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Aust. J. Chem. **2014**, *67*, 1288–1295
http://dx.doi.org/10.1071/CH14155

Full Paper

Unexpected Pyrolytic Behaviour of Substituted Benzo[*c*]thiopyran and Thieno[2,3-*c*]thiopyran *S*,*S*-dioxides

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Flash vacuum pyrolysis (FVP) of benzo[*c*]thiopyran *S*,*S*-dioxide (**1**) results in formation of indene and 2-vinylbenzaldehyde as previously described. A range of eight analogues with various substitution patterns are found to behave differently. In general, there is no extrusion of SO_2 to give products analogous to indene, but unsaturated carbonyl products analogous to 2-vinylbenzaldehyde are formed in most cases by way of ring expansion to a 7-membered ring sultine, extrusion of SO, and intramolecular hydrogen atom transfer. Other processes observed include formation of anthracene via an isomeric 7-membered sultine with loss of SO, CO and methane or butane, and formation of 4-ethylidene-4,5-dihydrocyclobuta[*b*]thiophenes by way of SO loss, a radical rearrangement, and extrusion of acetone. The analogues with a halogen substituent at position 8 on the benzene ring require a higher temperature to react and give naphthalene resulting from net elimination of HX and SO_2. The X-ray crystal structure of **1** is also reported.

Manuscript received: 16 March 2014.
Manuscript accepted: 23 April 2014.
Published online: 30 May 2014.

Introduction

Thermal decomposition of cyclic sulfones, resulting in extrusion of either SO_2 or other fragments, has been extensively investigated and forms the basis of several useful synthetic methods.[1,2] In this context, the benzo[*c*]thiopyran *S*,*S*-dioxide ring system has been relatively little studied, although brief reports of both pyrolysis[3] and photolysis[4] of the parent compound **1** have appeared some years ago. Recently, some of us have developed a new synthetic approach to substituted compounds of this type.[5] In this paper, we describe the pyrolytic behaviour of a wide range of differently substituted aromatic-fused thiopyran *S*,*S*-dioxides **2**–**9** (Chart 1).

Results and Discussion

Before embarking on the pyrolysis of the new compounds, we decided to re-examine the parent compound **1**. The preparation of **1** was first described by Pagani and co-workers in 1967,[6] but with few details. The synthetic sequence used is shown in Scheme 1, and since details of many of the steps and intermediates have not been readily accessible to date, the detailed procedures are given in the Experimental section. The starting material benzylthioacetic acid (**10**) was readily prepared by reaction between chloroacetic acid and benzyl mercaptan,[7] and when this was treated with P_2O_5 in hot toluene, rather than the benzene used in the literature procedure,[7] the cyclic ketone **11** was formed in moderate yield. Using a base extraction for the work-up, any unreacted **10** could be recovered for re-use. Oxidation of **11** to the corresponding sulfone **12** proved to be the lowest yielding step of the synthesis. Still and co-workers obtained a 42-% yield using peracetic acid,[8] but we found that our method using potassium permanganate under phase-transfer conditions in the presence of benzoic acid[9] was slightly better. The borohydride reduction of **12** proceeded smoothly under the reported conditions[10] to give alcohol **13** for which ^{1}H and ^{13}C NMR data are reported for the first time. Stirring alcohol **13** in concentrated sulfuric acid resulted in dehydration to give the target compound **1** as colourless crystals. Remarkably, no ^{13}C NMR data of such a fundamental compound appear to have been reported to date.

Slow evaporation of a solution of **1** in diethyl ether gave good quality crystals suitable for X-ray diffraction analysis and the resulting structure is illustrated in Fig. 1. This shows rather long C–S bonds, the presence of sp^3 C(1) in the ring with SO_2, and C=C all fused to the benzene ring resulting in significant non-planarity with the SO_2 being slightly above and C(1) significantly below the plane defined by C(8A), C(4A), C(4), and C(3).

As far as we can determine, no X-ray structure of a compound with the benzo[*c*]thiopyran ring system has been reported previously and certainly no *S*,*S*-dioxide. However, there are a few examples of sulfones of the isomeric benzo[*b*]thiopyran structure such as **14**,[11] **15**,[12] **16**,[13] and the *trans*-cyclopentane-fused compounds **17** and **18**.[14] Among these, **16** shows a very similar non-planarity to **1** at adjacent CH_2 and SO_2 groups (Chart 2).

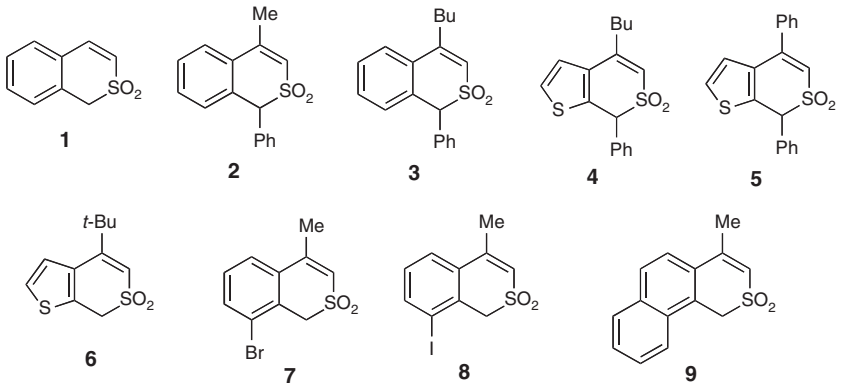
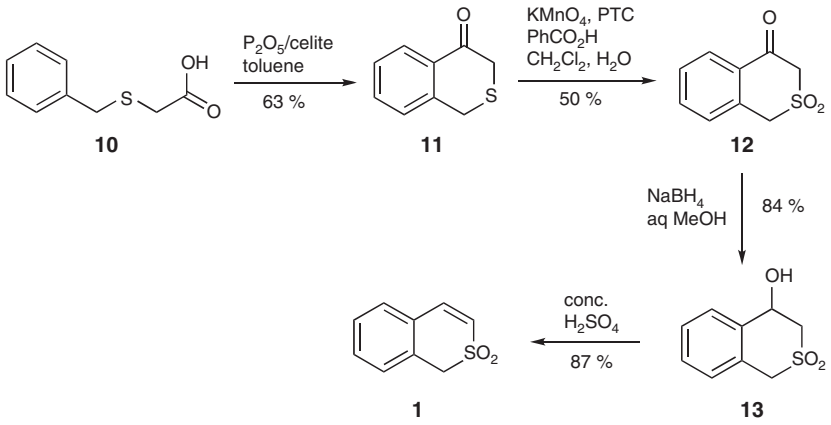


Chart 1.



Scheme 1. Synthesis of compound **1**.

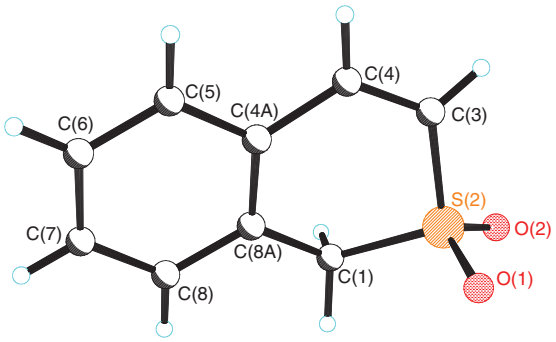


Fig. 1. X-ray structure of compound **1**. Selected bond lengths, angles, and torsion angles: C(4A)–C(4) 1.462(4), C(4)–C(3) 1.342(5), C(3)–S(2) 1.726 (3), S(2)–C(1) 1.767(3), C(1)–C(8A) 1.509(4), C(8A)–C(4A) 1.402(4) Å; C(4A)–C(4)–C(3) 125.7 (3), C(4)–C(3)–S(2) 120.3(2), C(3)–S(2)–C(1) 102.90(15), S(2)–C(1)–C(8A) 115.0(2), C(1)–S(2)–C(3)–C(4) 30.9(4), S (2)–C(3)–C(4)–C(4A) −9.1(5), C(8A)–C(1)–S(2)–C(3) −40.2(3), S(2)–C (1)–C(8A)–C(4A) 30.6(4)°.

The pyrolytic behaviour of compound **1** was investigated. Conducting flash vacuum pyrolysis (FVP) in a 30 × 2.5 cm furnace tube, operating at pressures in the range of 10^{-3}–10^{-2} Torr, afforded an almost complete reaction at 700°C (~5–10 % starting material). In agreement with the previous report,[3] the major products were found to be indene (**19**) and 2-vinylbenzaldehyde (**20**) (Scheme 2). Direct extrusion of SO_2 to give indene (**19**) is the major process, in agreement with the typical behaviour of many cyclic sulfones.[1,2] The formation of **20** may be explained by an initial ring-expansion of the sulfone to a sultine isomer **21** that was isolated in the photolysis of **1**.[4] As reported previously,[3] homolysis of the S–O bond in **21** followed by loss of SO and intramolecular hydrogen atom abstraction readily give 2-vinylbenzaldehyde (**20**).

We now focused our attention on the substituted compounds, and **2** was also found to undergo almost complete reaction upon FVP at 700°C. The major product 2-isopropenylbenzophenone (**22**) (42 %) was readily identified based on its spectra. Although this compound was first reported long ago,[15] and its photochemistry has been of recent interest,[16] no spectroscopic data are available for comparison. However, the good quality of the resulting ^{1}H and ^{13}C NMR spectra allowed confirmation of the identity of the compound, particularly because this exact product is expected based from the process analogous to formation of 2-vinylbenzaldehyde (**20**) from **1**. Interestingly, the substituted indene expected from SO_2 extrusion was completely absent, although its spectra were available for comparison.[17] The other major product turned out quite unexpectedly to be anthracene (**24**) (20 %). It appears that two isomeric sultines are involved, with **25** giving the major product **22**, whereas the isomeric sultine **26** seems more likely to yield anthracene by sequential loss of SO, CO, and methane (Scheme 3).

Further support for these routes was provided by the pyrolysis of the 4-butyl compound **3** that behaved in an exactly analogous way upon FVP at 700°C, giving the unsaturated ketone **23** as the main product (39 %) after purification and anthracene (15 %) as minor product.

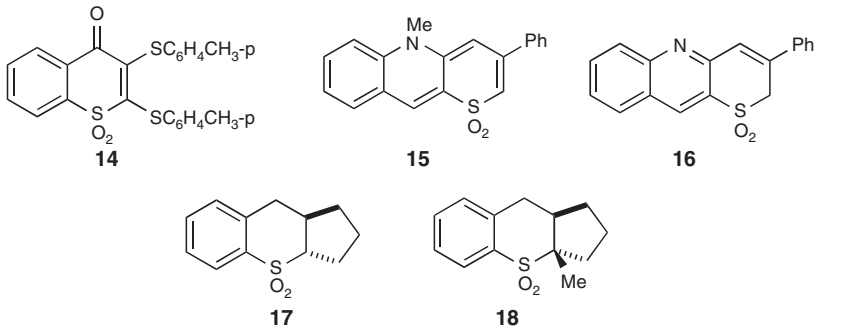
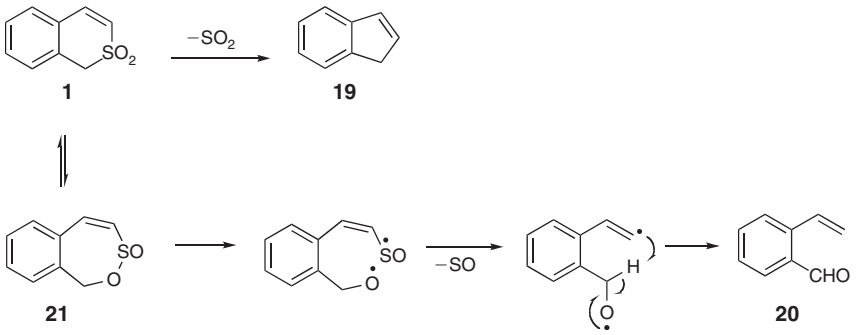
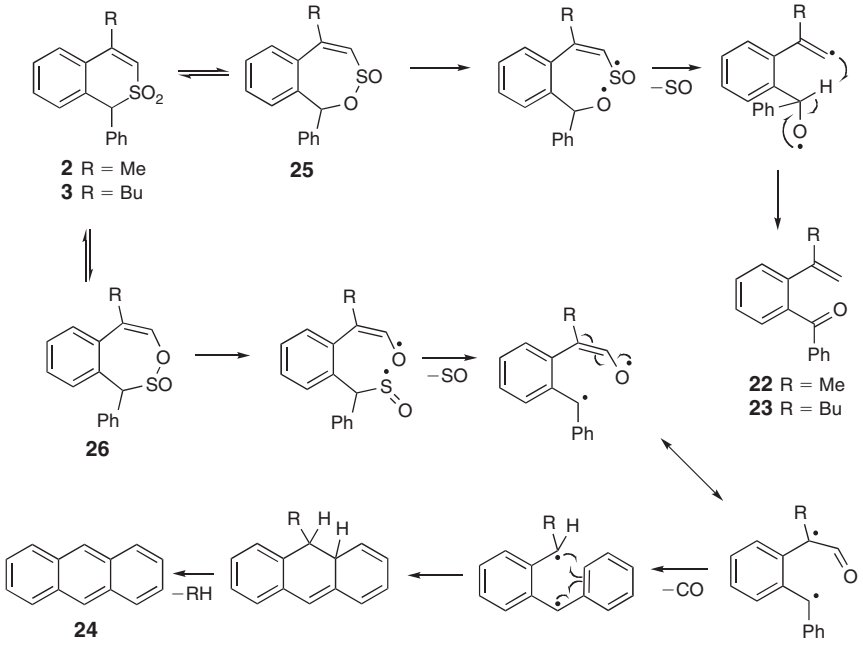


Chart 2.

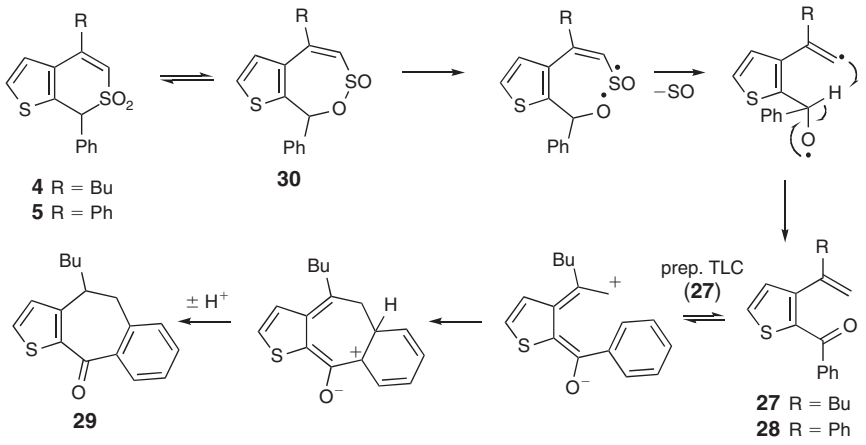


Scheme 2. Mechanisms observed in the FVP of **1** at 700°C.

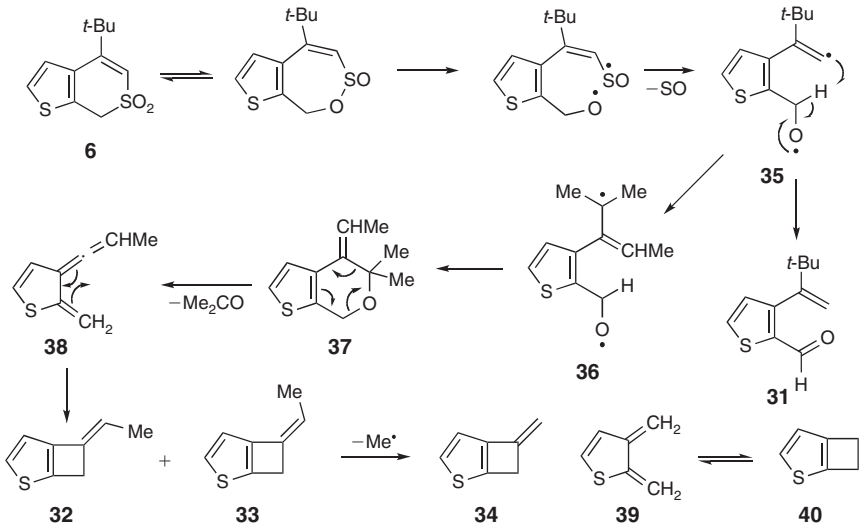


Scheme 3. Mechanisms proposed in the FVP of **2** and **3** at 700°C.

Under the same conditions, the thiophene-fused compounds **4** and **5** gave the unsaturated ketone products **27** and **28**, respectively, in agreement with the behaviour of **2** and **3**. In the case of **4**, an additional isomeric product was isolated after purification of the product **27** by preparative TLC on silica gel, and seemed likely to have the benzothienocycloheptadienone structure **29**. This was most obvious from the absence of signals corresponding to $=CH_2$ (δ_H 4.96, δ_C 116.1) and aromatic CH, to be replaced by adjacent aliphatic CH_2 (δ_H 3.55 or 3.04, δ_C 39.0) and CH (δ_H 3.20, δ_C 39.3) groups. This tricyclic product was absent in the initial pyrolysate and we speculate that it is formed on silica via a Friedel–Crafts-type intramolecular alkylation of the benzene ring by the highly electrophilic alkene function in **27** (Scheme 4). In this case, all the products identified were derived from the sultine **30** and there was no sign of products derived from ring-expansion in the other sense.



Scheme 4. Mechanisms proposed in the FVP of **4** and **5** at 700°C.

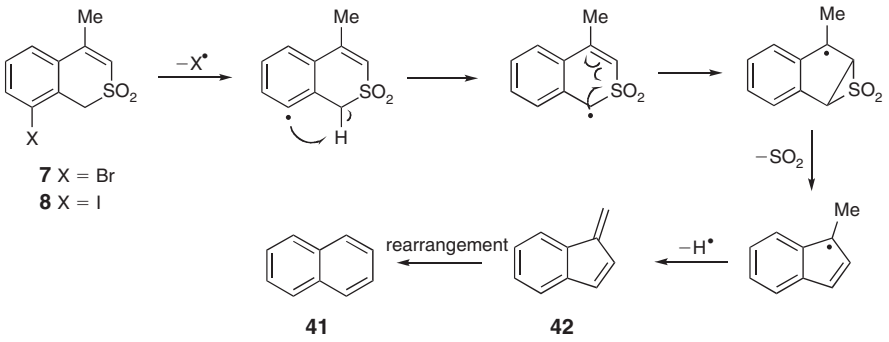


Scheme 5. Mechanisms proposed in the FVP of **6** at 700°C.

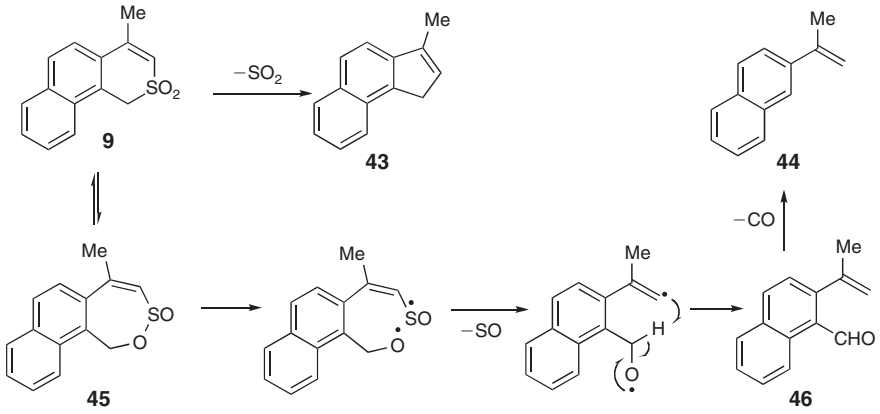
The other thiophene-fused compound investigated was **6**, with a *tert*-butyl group at the 4-position and an unsubstituted position 7. As before, the main product formed upon FVP at 700°C was the unsaturated aldehyde **31**, formed as usual by loss of SO from the sultine and intramolecular hydrogen atom abstraction (Scheme 5). This was obtained pure in 21 % yield by preparative TLC, but a second fraction proved to contain products with an unexpected structure. Detailed analysis of the ^{1}H NMR spectrum including COSY studies suggested these to be (*E*)- and (*Z*)-4-ethylidene-4,5-dihydrocyclobuta[*b*]thiophene (**32**) (6 %) and (**33**) (3 %), respectively, and 4-methylene-4,5-dihydrocyclobuta[*b*]thiophene (**34**) (1 %). The spectroscopic data were in almost perfect agreement with those of the corresponding ethylidene- and methylene-benzocyclobutenes, and the consistent pattern of chemical shifts also allowed assignment of the (*E*) and (*Z*) isomers.[18]

The formation of these products can be explained, as shown in Scheme 5, by an alternative process open to the diradical **35**, namely a 1,3-methyl group shift from the *tert*-butyl group to the alkenyl radical giving **36**. Although no analogous radical process has apparently been observed before in solution, the conversion of the non-stabilised vinyl radical **35** into the tertiary allylic radical **36** is expected to be highly favourable. The resulting stable tertiary radical site can pair up with the alkoxy radical to give the thienopyran **37** which is then ideally set up to extrude acetone. Acetone was present in the crude pyrolysate, as indicated by its NMR signals at δ_H 2.10 and δ_C 30.5 and 205.4. The electrocyclic ring closure of the resulting species **38** to give **32** and **33** is of some interest[19] since the corresponding 2,3-bis (methylene)-2,3-dihydrothiophene **39** was generated under similar conditions and found not to undergo ring-closure to the dihydrocyclobutathiophene **40**.[20] This finding was confirmed later by gas phase equilibrium studies, which did however report such a cyclisation being achieved photochemically in an argon matrix.[21] It appears that by adding an extra carbon, the equilibrium position can be reversed such that **38** is an unstable intermediate involved in the subsequent formation of the stable electrocyclisation products **32** and **33**. In the corresponding benzo-fused system, this is also the case with the two stable ethylidenebenzocyclobutene isomers undergoing interconversion via an unstable ring-opened allenic form.[18]

The next compounds examined were the 8-halo-4-methyl compounds **7** and **8**. Rather surprisingly, these were recovered unchanged from FVP at 700°C. It was only at 800°C that compounds **7** and **8** reacted completely to give single major product naphthalene (**41**) (50 % from **7**, 65 % from **8**). Elemental



Scheme 6. Mechanism proposed in the pyrolysis of **7** and **8** at 800°C.



Scheme 7. Mechanisms proposed in the pyrolysis of **9** at 700°C.

iodine was also observed in the cold trap in the latter case and it seemed likely that there was an initial loss of a halogen atom, generating the aryl radical (Scheme 6). This then undergoes intramolecular hydrogen atom abstraction to give the stabilised benzylic radical which is set up to cyclise upon interaction with the double bond to give a new episulfone-containing benzylic radical. Loss of SO_2 is expected to occur readily[1] and further loss of a hydrogen atom would give benzofulvene (**42**). From the seminal work of Brown, this is well known to isomerise readily to naphthalene under such FVP conditions.[22] The markedly higher reaction temperature requirements for these two compounds when compared with those employed for other compounds are believed to be due to steric buttressing from the large halogen atom, discouraging ring expansion or diradical formation and preventing reaction until sufficient energy is present for C–X bond fission. A similar effect has been reported recently in Grainger's work on 2,7-di-*tert*-butylnaphtho[1,8-*c*,*d*][1,2]dithiole 1,2-dioxides.[23]

Finally, the naphtho-fused compound **9** was examined and was found to react completely upon FVP at 700°C, producing a mixture of two hydrocarbons: methylcyclopenta[*a*]naphthalene (**43**) formed by simple extrusion of SO_2 and 2-isopropenylnaphthalene (**44**). The latter was readily identified by comparison with literature NMR data,[24,25] and its formation involved initial ring expansion to the sultine **45**, followed by the usual loss of SO and hydrogen atom transfer giving the aldehyde **46**, followed by decarbonylation (Scheme 7).

Conclusions

Examining a variety of substituted analogues of benzo[*c*]thiopyran *S*,*S*-dioxide **1** under FVP conditions reveals that direct extrusion of SO_2 is uncommon with most products formed via ring expansion to 7-membered ring sulfines that subsequently lose SO, and the resulting diradicals undergo further transformations. Thus, compounds **2**–**6** all give an unsaturated carbonyl compound as the main product (**22**, **23**, **27**, **28**, and **31**), whereas an isomeric sultine leads to anthracene as a minor product in the case of **2** and **3** and product **27** is observed to undergo an interesting cyclisation on silica. Unexpectedly, reaction involving **6** produces (*E*) and (*Z*) isomers of 4-ethylidene-4,5-dihydrocyclobuta[*b*]thiophene (**32**) and (**33**) as a result of a novel rearrangement of the diradical **35** to give **36**, followed by extrusion of acetone from the thieno[2,3-*c*]pyran intermediate **37**. The two 8-halo-4-methyl compounds **7** and **8** react only at a higher temperature than the other compounds and give naphthalene as the only major product in a mechanism involving a series of rearrangements and formation and isomerisation of benzofulvene. The naphtho compound **9** undergoes direct loss of SO_2 to give **43** as the main product and in this case, aldehyde **46** expected from the usual sultine route undergoes loss of CO to afford a minor hydrocarbon product **44**. Overall, the pattern of reactivity appears to be highly sensitive to the nature and position of substituents, suggesting that examination of a wider range of such substrates may lead to the discovery of further unexpected and novel thermal processes.

Experimental

Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (at 300 and 75 MHz, respectively); chemical shifts are reported in ppm (δ) using TMS as internal reference and coupling constants (*J*) are

given in Hz. High-resolution mass spectrometry (HRMS) data were obtained on a Micromass GCT mass spectrometer using electrospray ionisation. Compounds **2**–**9** were prepared as previously reported.[5]

*3,4-Dihydrobenzo[c]thiopyran-4-one (**11**)*

A solution of benzylthioacetic acid (**10**)[7] (20.1 g, 110 mmol) in toluene (75 mL) was stirred vigorously while a thin paste of P_2O_5 (30 g, 211 mmol) and celite (15 g) in toluene (100 mL) were added slowly. After the addition, the mixture was heated under reflux for 3 h. The solution was filtered and the filtrate was washed with 2 M NaOH to remove any uncyclised starting material (the NaOH extract could be neutralised with 2 M HCl and extraction with toluene, drying, and evaporation led to recovery of unreacted **10**). Drying and evaporation under reduced pressure then gave the product **11** (11.42 g, 63 %) as a yellow oil. δ_H 8.07 (1H, dd, *J* 7.5, 1.5), 7.44 (1H, td, *J* 7.5, 1.5), 7.35 (1H, t, *J* 7.5), 7.18 (1H, d, *J* 7.5), 3.90 (2H, s), 3.53 (2H, s). The data are in agreement with the literature.[26]

*3,4-Dihydrobenzo[c]thiopyran-4-one 2,2-Dioxide (**12**)*

A solution of **11** (11.42 g, 69.6 mmol) and benzoic acid (8.49 g, 69.6 mmol) in CH_2Cl_2 (500 mL) were stirred vigorously with a solution of $KMnO_4$ (22 g, 139 mmol) and benzyltriethylammonium chloride (1.58 g, 7 mmol) in water (1 L) for 18 h. Solid sodium metabisulfite was added to dissolve the MnO_2 present and the mixture was filtered. The organic layer was separated, washed with aqueous hydrazine hydrochloride solution, dried, and evaporated under reduced pressure to give the product **12** (6.94 g, 50 %) as a yellow oil. δ_H 8.23 (1H, dd, *J* 7.8, 1.5), 7.68 (1H, td, *J* 7.8, 1.5), 7.55 (1H, t, *J* 7.8), 7.37 (1H, d, *J* 7.8), 4.55 (2H, s), 4.25 (2H, s); the data are in agreement with the literature.[27] δ_C 186.2 (CO), 135.3 (CH), 132.3 (C), 130.6 (C), 130.3 (CH), 129.6 (CH), 129.5 (CH), 62.0 (CH_2), 55.2 (CH_2); the data are in agreement with the literature.[28]

*3,4-Dihydro-4-hydroxybenzo[c]thiopyran 2,2-Dioxide (**13**)*

A suspension of **12** (2.34 g, 11.9 mmol) in methanol/water (3 : 1, 60 mL) was stirred while a solution of $NaBH_4$ (0.51 g, 13.3 mmol) in water (20 mL) was added dropwise. After stirring for 12 h, 2 M HCl was added until pH 3 was reached and then the mixture was partly evaporated to remove the methanol. The residue was extracted with CH_2Cl_2, and was dried and evaporated to give the product **13** (1.98 g, 84 %) as a yellow oil. ν_{max} (neat)/cm^{-1} 3470, 1601, 1456, 1305, 1124, 704, 696. δ_H 7.52 (1H, dd, *J* 7.5, 1.5), 7.44–7.34 (2H, m), 7.16 (1H, d, *J* 7.5), 5.27 (1H, t, *J* 4.8), 4.41 and 4.26 (2H, AB pattern, *J* 15.6), 3.52 (2H, d, *J* 4.8), 3.25 (1H, br s). δ_C 135.3 (C), 129.9 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 127.4 (C), 69.1 (CH), 55.8 (CH_2), 54.6 (CH_2).

*Benzo[c]thiopyran 2,2-Dioxide (**1**)*

A mixture of **13** (2.3 g) and concentrated H_2SO_4 (10 mL) was stirred at room temperature (RT) for 3 h. The resulting clear brown solution was poured onto ice and the mixture was extracted with petroleum (2 × 25 mL), and dried and evaporated to give the product **1** (1.84 g, 87 %) as colourless crystals, mp 108–110°C (lit. 111°C[10]). δ_H 7.43–7.34 (3H, m), 7.30–7.25 (1H, m), 7.16 (1H, d, *J* 10.5, 4-H), 6.63 (1H, dt, *J* 10.5, 0.6, 3-H), 4.41 (2H, d, *J* 0.6); the data are in agreement with the literature.[10,27] δ_C 137.9 (CH), 130.4 (CH), 130.0 (CH), 129.9 (CH), 129.2 (CH), 128.7 (C), 128.4 (C), 127.2 (CH), 54.5 (CH_2).

*Crystallographic Data for **1***

Compound **1**, $C_9H_8O_2S$, *M* 180.21, colourless platelet. Monoclinic, space group *Cc*, *a* 9.543(9), *b* 11.071(8), *c* 8.888 (8) Å, *β* 118.785(18)°, *V* 823.0(12) $Å^3$, *Z* 4, D_c 1.454 Mg m^{-3}, *T* 125(2) K, 3072 reflections, 1307 unique (R_{int} 0.049). R_1 0.0354, wR_2 0.0856, *R* indices based on 1295 data with $I > 2\sigma(I)$, 109 parameters. Data were recorded using a Rigaku MM007, $Mo_{K\alpha}$ radiation (confocal optic, *λ* 0.71073 Å) and Saturn detector. The structure was solved by direct methods and refined using full-matrix least-squares methods.

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-782442. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336 033; email: deposit@ccdc.cam.ac.uk.

Flash Vacuum Pyrolysis (FVP)

The apparatus used for this study was as described previously.[29] All pyrolyses were conducted at pressures in the range of 10^{-3}–10^{-2} Torr. Under these conditions, the contact time in the hot zone was estimated to be 1–10 ms. Products were identified by NMR comparison with authentic materials and yields were determined by calibration of the ^1H NMR spectra by adding an accurately weighed quantity of a solvent, such as CH_2Cl_2, and comparing integrals, a procedure estimated to be accurate to ±10 %.

*FVP of Benzo[c]thiopyran S,S-dioxide (**1**)*

Compound **1** (500 mg) was subjected to FVP at 700°C and the major products were identified as follows. Indene (**19**) (23 % yield). δ_H 7.60–7.20 (4H, m), 6.88 (1H, dtd, *J* 5, 2, 1), 6.55 (1H, dt, *J* 5, 2), 3.39 (2H, m); the data are in agreement with the literature.[30] δ_C 144.8 (C), 143.6 (C), 133.8 (CH), 132.0 (CH), 126.2 (CH), 124.5 (CH), 123.7 (CH), 120.9 (CH), 39.0 (CH_2); the data are in agreement with the literature.[31]

2-Vinylbenzaldehyde (**20**) (18 % yield). δ_H 10.28 (1H, s), 7.84 (1H, dd, *J* 7, 1), 7.70–7.50 (4H, m), 5.69 (1H, dd, *J* 17, 1), 5.51 (1H, dd, *J* 11, 1); the data are in agreement with the literature.[32] δ_C 192.4 (CO), 140.5 (C), 134.1 (CH), 133.3 (CH), 132.8 (C), 131.2 (CH), 127.9 (CH), 127.4 (CH), 119.4 (CH_2); the data are in agreement with the literature.[33]

*FVP of 4-Methyl-1-phenylbenzo[c]thiopyran S,S-dioxide (**2**)*

Compound **2** (200 mg) was subjected to FVP at 700°C and the products were isolated by preparative TLC (SiO_2, hexane/diethyl ether, 4 : 1) and identified spectroscopically as follows. 2-Isopropenylbenzophenone (**22**) (69 mg, 42 %). R_F 0.60. ν_{max} (neat)/cm^{-1} 1717, 1674, 1598, 1493, 1447, 1263, 1073, 700. δ_H 7.75–7.72 (2H, m), 7.60–7.35 (7H, m), 4.954 (1H, quin, *J* 1.5, =CH), 4.851 (1H, dq, *J* 1.5, 0.9, =CH), 1.94 (3H, dd, *J* 1.5, 0.9, CH_3). δ_C 198.8 (CO), 143.8 (C), 142.8 (C),138.2 (C), 137.8 (C), 132.9 (CH), 130.0 (CH), 129.8 (2CH), 128.4 (CH), 128.2 (2CH), 127.8 (CH), 126.8 (CH), 117.3 (=CH_2), 23.7 (CH_3). *m/z* (HRMS) 223.1116; M^++H requires 223.1123.

Anthracene (**24**) (26 mg, 20 %). R_F 0.85. δ_H 8.43 (2H, s, 9/10-H), 8.01 (4H, m, 1/4/5/8-H), 7.46 (4H, m, 2/3/6/7-H);

second-order pattern is in agreement with simulation using $J_{1,2} = J_{3,4} = 8.5$, $J_{2,3} = 6$, $J_{1,3} = J_{2,4} = 0.5$. δ_C 128.1 (4CH), 126.2 (2CH), 125.3 (4CH); the data are in agreement with the literature.[30]

*FVP of 4-Butyl-1-phenylbenzo[c]thiopyran S,S-dioxide (**3**)*

Compound **3** (201 mg) was subjected to FVP at 700°C and the products were isolated by preparative TLC (SiO_2, petroleum/diethyl ether, 20 : 1) and identified as follows. 2-(Hex-1-en-2-yl) benzophenone (**23**) (65 mg, 39 %) as a red oil. R_F 0.40. ν_{max} (neat)/cm^{-1} 2960, 1707, 1666, 1597, 1449, 1265, 738, 700. δ_H 7.76–7.72 (2H, m, ArH), 7.57–7.31 (7H, m, ArH), 4.96 (1H, q, *J* 1.5, $=CH_2$), 4.91 (1H, dt, *J* 1.5, 0.6, $=CH_2$), 2.23 (2H, t, *J* 7.8, CH_2), 1.26–1.17 (4H, m, $2 \times CH_2$), 0.80 (3H, t, *J* 7.2, CH_3). δ_C 198.8 (CO), 148.5 (C), 142.7 (C), 138.3 (C), 137.8 (C), 132.9 (CH), 129.94 (2CH), 129.90 (CH), 128.5 (CH), 128.3 (CH), 128.2 (2CH), 126.6 (CH), 115.7 ($=CH_2$), 36.7 (CH_2), 29.9 (CH_2), 22.3 (CH_2), 13.9 (CH_3). *m*/*z* (HRMS) 265.1593; M^++H requires 265.1592.

Anthracene (**24**) (16 mg, 15 %). R_F 0.75. Spectrum is as above.

*FVP of 4-Butyl-7-phenylthieno[2,3-c]thiopyran 6,6-dioxide (**4**)*

Compound **4** (130 mg) was subjected to FVP at 700°C and the products were isolated by preparative TLC (SiO_2, petroleum/diethyl ether, 20 : 1) and identified as follows. 3-(Hex-1-en-2-yl)-2-thienyl phenyl ketone **27** (17.1 mg, 16 %) as a brown oil. R_F 0.60. δ_H 8.04 (1H, dd, *J* 7.8, 1.5, ArH), 7.79 (1H, dd, *J* 8.4, 1.5, ArH), 7.57–7.36 (5H, m, ArH), 4.96 (2H, m, $=CH_2$), 2.21 (2H, t, *J* 7.2, CH_2), 1.30–1.20 (4H, m, $2 \times CH_2$), 0.83 (3H, t, *J* 7, CH_3). δ_C 132.5 (CH), 129.8 (CH), 129.7 (CH), 129.5 (2CH), 128.1 (2CH), 116.1 ($=CH_2$), 36.4 (CH_2), 30.1 (CH_2), 22.3 (CH_2), 13.89 (CH_3), five C not apparent.

4-Butyl-4*H*-benzo[5,6]cyclohepta[1,2-*b*]thiophen-10(5*H*)-one (**29**) (9.4 mg, 10 %) as a brown oil. R_F 0.50. δ_H 8.03 (1H, dd, *J* 7.5, 1.8, ArH), 7.56 (1H, d, *J* 5.1, ArH), 7.55–7.38 (3H, m, ArH), 6.95 (1H, d, *J* 5.1, ArH), 3.55 (1H, dd, *J* 14.1, 2.4, CH_2), 3.15–3.25 (1H, m), 3.04 (1H, dd, *J* 14.1, 6.0, CH_2), 1.55–1.60 (2H, m, CH_2), 1.45–1.30 (2H, m, CH_2), 1.30–1.20 (2H, m, CH_2), 0.80 (3H, t, *J* 7, CH_3). δ_C 133.6, 132.5, 131.1, 130.8, 130.5, 127.0, 39.3 (CH), 39.0 (CH_2), 33.2 (CH_2), 29.8 (CH_2), 22.6 (CH_2), 13.95 (CH_3), five C not apparent.

Data for mixture of **27** and **29**: ν_{max} (neat)/cm^{-1} 1771, 1721, 1619, 1594, 1449, 1416, 1312, 1268. *m*/*z* (HRMS) 293.0983; M^++Na requires 293.0976.

*FVP of 4,7-Diphenylthieno[2,3-c]thiopyran 6,6-dioxide (**5**)*

Compound **5** (41.7 mg) was subjected to FVP at 700°C and a single product was identified as follows: 3-(1-phenyl-1-ethenyl)-2-thienyl phenyl ketone **28** (29.4 mg, 82 %) as a dark oil. ν_{max} (neat)/cm^{-1} 1640, 1597, 1447, 1394, 1264, 694. δ_H 7.58 (1H, d, *J* 5.1, CH), 7.54–7.10 (8H, m, ArH), 7.14 (1H, d, *J* 5.1, CH), 6.92–6.89 (2H, m, ArH), 5.42 (1H, d, *J* 0.9, $=CH_2$), 5.29 (1H, d, *J* 0.9, $=CH_2$). δ_C 190.0 (CO), 146.2 (=C), 144.1 (C), 140.7 (C), 138.1 (C), 132.2 (CH), 131.2 (CH), 129.9 (CH), 129.0 (2CH), 128.1 (2CH), 127.8 (2CH), 127.6 (CH), 126.7 (2CH), 116.8 ($=CH_2$), one quaternary C not apparent. *m*/*z* (HRMS) 313.0658; M^++Na requires 313.0663.

*FVP of 4-(Tert-butyl)thieno[2,3-c]thiopyran 6,6-dioxide (**6**)*

Compound **6** (65.6 mg) was subjected to FVP at 700°C and the products were separated by preparative TLC (SiO_2, hexane/diethyl ether, 1 : 1) to give two fractions: (1) 3-(2,2-dimethyl-1-methylenepropyl)thiophene-2-carbaldehyde (**31**) (11 mg, 21 %) as a colourless oil. R_F 0.70. ν_{max} (neat)/cm^{-1} 1706, 1603, 1439, 1367, 1265, 1163, 737. δ_H 9.81 (1H, d, *J* 1.3, CHO), 7.62 (1H, dd, *J* 5.0, 1.3, ArH), 7.02 (1H, d, *J* 5.0, ArH), 5.45 (1H, d, *J* 1.3, =CH), 4.97 (1H, d, *J* 1.3, =CH), 1.15 (3H, s, CH_3). δ_C 184.6 (CHO), 154.4 (C), 151.4 (C), 132.7 (CH), 130.5 (CH), 116.2 ($=CH_2$), 43.0 (C), 29.6 (CH_3). *m*/*z* (HRMS) 217.0659; M^++Na requires 217.0663; and (2) and a yellow oil, R_F 0.50, and proved to be a mixture of the following compounds. (*E*)-4-ethylidene-4,5-dihydrocyclobuta[*b*]thiophene (**32**) (6 % yield). δ_H 7.84 (1H, d, *J* 4.8, ArH), 7.18 (1H, d, *J* 4.8, ArH), 6.05 (1H, qt, *J* 7.0, 1.7, =CH), 3.44 (2H, dq, *J* 1.7, 0.8, CH_2), 1.85 (3H, dt, *J* 7.0, 0.8, CH_3).

(*Z*)-4-Ethylidene-4,5-dihydrocyclobuta[*b*]thiophene (**33**) (3 % yield). δ_H 7.92 (1H, d, *J* 5.0, ArH), 7.39 (1H, d, *J* 5.0, ArH), 5.68 (1H, qt, *J* 7.2, 1.2, =CH), 3.50 (2H, quin, *J* 1.2, CH_2), 2.05 (3H, dt, *J* 7.2, 1.2, CH_3).

m/*z* (HRMS) 137.0384; M^++H requires 137.0425.

4-Methylene-4,5-dihydrocyclobuta[*b*]thiophene (**34**) (1 % yield). δ_H 7.88 (1H, d, *J* 4.8, ArH), 7.25 (1H, d, *J* 4.8, ArH), 5.54 (1H, t, *J* 1.8, =CH), 5.23 (1H, t, *J* 1.3, =CH), 3.53 (2H, dd, *J* 1.8, 1.3, CH_2).

*FVP of 8-Bromo-4-methylbenzo[c]thiopyran S,S-dioxide (**7**)*

Compound **7** (36.7 mg) was subjected to FVP at 800°C and gave a single product identified as naphthalene **41** (50 %). δ_H 7.84 (4H, m, 1/4/5/8-H), 7.48 (4H, m, 2/3/6/7-H). δ_C 133.5 (2C), 127.8 (4CH), 125.8 (4CH).

*FVP of 8-Iodo-4-methylbenzo[c]thiopyran S,S-dioxide (**8**)*

Compound **8** (100 mg) was subjected to FVP at 800°C and the product was identified spectroscopically as naphthalene (**41**) (65 % yield); spectrum is as above.

*FVP of 4-Methylnaphtho[1,2-c]thiopyran 2,2-dioxide (**9**)*

Compound **9** (52.3 mg) was subjected to FVP at 700°C and the products were identified as follows. 3-Methyl-1*H*-cyclopent[*a*]naphthalene (**43**) (30 % yield). δ_H 7.90–7.25 (6H, m, ArH), 6.29 (1H, m, CH), 3.63 (2H, m, CH_2), 2.26 (3H, m, CH_3). δ_C 128.8 (CH), 127.9 (CH), 126.9 (CH), 126.0 (CH), 124.4 (CH), 123.5 (CH), 118.5 (CH), 36.5 (CH_2), 13.3 (CH_3).

2-Isopropenylnaphthalene (**44**) (15 % yield). δ_H 7.90–7.25 (7H, m, ArH), 5.53 (1H, s), 5.19 (1H, s), 2.26 (3H, s, CH_3); the data are in agreement with the literature.[24] δ_C 128.2 (CH), 127.7 (CH), 127.5 (CH), 126.1 (CH), 125.8 (CH), 124.2 (CH), 123.9 (CH), 113.0 (CH_2), 21.9 (CH_3); the data are in agreement with the literature.[25]

Supplementary Material

^1H and ^{13}C NMR spectra of all new compounds are available on the Journal's website.

Acknowledgement

MSH and ALS thank NSERC of Canada for support of this research.

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