24 (*m*, 1 H), 6.96-6.94 (*m*, 2 H), 4.75 (*s*, 2 H), 2.63 (*br*, 1 H); ^{13}C NMR ($CDCl_3$) δ 143.88, 126.74, 125.40, 125.33, 59.64; MS (LR) m/z (%) 114 (M^+, 96), 113 (36), 111 (10), 97 (68), 85 (100), 81 (43), 69 (19), 59 (10), 58 (29), 57 (25), 53 (30), 51 (16), 50 (15), 45 (90), 44 (11), 41 (12); Anal. Calcd for C_5H_6OS: C, 52.60; H, 5.30. Found: C, 52.59; H, 5.27. Without further purification, the alcohol **7** (10.00 g, 87.72 mmol) was converted to **4**, using the procedure described for the synthesis of 2-methyl-3-furylmethyl benzoate.[14] The benzoate was purified by column chromatography on silica gel (5% ethyl acetate in hexane, Rf=0.28) to yield **4** (17.90 g, 82.11 mmol, 93%): m.p.=50-51 °C [lit.[15] m.p.=58-59 °C]; IR (KBr, cm^{-1}) 3100, 2950, 1720, 1600, 1590, 1450, 1380, 1360, 1320, 1230, 1180, 1150, 1070, 1030, 980, 920, 840, 810, 760, 720, 630, 520; ^1H NMR ($CDCl_3$) δ 8.10-8.07 (*m*, 2 H), 7.57-7.54 (*m*, 1 H), 7.47-7.42 (*m*, 2 H), 7.36-7.34 (*m*, 1 H), 7.2-7.19 (*m*, 1 H), 7.04-7.01 (*m*, 1 H), 5.53 (*s*, 2 H); ^{13}C NMR ($CDCl_3$) δ 166.08, 137.90, 132.97, 129.80, 129.61, 128.24, 128.07, 126.72, 60.90; MS (LR) m/z (%) 218 (M^+, 14), 105 (100), 97 (89), 96 (45), 77 (33), 51 (12); Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62. Found: C, 65.96; H, 4.59.

3-Thenyl Benzoate (5)

The synthetic procedure of **5** was the same as that of **4**. 3-Thenyl alcohol (96% yield): IR (neat, cm^{-1}) 3300 (*br*), 2850, 1410, 1240, 1150, 1100, 850, 825, 770; ^1H NMR ($CDCl_3$) δ 7.32-7.29 (*m*, 1 H), 7.20-7.19 (*m*, 1 H), 7.08-7.06 (*m*, 1 H), 4.64 (*s*, 2 H), 2.65 (*br*, 1 H); ^{13}C NMR ($CDCl_3$) δ 142.12, 126.71, 126.14, 121.85, 60.44; MS (LR) m/z (%) 114 (M^+, 97), 97 (52), 85 (100), 81 (30), 69 (18), 58 (12), 57 (20), 53 (11), 50 (18), 45 (57), 44 (22), 40 (16); Anal. Calcd for C_5H_6OS: C, 52.60; H, 5.30. Found: C, 52.46; H, 5.43. 3-Thenyl benzoate (**5**) (95% yield): IR (neat, cm^{-1}) 3090, 2950, 1720, 1600, 1580, 1450, 1360, 1310, 1260, 1170, 1150, 1100, 1060, 1020, 930, 850, 770, 700; ^1H NMR ($CDCl_3$) δ 8.10-8.07 (*m*, 2 H), 7.60-7.54 (*m*, 1 H), 7.47-7.33 (*m*, 4 H), 7.20-7.18 (*m*, 1 H), 5.38 (*s*, 2 H); ^{13}C NMR ($CDCl_3$) δ 166.32, 136.86, 132.98, 130.08, 129.65, 128.33, 127.56, 126.21, 124.23, 61.78; MS (LR) m/z (%) 218 (M^+, 22), 105 (100), 97 (40), 96 (10), 77 (26), 45 (10); Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62. Found: C, 66.28; H, 4.84.

General Pyrolysis Procedure[5]

The furnace was maintained at temperatures in the range 550-900 °C. A sample of benzoate (0.10-0.15 g) or methylthiophene (0.20-0.50 g) was placed into the sample chamber and the system was evacuated to ca. 10^{-2} torr. During the pyrolysis $CHCl_3$ was deposited into the trap through a side arm. After the pyrolysis was completed, nitrogen was introduced into the system, the liquid-nitrogen-cooled trap was warmed to room temperature and the pyrolysate was collected. All the pyrolysis products of benzoates or methylthiophenes are known compounds. After separation, the pyrolysis products were identified by comparison of their NMR and/or GC and MS spectral data with those of authentic samples. The yields of all the pyrolysis products were measured by quantitative analysis of GC with weighed dibenzyl as an internal standard.

2,2'-Dithenyl (15)[16]

The pyrolysate from FVP of **4** at 650 °C was collected in $CHCl_3$. After the $CHCl_3$ solution was dried over $MgSO_4$ and the solvent was removed, the compound **15** was separated by column chromatography on silica gel (hexane). ^1H NMR ($CDCl_3$) δ 7.13 (d, J=5.1 Hz, 2 H), 6.92 (dd, J=5.1, 3.6 Hz, 2 H), 6.80 (d, J=3.6 Hz, 2 H), 3.20 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 143.67, 126.72, 124.61, 123.29, 32.14; MS (LR) m/z (%) 194 (M^+, 15), 97 (100), 53 (15), 45 (19). HRMS Calcd for $C_{10}H_{10}S_2$: 194.0225. Found: 194.0224.

3,3'-Dithenyl (32)[17]

The pyrolysate from FVP of **5** at 650 °C was collected in $CHCl_3$. After the $CHCl_3$ solution was dried over $MgSO_4$ and the solvent was removed, the compound **32** was separated by column chromatography on silica gel (hexane). ^1H NMR ($CDCl_3$) δ 7.25-7.23 (m, 2 H), 6.94 (s, 2 H), 6.92 (s, 2 H), 2.96 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 142.00, 128.13, 125.25, 120.34, 31.25; MS (LR) m/z (%) 194 (M^+, 48), 97 (100). HRMS Calcd for $C_{10}H_{10}S_2$: 194.0225. Found: 194.0230.

ACKNOWLEDGMENT

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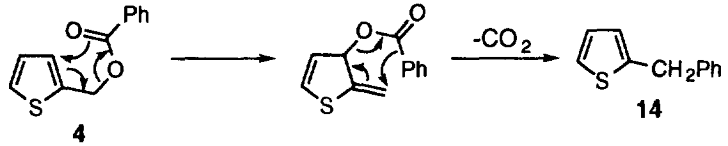
REFERENCES AND NOTES

1. Chen, P.S.; Chou, C.H. *J. Chin. Chem. Soc.* **1994**, *41*, 597-599.
2. Trahanovsky, W.S.; Park, M.-G. *J. Am. Chem. Soc.* **1973**, *95*, 5412.
3. Trahanovsky, W.S.; Park, M.-G. *J. Org. Chem.* **1974**, *39*, 1448-1449.
4. Fringguelli, F.; Marino, G.; Taticchi, A.; Grandolini, G. *J. Chem. Soc. Perkin Trans. II* **1974**, 332-337.
5. Chou, C.H.; Trahanovsky, W.S. *J. Am. Chem. Soc.* **1986**, *108*, 4138-4144.
6 Kellogg, R.M.; Dik, J.K.; van Driel, H; Wynberg, H. *J. Org. Chem.* **1970**, *35*, 2737-2741.
7. The route involved phenyl migration could not be ruled out as an alternative way to give **14**.



8. Reinecke, M.G.; Newsom, J.G. *J. Am. Chem. Soc.* **1976**, *98*, 3021-3022.
9. Wynberg, H.; Bantjes, A. *J. Org. Chem.* **1959**, *24*, 1421-1423.
10. Wynberg, H.; van Driel, H. *J. Am. Chem. Soc.* **1965**, *87*, 3998-4000.
11. Barltrop, J.A.; Day, A.C.; Irving, E. *J. Chem. Soc. Chem. Commun.* **1979**, 966-968, and the references cited therein.
12. Gilchrist, G.L. *Heterocyclic Chemistry*; Wiley: New York, **1992**, 2nd Edition, p 222.
13. Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, **1967**, Vol. 1, p 584.
14. Trahanovsky, W.S.; Cassady, T.J.; Wood, T.L. *J. Am. Chem. Soc.* **1981**, *103*, 6691-6695.
15. Cairns, T.L.; McKusick, B.C. *J. Org. Chem.* **1950**, *15*, 790-794.
16. Giumanini, A.G.; Trombini, C.; Lercker, G. *J. Org. Chem.* **1976**, *41*, 2187-2193.
17. Yom-Tov, B.; Gronowitz, S. *Chem. Scr.* **1973**, *3*, 37-47.

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