Carbene Reactions. Part 16.¹ Thermolyses of Norbornadiene-7-spiro-2'-(1',3'-dithiolane) S-Oxides ¹

Reinhard W. Hoffmann * and Wolfgang Barth

Fachbereich Chemie der Philipps-Universität D-3550 Marburg, W. Germany Lars Carlsen * and Helge Egsgaard Chemistry Department Risø National Laboratory DK-4000 Roskilde, Denmark

The gas-phase thermolysis of the norbornadienespirodithiolane S-oxides (5) and (7) led to benzene, ethylene, and carbon disulphide as the major products, possibly involving carbon disulphide oxides as intermediates. Thermolyses of the related sulphones (9) or (14) led to completely different product patterns.

The generation of carbon disulphide S-oxides 2,3 has been attempted either by oxygenation of carbon disulphide⁴ or by sulphurization of carbon oxysulphide.⁵ Whereas no direct evidence for the intermediates (1) has accrued so far, the fragmentation products obtained suggest the intermediacy of structures such as (1). It may be hoped that other methods to generate any member of the set of intermediates (1) may shed some light on their interconversions as well as preferred modes of fragmentation.

Since sulphines themselves have been generated by cycloreversions ² creating the C=S bond, it seemed attractive to modify some of the cycloreversion reactions that generate carbon disulphide ⁶⁻⁸ in such a manner that the reaction leads to the S-oxide of carbon disulphide instead. Such modification seems possible for the decay of the carbene (15) which itself is generated by cycloelimination ⁹ from a 7,7-disubstituted norbornadiene: it has been reported ⁸ that thermolysis of the quadricyclane (2) gave benzene, ethylene, and carbon disulphide. Hence we set out to study the thermal behaviour of compound (4) which might liberate the intermediate (1a) in analogy. The related compounds (6)—(11) have also been included in this study.

Results and Discussion

Syntheses.—Compound (2) was prepared from quadricyclanone ¹⁰ as described.⁸ We succeeded in isomerising the quadricyclane (2) quantitatively to the norbornadiene (3) by using dicarbonylbis(triphenylphosphine)nickel ¹¹ as catalyst, which has not previously been applied for such isomerisation reactions. Oxidation of compound (2) with one equivalent of NaIO₄ gave the sulphoxide (4) in 67% yield. Oxidation with two equivalents of NaIO₄ led to the bis-sulphoxide (6). The crystalline material obtained in \geq 50% yield was the *trans*isomer, as judged from the C₂-symmetry evident in the ¹³C n.m.r. spectrum of the derived norbornadiene (7).

Oxidation of compound (2) with H_2O_2 in acetic acid furnished 81% of the tetraoxide (8). Isomerisation of the quadricyclanes (8) and (6) to the norbornadienes (9) and (7) could readily be effected with chloronorbornadienerhodium(1)dimer,¹² whereas compound (4) has so far resisted attempts at effective catalysed isomerisation to the norbornadiene (5). In addition compound (10) was prepared in 89% yield from quadricyclanone and propane-1,3-dithiol and isomerised by the nickel catalyst to compound (11).

The compounds (12)—(14) were considered to be potential products or intermediates of the pyrolyses of the compounds (2), (4), and (9). While the heterocycles (12) and (14) were known,^{13,14} the sulphoxide (13) was prepared by NaIO₄ oxidation of the dithiolane (12) in 83% yield. The sulphoxide (13) was formed as a single stereoisomer, the relative con-



figuration of which was not assigned. Heating the sulphoxide (13) to 150 $^{\circ}$ C led to equilibration with the other diastereoisomer.

Thermolyses.—In order to test our experimental set-up ¹⁵ compound (3) was thermolysed at 300 °C yielding quantitatively benzene and CS₂. Cleavage of the sulphoxide (4) could be effected at 450 °C in line with the facile thermal isomerisation of quadricyclane to norbornadiene derivatives.^{15,16} Aside from a quantitative formation of benzene only CS₂ and

J. CHEM. SOC. PERKIN TRANS. II 1983



sulphur could be identified. Hence, this experiment was rather inconclusive with respect to the formation of a reactive intermediate such as (1a). Formation of the intermediate (1a) would be expected primarily if the carbene (16) were to collapse in a concerted process.^{9,17}

However, in view of the high temperature applied, stepwise fragmentation of such carbenes should be considered,¹⁸ because single-bond dissociation should be favoured over concerted processes on entropy grounds at high temperatures.¹⁹ Hence, homolytic cleavage of the carbene (16) could initiate not only formation of ethylene and the intermediate (1), but perhaps also a direct cleavage to the thiirane (17) and carbon oxysulphide. The feasibility of such homolytic processes under our thermolysis conditions was clearly underscored by the thermolysis of the compounds (10) and (11) at 450 °C: again benzene was the main product and carbon disulphide as well as cyclopropane could be shown to be formed. In as much as formation of cyclopropane from the carbene (18) is not obvious in a concerted process ²⁰ this signals a tendency for



homolytic decay 8,19 of the carbenes formed under our conditions.

The thermolyses of the bis-sulphoxide (7) at 450 $^{\circ}$ C revealed a diversion of reaction pathways. Cheletropic elimination of the bridge is no longer the sole pathway, since aside from benzene (50%) benzaldehyde was formed in significant amounts (21%).

On thermolyses of the bis-sulphone (9) benzene is not obtained at all. The formation of indan (31%) and cisstilbene was accompanied by small amounts of indene and benzaldehyde. We assumed that instead of cycloelimination, rearrangement of the norbornadiene (9) to the benzyl derivative (14) could have happened, since it seemed conceivable that pyrolysis of the sulphone (14) could proceed to indan and stilbene. However, thermolysis of an authentic sample of bis-sulphone (14) led to benzaldehyde (51%) and phenylcyclopropane (19%) instead. The latter is known²¹ to give neither stilbene on pyrolysis nor indan. This demonstrates beyond doubt that the bis-sulphone (14) is not an intermediate in the pyrolysis of the norbornadiene (9). Hence, the mechanism of the formation of indan and stilbene from the bis-sulphone (9) remains obscure, whereas formation of an aldehyde, e.g. benzaldehyde from compound (14) is in accord with observations on other 1,3-bis-sulphone pyrolyses.²²

This study revealed that cycloelimination to benzene and presumably a carbene is the main process in the thermolyses of the compounds (3) and (4). This process becomes less important on thermolyses of the bis-sulphoxide (7) and disappears on pyrolysis of the highly oxygenated derivative (9). A chance to scrutinize further the potential formation of carbon disulphide oxides is hence given in the pyrolyses of compound (4), which could proceed *via* the carbene (16) to the intermediate (1a). In order to obtain more information a detailed study of the thermolyses of the sulphoxide (4) was undertaken by a 'real-time-analysis' using Curie-point pyrolysis-mass spectrometry.²³ In order to eliminate possible surface-pro-

	Ethylene	Formaldehyde	Ethylene sulphide	Carbon disulphide	Benzene	Benzaldehyde	Thiophenol	C7H6S
(2)	0.35		0.54 ª	0.55	1.0		0.03 ª	
(4)	0.43 ª			0.30	1.0	0.35 ª		0.14 ª
(7)	0.29 ª	0.67 ª		0.32 ª	1.0	0.74		0.45 ª
(12)	1.00		13.18		1.0		1.73	
(13)	0.39		1.70 %	0.59	1.0	2.23		

Relative abundances of the single pyrolysis products observed following Curie-point pyrolysis [1 043 K (Au)] of (2), (4), (7), (12), and (13), relative to benzene

^a Compounds found by Curie-point pyrolysis-mass spectrometry investigations only. ^b May contain a minor COS contribution.

moted reactions, due to the presence of hot metal surfaces, gold-plated filaments were applied.²⁴ By this technique we studied the pyrolysis of compounds (2), (4), (7), and, for comparison, the isomeric structures (12) and (13). In the Table the relative abundances of the single pyrolysis products observed following Curie-point pyrolysis at 1 043 K are shown, relative to benzene.*

Qualitatively, the picture observed to a certain extent matches that described above, involving product isolation. However, some significant differences can be noted (*see* Table).

Pyrolysis of compound (2) afforded besides the previously reported benzene, carbon disulphide, and ethylene⁸ minor amounts of ethylene sulphide and, surprisingly, thiophenol. Comparison of the product distribution following pyrolysis of compounds (2) and (12), respectively (Table), suggests that parallel to the above described elimination of carbene (15) from compound (2) isomerisation to compound (12) takes place followed by consecutive decomposition of the latter. On the other hand, comparing the pyrolyses of compounds (4) and (13), an analogous rearrangement of the sulphoxide (4) into compound (13) does not apparently take place, as no ethylene sulphide was seen in the case of the pyrolysis of the sulphoxide (4). Apparently the formation of benzene in the pyrolyses of compounds (4) and (7) is, as in the pyrolysis of compound (2), a result of elimination of the carbenes (16) and (19), respectively, the fate of these carbenes, however, being unclear, although it is suggested that they play a role in the formation of carbon disulphide and, at least to a certain extent, of ethylene. On the other hand, it is obvious that, in the pyrolyses of the compounds (4) and (7), a parallel decomposition mechanism, leading to the formation of benzaldehyde and the C_7H_6S isomer (possibly thiotropone, see Experimental section) is operating. Pyrolytic decomposition of thiobenzophenone S-oxide (diphenyl sulphide) leads to a mixture of benzophenone and thiobenzophenone,26 and we therefore suggested sulphine (C_7H_6SO) formation, consecutively giving rise to the ketone and the thicketone. Surprisingly, however, in the pyrolysis of the sulphoxide (4) no formation of ethylene sulphide is seen which suggests a two-step mechanism involving ethylene elimination directly from the sulphoxide (4) followed by loss of elemental sulphur leading to the intermediate species (20), the latter eventually decomposing to benzaldehyde and C7H6S.

In the pyrolysis of the bis-sulphoxide (7) we are unable to draw analogous conclusions, since we should not be able to detect possible eliminated ethylene sulphoxide, due to the thermal lability of the latter under the reaction conditions applied.²⁷ The presence of a common intermediate such as (20)



seems, however, conceivable. The origin of thiophenol and formaldehyde during the pyrolysis of the bis-sulphoxide (7) is obscure.

The sum of the above presented experiments does, unfortunately, not give occasion for any conclusions on the possible intermediacy of a carbon disulphide oxide structure (1a-d) in the decomposition of 7-norbornadienespiro-2-(1,3-dithiolane) oxides. However, it cannot be excluded that the intermediates (1) may be involved in the formation of carbon disulphide, a major product in the thermolysis of both sulphoxides (4) and (7).

Experimental

M.p.s were determined with a Kofler apparatus and are uncorrected. ¹H and ¹³C n.m.r. spectra were recorded with Varian T-60 and JEOL FX 100 spectrometers. G.c. analyses were performed with a Perkin-Elmer 900 gas chromatograph with a 2.50 m \times 0.30 cm column with 4% SE 52 on Chromosorb G AW-DMCS (80–100 mesh), with 40 cm³ N₂ min⁻¹. For g.c.-mass spectral analyses a Varian 1700 gaschromatograph coupled to a Varian MAT 711 mass spectrometer was used with the column and conditions above.

Syntheses.—(1) Tetracyclo[$3.2.0.0^{2.7}.0^{4.6}$]heptane-3-spiro-2'-(1',3'-dithiolane) (2).⁸ To quadricyclanone (2.00 g, 18.9 mmol) in dry CH₂Cl₂ (60 ml) were added under stirring Na₂SO₄ (1 g), zinc chloride (1 g, freshly dried) and ethane-1,2-dithiol (2.00 ml, 23.8 mmol). After stirring for 30 min the solution was decanted and washed with 5% KOH (3×20 ml). After drying (MgSO₄) the solvent was removed *in vacuo* leaving light tan crystals (2.5 g, 70%), which were recrystallized from

^{*} The relative abundances of the single product can be compared vertically only. The figures given horizontally do not reflect the chemical yields of the products, since no corrections due to differences in flame ionization sensitivities ^{23,25} have been made.

light petroleum, m.p. 99–100 °C (lit.,⁸ 97–98 °C); $\delta_{\rm H}$ (CCl₄) 1.47–1.90 (m, 6 H) and 3.41 (s, 4 H).

(2) Bicyclo[2.2.1]heptadiene-7-spiro-2'-(1',3'-dithiolane) (3).— A solution of the quadricyclane (2) (1.5 g, 8.2 mmol) in chloroform (30 ml) was stirred at room temperature with $(Ph_3P)_2$ -Ni(CO)₂ (10 mg, 0.015 mmol) for one week. After stripping the solvent the *product* (3) was obtained by sublimation (60 °C and 1 Torr) and recrystallized from light petroleum (0.9 g, 60%), m.p. 69—70 °C; $\delta_{\rm H}$ (CDCl₃) 3.14 (s, 4 H), 3.90 (p, 2 H), and 6.73 (t, 4 H); $\delta_{\rm C}$ (CDCl₃) 38.9, 63.4, 115.2, and 142.8 p.p.m. (Found: C, 59.5; H, 5.6. C₉H₁₀S₂ requires C, 59.3; H, 5.55%).

(3) Tetracyclo[$3.2.0.0^{2.7}.0^{4.6}$]heptane-3-spiro-2'-(1',3'-dithiolane) S-oxide (4).—To a solution of the dithiolane (2) (2.00 g, 11.0 mmol) in THF (50 ml) was added a solution of NaIO₄ (2.5 g, 12 mmol) in water (5 ml). After stirring for 3 d the solution was filtered and, after addition of water (50 ml), extracted with CH₂Cl₂ (3 × 20 ml). The organic layer was dried (MgSO₄) and stripped of solvent. The crystalline residue was recrystallized twice from light petroleum (1.5 l) to give the product (1.45 g, 67%), m.p. 79–80 °C; $\delta_{\rm H}$ (CDCl₃) 1.29–1.50 (m, 1 H), 1.83–2.23 (m, 5 H), and 3.00–4.40 (m, 4 H) (Found: C, 54.6; H, 5.35; S, 32.15. C₉H₁₀OS₂ requires C, 54.5; H, 5.1; S, 32.35%).

(4) Tetracyclo[$3.2.0.0^{2.7}.0^{4.6}$]heptane-3-spiro-2'-(1',3'-dithiolane) 1',3'-dioxide (6). A solution of the dithiolane (2) (2.0 g, 11 mmol) in THF (60 ml) was combined with a solution of NaIO₄ (5.0 g, 23 mmol) in H₂O (10 ml) and was refluxed for 8 h. After filtration, the solution was evaporated to dryness. The residue was taken up in CH₂Cl₂ (200 ml), filtered, and evaporated to dryness. The crystalline residue (2.3 g, 98%) was crystallized from DMSO (20 ml) giving the product (1.2 g, 50%), m.p. 221 °C (decomp.); $\delta_{\rm H}$ (D₂O) 1.80–2.36 (m, 6 H) and 4.06 (s, 4 H) (Found: C, 50.6; H, 4.75; S, 30.2. C₉H₁₀O₂S₂ requires C, 50.45; H, 4.7; S, 29.9%).

(5) Bicyclo[2.2.1]heptadiene-7-spiro-2'-(1',3'-dithiolane) 1',3'dioxide (7). The quadricyclane derivative (6) (700 mg, 3.3 mmol) was stirred in chloroform (30 ml) with (norbornadienerhodium chloride)₂ (40 mg, 0.17 mmol) for 3 d. After removal of the solvent the product (500 mg, 79%) was obtained by sublimation (120 °C and 1 Torr), m.p. 192— 194 °C (decomp.); $\delta_{\rm H}$ (CDCl₃) 3.30—3.83 (m, 4 H), 3.90 (p, 2 H), and 6.95 (m, 4 H); $\delta_{\rm C}$ (CDCl₃) 49.26, 51.55, 136.73, 141.61, and 144.07 p.p.m. Trace amounts of the isomeric ciscompound displayed signals at δ 48.32, 52.37, 52.60, 139.79, and 143.49 p.p.m. (Found: C, 50.55; H, 4.8; S, 29.8. C₉H₁₀-O₂S₂ requires C, 50.45; H, 4.7; S, 29.9%).

(6) Tetracyclo[$3.2.0.0^{2.7}.0^{4.6}$]heptane-3-spiro-2'-(1',3'-dithiolane) 1',1',3',3'-Tetraoxide (8). The dithiolane (2) (1.0 g, 5.5 mmol) in acetic acid (30 ml) was stirred with 30% hydrogen peroxide (3.75 g, 33 mmol). Upon warming to 80—90 °C for 2 h crystals were deposited. After cooling, saturated aqueous Na₂SO₃ solution (10 ml) was added. After stirring for 15 min the crystals were filtered and washed with water giving the product (1.1 g, 81%), m.p. 269 °C (decomp.); $\delta_{\rm H}$ (hot [${}^{2}{\rm H}_{6}$]-DMSO) 1.80—2.20 (m, 6 H) and 4.12 (s, 4 H) (Found: C, 43.7; H, 4.0; S, 26.05. C₉H₁₀O₄S₂ requires C, 43.85; H, 4.1; S, 26.05%).

(7) Bicyclo[2.2.1]heptadiene-7-spiro-2'-(1',3'-ditholane) 1',1',-3',3'-Tetraoxide (9). The quadricyclane derivative (8) (500 mg, 2.0 mmol) and (norbornadienerhodiumchloride)₂ (20 mg, 0.087 mmol) were stirred for 2 days in CH₂Cl₂ (10 ml). After removal of the solvent the product (450 mg, 90%) was obtained by sublimation (160 °C and 1 Torr), m.p. 247 °C (decomp.); $\delta_{\rm H}$ (hot [²H₆]DMSO) 3.70 (s, 4 H), 3.93 (p, 2 H), and 6.90 (t, 4 H) (Found: C, 44.05; H, 4.05; S, 25.9. C₉H₁₀O₄S₂ requires C, 43.85; H, 4.1; S, 26.05%).

(8) $Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]$ heptane-3-spiro-2'-(1',3'-dithiane)

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(10). Quadricyclanone (2.00 g, 18.9 mmol) was dissolved in dry CH₂Cl₂ (40 ml). Dry Na₂SO₄ (0.5 g), boron trifluoride–ether (0.3 ml), and propane-1,3-dithiol (2.00 ml, 22.1 mmol) were rapidly added under stirring. After 30 min, the solution was extracted with 10% KOH (3 × 25 ml). After drying (MgSO₄) the solvent was removed *in vacuo*, yielding light tan *crystals* (3.3 g, 89%) which were recrystallized from light petroleum, m.p. 103–106 °C; $\delta_{\rm H}$ (CDCl₃) 1.90 (s), 1.95–2.3 (m, 8 H), and 3.05 (t, 4 H) (Found: C, 61.35; H, 6.25; S, 32.75. C₁₀H₁₂S₂ requires C, 61.2; H, 6.15; S, 32.65%).

(9) Bicyclo[2.2.1]heptadiene-7-spiro-2'-(1',3'-dithiane) (11). The quadricyclane derivative (10) (0.50 g, 2.6 mmol) and (Ph₃-P)₂Ni(CO)₂ (10 mg, 0.015 mmol) were stirred for 15 days in CH₂Cl₂ (30 ml). After removal of the solvent the crude product was obtained by sublimation (80 °C and 1 Torr) and purified by crystallization from light petroleum, yielding crystals (0.31 g, 62%), m.p. 82–84 °C; $\delta_{\rm H}$ (CDCl₃) 1.60–2.11 (p, 2 H), 2.80 (t, 4 H), 3.88 (p, 2 H), and 6.92 (t, 4 H) (Found: C, 61.4; H, 5.9. C₁₀H₁₂S₂ requires C, 61.2; H, 6.15%).

(10) 2-Phenyl-1,3-dithiolane 1-oxide (13). To a solution of NaIO₄ (2.50 g, 12 mmol) in H₂O (10 ml) was added dropwise 2-phenyl-1,3-dithiolane (2.00 g, 11 mmol) dissolved in acetone (30 ml) over 10 min. After stirring for 20 h the mixture was filtered and the filtrate freed of solvent. The residue was triturated with water (40 ml) and extracted with CH₂Cl₂ (3 × 20 ml). The extracts were dried over Na₂SO₄. Removal of the solvent left a light tan oil. The crude product was purified by chromatography with ethyl acetate over a Merck LOBAR column giving an *oil* (1.80 g, 83%), $\delta_{\rm H}$ (CDCl₃) 2.57–4.25 (m, 4 H), 5.50 (s, 1 H), and 7.47–7.92 (m, 5 H) (Found: C, 54.2; H, 5.1; S, 32.1. C₉H₁₀OS₂ requires C, 54.5; H, 5.1; S, 32.3%).

(11) 2-Phenyl-1,3-dithiolane 1,1,3,3-tetraoxide (14). To a solution of 2-phenyl-1,3-dithiolane (1.0 g, 5.5 mmol) in CHCl₃ (100 ml) was added 79% *m*-chloroperbenzoic acid (5.8 g, 23.5 mmol). In an exothermic reaction the mixture slowly deposited a thick precipitate which after 1 h was dissolved by stirring with CH₂Cl₂ (100 ml) and aqueous saturated NaHCO₃ solution (100 ml). The organic phase was washed with 10% aqueous Na₂SO₃ solution (80 ml) and twice with saturated NaHCO₃ solution. After drying (Na₂SO₄) the solvent was removed leaving (14) as *crystals* (0.55 g, 41%), m.p. 250–255 °C (decomp.); $\delta_{\rm H}$ ([²H₆]DMSO, external Me₄Si), 4.15 (s, 4 H), 6.2 (s, 1 H), and 7.5 (s, 5 H) (Found: C, 44.3; H, 4.1. C₉H₁₀O₄S₂ requires C, 43.85; H, 4.1%).

Thermolyses.—The substances were vapourized into an electrically heated tube of 25 cm length and 1.2 cm diameter. The horizontally arranged tube was directly connected to the vacuum system via a U-tube cold trap. Before each run the tube and trap were carefully cleaned with acetone. At the end of a run a defined volume of CCl_4 solution of acetone (internal standard) was injected into the cold trap. Product yields were then determined by ¹H n.m.r. spectroscopy.

(1) Thermolysis of spiro-compound (3). Compound (3) (35.5 mg, 0.195 mmol) was thermolysed at 300 °C and 10^{-4} Torr over 2 h. The ¹H n.m.r. spectrum of the condensate revealed the presence of benzene (0.197 mmol). The i.r. spectrum showed the characteristic absorptions of benzene ²⁸ and carbon disulphide.²⁸

(2) Thermolysis of spiro-compound (4). Compound (4) (38.7 mg, 0.195 mmol) was pyrolysed at 450 °C and 10^{-4} Torr over 8 h. From the ¹H n.m.r. spectrum of the condensate the formation of 98% benzene was evident. G.c. (30–130 °C)-m.s. analyses revealed the presence of benzene,²⁹ carbon disulphide,²⁹ and small peaks corresponding to molecular weights 104, 110, 106, and 180. The yellow deposit at the entrance of the U-tube was taken up in carbon disulphide. After

1690

removal of the solvent it was identified by the action of pyridine and NaOH as elemental sulphur.³⁰

(3) Thermolysis of spiro-compound (11). Compound (11) (94.0 mg, 0.173 mmol) was pyrolysed at 400 °C and 10^{-4} Torr over 4 h. After the run, the cold trap was connected with an i.r. gas-cell and allowed to warm to -20 °C. The i.r. spectrum was a superposition of the absorptions of carbon disulphide,²⁸ benzene,²⁸ and cyclopropane.²⁸ The ¹H n.m.r. spectrum showed the presence of small amounts of cyclopropane ³¹ besides 84% benzene.

(4) Thermolysis of spiro-compound (7). Compound (7) (34 mg, 0.16 mmol) was pyrolysed at 400 °C and 10^{-4} Torr over 4 h. The orange-red colour of the cold trap changed rapidly to yellow upon removal of the liquid nitrogen cooling bath. The ¹H n.m.r. spectrum of the condensate showed the presence of 45—50% benzene ³¹ and *ca.* 21% benzaldehyde.³¹ The i.r. spectrum was a composite from the absorptions of benzene,²⁸ carbon disulphide,²⁸ and benzaldehyde.²⁸ G.c. (30—230 °C)-m.s. analyses showed the presence of carbon disulphide,²⁹ benzene, ²⁹ and benzaldehyde.²⁹ Small peaks corresponded to compounds with molecular weights 83, 122, 106, and 180.

(5) Thermolysis of spiro-compound (9). Compound (9) (62 mg, 0.25 mmol) was thermolysed at 450 °C and 10⁻⁴ Torr over 10 h. The ¹H n.m.r. spectrum of the condensate revealed the presence of indan,³¹ indene, *cis*-stilbene,³¹ and benzaldehyde³¹ as well as several unassigned signals. G.c. (30–230 °C)-m.s. analyses showed the presence of ten substances. By comparison of their mass spectra benzaldehyde,²⁹ indan,²⁹ and stilbene ²⁹ could be identified. Benzene was clearly absent. Of the other minor constituents four had a molecular mass of 118, two of 92, and one of 116. When the cold trap of the thermolysis was warmed up, the formation of SO₂ was evident.

(6) Thermolysis of 2-phenyl-1,3-dithiolane 1,1,3,3-tetraoxide (14). Compound (14) (46.6 mg, 0.189 mmol) was thermolysed at 800 °C and 10^{-2} Torr. The ¹H n.m.r. spectrum of the condensate revealed the presence of 51% benzaldehyde and 19% phenylcyclopropane. The latter was identified by comparison with an authentic sample ³² on several g.c. columns. G.c. (30-230 °C)-m.s. analyses documented the presence of benzaldehyde ²⁹ and of phenylcyclopropane and showed the presence of two minor constituents of mass 118 and 180, which were not assigned.

(7) Curie-point pyrolyses. The Curie-point pyrolysis-mass spectrometry investigations were carried out using the experimental set-up previously described,²³ which is based on a direct connection between a Pye-Unicam PV4000 Curiepoint pyrolyser and the ion source of a double-focusing Varian MAT CH5 D mass spectrometer. Samples, suspended in methanol, were applied to the gold-plated filaments²⁴ by the dip-coating technique.33 The pyrolyses were carried out at 1043 K (Curie temperature of iron), the reaction mixture being analysed by field ionization mass spectrometry.23 Identification of the single components in the pyrolysis mixtures was obtained by collision activation mass spectrometry (c.a.m.s.) of the field-ionized molecular ions by comparison with authentic samples (see ref. 23). The c.a.m.s. analysis of the C_7H_6S compound formed in the pyrolysis of the sulphoxides (4) and (7) was equivocal, since the spectrum a priori, based on the observed fragmentation pattern, was to be assigned to thiobenzaldehyde. However, we were, for some unknown reason, unable to obtain the mass spectrum of authentic thiobenzaldehyde, the latter being reported to arise by pyrolysis of allyl benzyl sulphide.³⁴ Similarly, it was expected that pyrolysis of thioacetal (12) would give rise to thiobenzaldehyde ³⁵ in addition to ethylene sulphide. No C₇H₆S was observed. Against this background we suggest that the C7H6S generated by pyrolysis of the sulphoxides (4) and (7) is an isomeric species, e.g. thiotropone,³⁶ the alternative structure,

tetracyclo[3.2.0^{2.7}.0^{4.6}]heptane-3-thione most probably being too labile to be observed, *i.e.* t_{\pm} less than *ca.* 10⁻³ s.²³ The results of the pyrolyses of the compounds (2), (4), (7), (12), and (13) are summarized in the Table.

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