Studies on the Flash Vacuum Thermolysis of Thiones of Selected N-, O-, and S-Heterocycles

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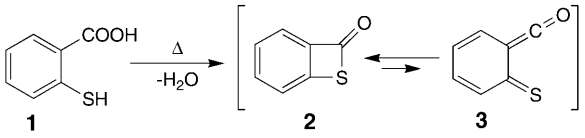
Thermal decomposition of thiones of selected N-, O- and S-heterocycles under flash vacuum thermolysis conditions was investigated. In the case of six-membered 4*H*-3,1-benzoxathiin-4-thione **6**, the course of the reaction depended on the substitution pattern at C(2) (*Scheme 3*). Thus, the 2-unsubstituted derivative **6a** led to the unstable product **2**, which upon treatment with MeOH was converted quantitatively into methyl 2-mercaptobenzoate (**7**). The analogous thermolysis of the 2,2-dimethyl derivative **6b** yielded 2-methyl-4*H*-1-benzothiopyran-4-thione (**8**) as a sole product. In the case of thiophthalide derivatives **15**, a thermal rearrangement in the gas phase leading to the corresponding benzo[*c*]thiophen-1(3*H*)-ones **16** in high yields was observed (*Scheme 6*). Unexpectedly, thionation of 1,3-oxathiolan-5-one **17** with *Lawesson*'s reagent under standard conditions led to 1,2-dithietane derivative **19**, which, after the gas-phase thermolysis, underwent a ring enlargement to yield 3*H*-1,2-dithiole **20** (*Scheme 7*). The six-membered 4*H*-1,3-benzothiazine-4-thione **21** was shown to give three products: phenanthro[9,10-*c*]-1,2-dithiete (**22**), 3*H*-1,3-benzodithiole-3-thione (**23**), and *N*-(3*H*-1,2-benzodithiol-3-ylidene)prop-2-en-1-amine (**24**) (*Scheme 8*). The latter is the product of the initial reaction, whereas **22** and **23** are postulated to be formed as secondary products of the conversion of the intermediate 6-(thioxomethylene)cyclohexa-2,4-diene-1-thione (**26**) (*Schemes 9* and *10*).

1. Introduction. – It is well documented that the flash vacuum thermolysis of 2-mercaptobenzoic acid (**1**) leads to the formation of benzothiet-2-one (**2**) (*Scheme 1*) [1]. The same product can be obtained thermally from benzothiophene-2,3-dione [1] as well as photolytically starting either from 4*H*-1,2,3-benzothiadiazin-4-one [2] or from 2-phenyl-4*H*-3,1-benzoxathin-4-one [3]. The benzothiet-2-one (**2**) is postulated to exist in an equilibrium with α-thioxo ketene **3** being its ring-opened isomer. The heterocycle **2** is stable only below $-20°$, whereas the analogous naphtho[2,3-*b*]thiet-2-one was successfully isolated and identified at room temperature [4]. It is worth mentioning that the treatment of 2-mercaptobenzoic acid with molecular sieves at room temperature in the presence of suitable dienophiles, *e.g.*, dimethyl fumarate, yields hetero-*Diels–Alder* cycloadducts in excellent yields [5]. This result shows that the elimination of H_2O leading to highly reactive heterocumulene occurs even under very mild conditions.

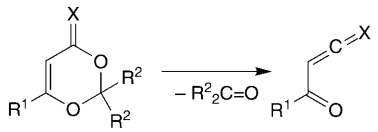
[1]) Part of the planned Ph. D. Thesis by *T. Drewnowski*, University of Łódź.

Scheme 1



The generation of heterocumulenes of type **5** is based on the thermolysis of 4*H*-1,3-dioxin-4-ones **4**, which are known to eliminate a molecule of ketone (*Scheme 2*). As already reported, the replacement of the C=O group by a C=S unit in the case of the substrates **4** does not influence the main course of the reaction [6–8].

Scheme 2



4 R^1 = Alk, Ar
R^2 = Alk

5 X = O, S

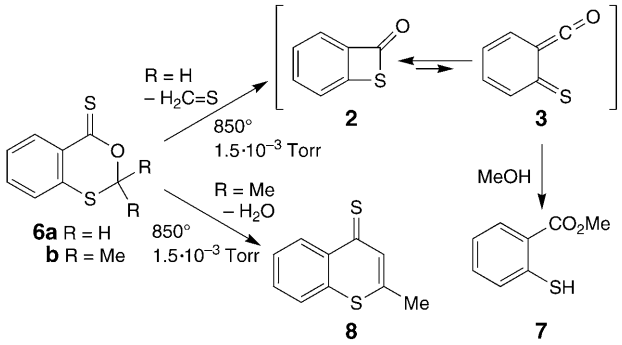
The present paper is aimed mainly at the study on the influence of the C=S group on the course of the gas-phase thermolysis of selected cyclic derivatives of 2-mercaptobenzoic acid. For comparison, some five-membered systems bearing a thioxo group as well as a cyclic six-membered thioamide are included for mechanistic investigations.

2. Results and Discussion. – The 4*H*-3,1-benzoxathiin-4-thione (**6a**) obtained after thionation of the corresponding oxo analogue [9] was used as the first compound in the study. Thermolysis carried out at 850°/1.5 · 10^{-3} Torr[2]) led to the formation of an orange pyrolyzate which, after warming to room temperature, immediately decomposed giving a colorless, viscous material. However, treatment of the colored product collected on the cooling finger at −78° with MeOH resulted in the formation of a compound, which could be easily isolated and identified as methyl 2-mercaptobenzoate (**7**) (*Scheme 3*). This result showed unambiguously that the initially formed product in the thermolysis of **6a** was benzothiet-4-one (**2**). The analogous experiment with 2,2-dimethyl-4*H*-3,1-benzoxathiin-4-thione (**6b**) gave a yellow solid, which did not change during the warming to room temperature. The spectroscopic data allowed to identify this product as the known 2-methyl-4*H*-1-benzothiopyran-4-thione (**8**) (*Scheme 3*) [10].

The comparison of the results obtained with **6a** and **6b** shows that the substituent R attached at C(2) governs the course of the reaction in the gas phase and thereby determines the type of the formed products. Whereas in the case of **6a**, elimination of thioformaldehyde took place, the reaction with **6b** proceeded by elimination of H_2O. In the light of available literature reports [6–8], the elimination of formaldehyde rather than

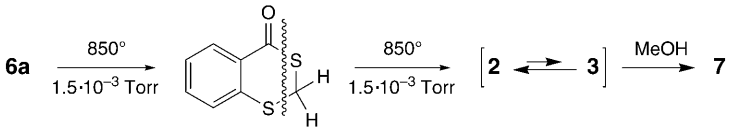
[2]) The temperature 850° is the lowest possible at which the starting material was not present in the pyrolyzate.

Scheme 3



thioformaldehyde could be expected in the case of **6a**. The preservation of the carbonyl group in the product can be rationalized by the assumption that the initial step of the reaction is the rearrangement of the *O*-substituted thiolactones into the *S*-substituted isomer, which finally eliminates of $H_2C{=}S$ (*Scheme 4*). This type of isomerization is known as the *Schönberg–Newman–Kwart* rearrangement, and to the best of our knowledge, hitherto it has been reported only for reactions carried out in solution but not in the gas phase [11].

Scheme 4

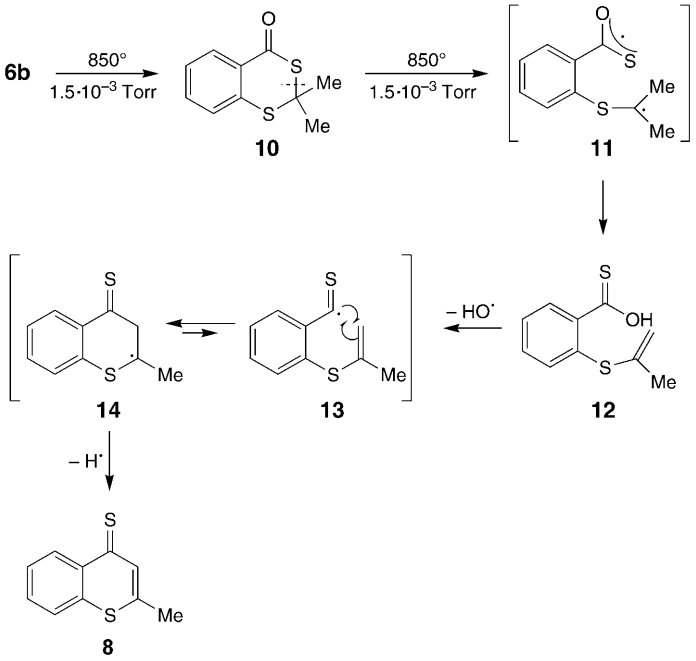


It is very likely that this type of rearrangement initiates also the conversions of **6b** in the gas phase (*Scheme 5*). Selective splitting of the C–S bond in the rearranged product **10** affords the biradical intermediate **11**, in which subsequent migration of an H-atom leads to the unstable thioacid **12**. The postulated abstraction of the H-atom by the O- and not the S-atom can be rationalized by the assumption that an O-atom displays higher affinity to an H-atom than an S-atom [12]. The next step of the conversion of **12** to **8** requires elimination of H_2O which presumably proceeds stepwise *via* homolytic cleavage of the C–OH bond leading to **13**, which undergoes cyclization to **14**. The latter eliminates the H-atom giving the final product **8** (*Scheme 5*).

The next compounds involved in the study were thiophthalides **15a**,**b**. Flash vacuum thermolysis of **15a** at 850°/1.5 · 10^{-3} Torr occurred smoothly, and the expected product of the gas-phase rearrangement, *i.e.*, benzo[*c*]thiophen-1(3*H*)-one (**16a**), was obtained in nearly quantitative yield. Similarly, the 3,3-dimethyl derivative **15b** was converted into the analogous thiophenone **16b** (*Scheme 6*). These results establish that the rearrangement of thio-*O*-lactones to thio-*S*-lactones by exchange of the positions of both heteroatoms proceeds easily also in the gas phase[3]). It is worth mentioning that in

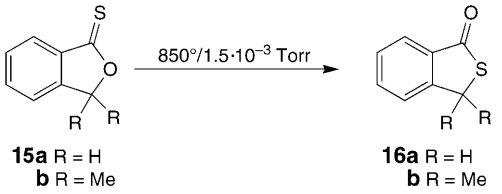
[3]) Heating of **15a** in boiling aniline was reported to yield **16a** [13], and **15b** was converted to **16b** by the reaction with triethyloxonium tetrafluoroborate and triethylamine [14].

Scheme 5



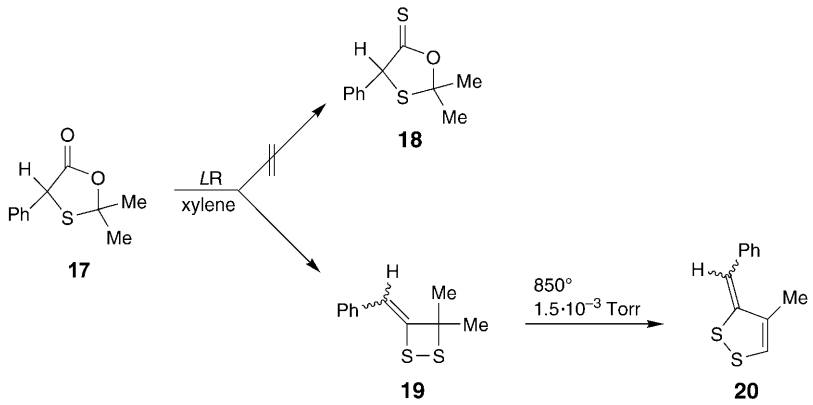
the case of **15b** the conversion analogous to **6b** → **8**, which requires elimination of H_2O (*Scheme* 5), was not observed.

Scheme 6



Cammeron and *Pinnick* reported that 1,3-oxathiolan-5-ones of type **17** eliminate CO_2 in the gas phase to generate the reactive 'thiocarbonyl' ylides (= sulfonium ylides), which underwent stereoselectively 1,3-dipolar electrocyclization to give the corresponding thiiranes [15]. In the light of the results described for **6**, it was of interest to examine whether the thioxo derivative **18** follows a reaction pathway similar to that presented for **6b**. However, the attempted thionation of **17** with *Lawesson*'s reagent (*L*R) in boiling xylene led to 1,2-dithietane **19**, as a single isomer (^{1}H- and ^{13}C-NMR) with unknown configuration, and the expected product **18** was not observed (*Scheme 7*). Having in hands this new, S-rich heterocycle **19**, we decided to examine its behavior in the gas-phase thermolysis. Under the conditions outlined in *Scheme 7*,

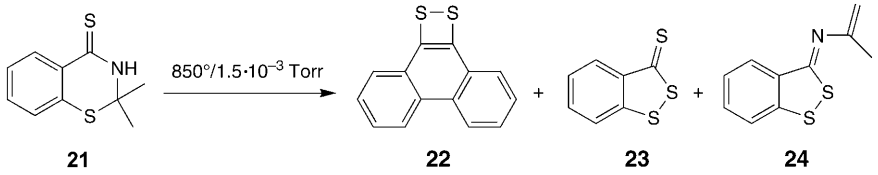
Scheme 7



3-benzylidene-4-methyl-3*H*-dithiolane (**20**) was obtained as a 1:3-(*E*)/(*Z*) mixture (based on the ^{13}C-NMR spectrum)[4]). Unfortunately, all attempts to separate the isomers by column chromatography or prep. TLC were in vain.

The 4*H*-1,3-benzothiazine-4-thione **21**, which is an N-analogue of **6b**, was obtained from the corresponding oxo derivative by treatment with *L*R in boiling xylene. Due to the replacement of an O- by an N-atom, this compound did not undergo the *Schönberg–Newman–Kwart* rearrangement. The gas-phase thermolysis led to a mixture of three products, which were separated by column chromatography. Based on the spectroscopic and physicochemical properties, their structures were elucidated as **22**–**24** (*Scheme 8*). This result suggests that the key intermediate in the reaction is the biradical **25**, which either eliminates propan-2-imine to give heterocumulene **26** or undergoes an intramolecular cyclization followed by the elimination of an H-atom leading finally to the isolated amine **24** (*Scheme 9*). It is very likely that the formation of **22** and **23** proceeds by initial dimerization of **26** and subsequent unsymmetrical fragmentation (the symmetrical cleavage would lead to the starting **26**) to give 3*H*-1,2-benzodithiole-3-thione (**23**) and phenanthro[9,10-*c*]-1,2-dithiete (**22**) as a result of the dimerization of the biradical or carbene (*Scheme 10*).

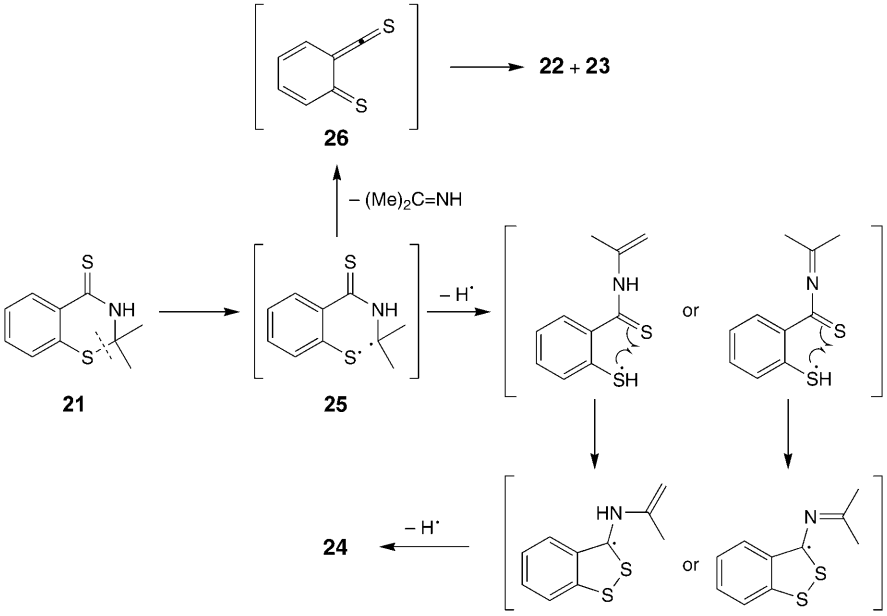
Scheme 8



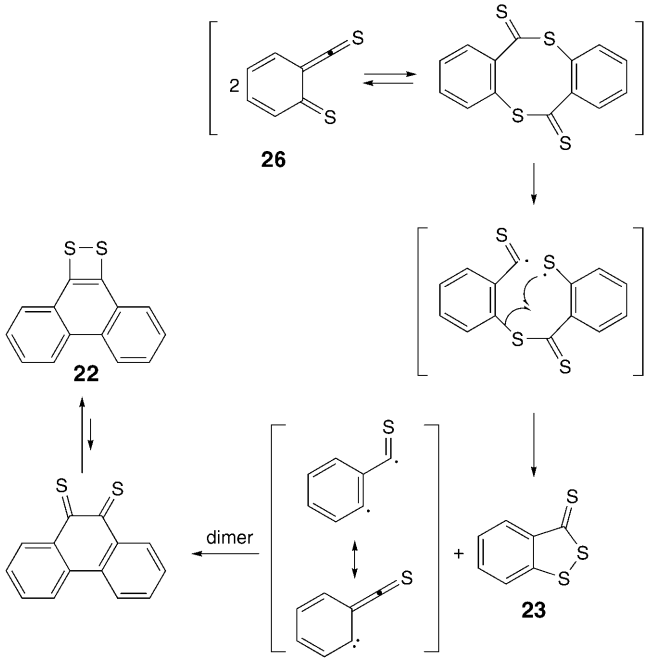
On the other hand, the higher yield of **22** in comparison with **23** (theoretically, 1 mol of **21** affords 0.5 mol of **23** and 0.25 mol **22**) suggests that the additional amount of com-

[4]) Interestingly, (*E*)- and (*Z*)-**20** showed identical chemical shifts for all groups of signals in the ^{1}H-NMR spectrum (200 MHz).

Scheme 9



Scheme 10



pound **22** originates from the decomposition of **23** initially formed in the gas phase. As a matter of fact, when pure **23** was pyrolyzed under the same conditions, a mixture of **22** and **23** was obtained. This result shows unequivocally that **22** was produced from the dimer of **26** as well as from **23**.

In summary, the present study shows that the replacement of the O-atom in the C=O group of the cyclic ester (lactone) by an S-atom results in the initial rearrangement in the gas-phase thermolysis. The next step of the conversion depends strongly on the substitution pattern at the C(2) atom of the heterocycle. Whereas in the case of a CH_2 group, the elimination of CH_2=S takes place to yield the reactive system **2** ⇌ **3**, the presence of a Me_2C moiety determines the formation of 4*H*-1-benzothiopyran-4-thione **8** *via* elimination of H_2O. Introduction of an N-atom into the six-membered heterocycle (thioamide instead of thioester) prevents the *Schönberg–Newman–Kwart* rearrangement and results in the competitive elimination of propan-2-imine or dehydrogenation.

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Experimental Part

1. *General*: Column chromatography (CC): silica gel (*Merck 60*, 63–200 microns). TLC: *Merck-5554* aluminium-backed SiO_2 plates; visualization by UV light. M.p.: *Boëtius* apparatus; uncorrected. IR Spectra: *Thermo-Nicolet-Nexus-FT-IR* spectrometer; in KBr or as films, in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Varian-Gemini-200-BB-VT* instrument, at 200.11 (^1H) and 50.33 MHz (^{13}C); $CDCl_3$ solns. at *ca.* 21°; chemical shifts δ in ppm rel. to $SiMe_4$, coupling constants *J* in Hz; assignments usually with ATP or DEPT experiments. EI-MS: *Finnigan-MAT-95* spectrometer at 70 eV; peaks ≥10% rel. intensity are given in *m*/*z* (rel.%).

2. *Starting Materials.* Compounds **15a**,**b** were prepared following the literature procedure, *i.e.*, isobenzofuran-1(3*H*)-thione (**15a**) [16] and 3,3-dimethyl-isobenzofuran-1(3*H*)-thione (**15b**) [14]. The remaining thiones **6a**,**b**, and **21** as well as **19** were prepared by thionation of their ketone precursors with *Lawesson* reagent (*L*R), *i.e.*, of 4*H*-3,1-benzoxathiin-4-one [9], 2,2-dimethyl-4*H*-3,1-benzoxathiin-4-one [9], 2,2-dimethyl-2,3-dihydro-4*H*-1,3-benzothiazin-4-one [17], and 2,2-dimethyl-4-phenyl-[1,3]oxathiolan-5-one (**17**) [18].

3. *Synthesis of* **6a,b**, **19** *and* **21**: *General Procedure.* A soln. of the corresponding ketone (5 mmol) and *L*R (3.24 g, 8 mmol) in xylene (20 ml) was heated to reflux for 4 h. Xylene was evaporated and the residue was subjected to CC (SiO_2, hexane/CH_2Cl_2 or hexane/AcOEt). Then, the products were purified additionally by recrystallization.

*4*H-*3,1-Benzoxathiin-4-thione* (**6a**). CC (hexane/CH_2Cl_2 1:1) and recrystallization from hexane gave 310 mg (34%) of **6a**. Red solid. M.p. 64–66° (hexane). IR (KBr): 3052*w*, 2976*s*, 1583*s*, 1449*s*, 1427*s*, 1296*m*, 1254*s*, 1224v*s*, 1135*m*, 1111*m*, 955*w*, 919*s*, 759v*s*, 713*w*, 642*m*. ^1H-NMR: 5.40 (*s*, 2 H); 7.14–7.52 (*m*, 3 H); 8.40–8.56 (*m,* 1 H). Anal. calc. for $C_8H_6OS_2$ (182.26): C 52.72, H 3.32, S 35.19; found: C 52.48, H 3.51, S 35.11.

*2,2-Dimethyl-4*H-*3,1-benzoxathiin-4-thione* (**6b**). CC (hexane/CH_2Cl_2 3:2) and recrystallization from hexane gave 631 mg (60%) of **6b**. Red solid. M.p. 67–69° (hexane). IR (KBr): 3065*w*, 3046*w*, 2978*m*, 2961*m,* 1581*s*, 1550*m*, 1446*s*, 1425*s*, 1366*m*, 1285*w*, 1259*s*, 1224v*s*, 1158*m*, 1132*m*, 1019v*s*, 1002*s*, 957*w*, 919*s*, 763v*s*, 696*w*. ^1H-NMR: 1.73 (*s*, 6 H); 7.20–7.48 (*m*, 3 H); 8.35–8.52 (*m*, 1 H). Anal. calc. for $C_{10}H_{10}OS_2$ (210.32): C 57.11, H 4.79, S 30.49; found: C 57.08, H 4.55, S 30.21.

*4-Benzylidene-3,3-dimethyl-1,2-dithietane (***19***)*. CC (hexane/AcOEt 97:3) and recrystallization from pentane gave 505 mg (45%) of **19**. M.p. 51–52° (pentane). IR (KBr): 3077*w*, 3052*w,* 2958*m*, 2921*m*, 1596*w*, 1577*m*, 1537*s*, 1489*m*, 1444*s*, 1382*w*, 1362*s*, 1170*m*, 1148*s*, 1107*m*, 1073*w*, 1030*w*, 920*m*, 823*m*,

740v*s*, 683*s*. ^{1}H-NMR: 1.89 (br. *s*, 6 H); 6.31 (*s*, 1 H); 7.18–7.51 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 31.8 (Me); 65.6 (C); 112.7 (CH); 126.7 (arom. C); 127.9 (arom. C); 128.8 (arom. C); 134.6 (C); 134.7 (C). MS: 208 (27, M^+), 194 (10), 193 (100), 134 (10). Anal. calc. for $C_{11}H_{12}S_2$ (208.35): C 63.41, H 5.81, S 30.78; found: C 63.38, H 5.84, S 30.41.

*2,2-Dimethyl-2,3-dihydro-4*H-*1,3-benzothiazine-4-thione* (**21**). CC (hexane/CH_2Cl_2 1:1) and recrystallization from hexane/CH_2Cl_2 gave 1005 mg (96%) of **21**. Yellow solid. M.p. 191–192° (hexane/CH_2Cl_2). IR (KBr): 3148*m* (NH), 3069*m*, 2984*m*, 2960*w*, 2937*w*, 1584*w*, 1567*s*, 1521v*s*, 1453*m*, 1425*s*, 1387*m*, 1367*m*, 1225v*s*, 1160*w*, 1148*w*, 1000*m*, 768v*s*, 753*w*, 722*m*. ^{1}H-NMR: 1.70 (*s*, 6 H); 7.10–7.45 (*m*, 3 H); 8.48–8.65 (*m*, 1 H); 8.95 (br. *s*, 1 H). Anal. calc. for $C_{10}H_{11}NS_2$ (209.33): C 57.38, H 5.30, N 6.69, S 30.49; found: C 57.35, H 5.29, N 6.60, S 30.24.

4. Thermolysis of Thiones: General Procedure. The flash vacuum thermolysis was carried out in a $30 \cdot 2.5$ cm^2 electrically heated horizontal quartz tube packed with quartz rings at $1.5 \cdot 10^{-3}$ Torr. The starting compounds (2 mmol) were slowly sublimed from a flask held at 40–50° (for **6a**,**b**, **15a**,**b**, and **19**) or 80° (for **21**) into the thermolysis tube preheated to 850°. The products were collected in a CO_2/aceton trap. After thermolysis, the system was brought to atmospheric pressure allowing a slow warming up to r.t., and the products were dissolved in MeOH or $CHCl_3$. The solvent was evaporated and the products were purified by CC (SiO_2), recrystallization, distillation, or prep. TLC.

Thermolysis of **6a**. The product of the thermolysis was rinsed from the cold finger with cold MeOH. After warming to r.t., excess MeOH was evaporated: 316 mg (94%) of *methyl 2-mercaptobenzoate* (**7**).

Thermolysis of **6b**. The product of the thermolysis was rinsed from the cold finger with $CHCl_3$. Evaporation and recrystallization from hexane gave 342 mg (89%) of *2-methyl-4*H-*1-benzothiopyran-4-thione* (**8**). M.p.107–108° ([10]: 107–108°). Spectral data: identical with those of an authentic sample [10].

Thermolysis of **15a**,**b**. The products of the thermolysis were rinsed from the cold finger with $CHCl_3$. Evaporation, CC (SiO_2, hexane/AcOEt 99:1), and recrystallization from petroleum ether gave 291 mg (97%) of *benzo[*c*]thiophen-1(3*H*)-one* (**16a**) or 338 mg (95%) of *3,3-dimethyl-benzo[*c*]thiophen-1(3*H*)-one* (**16b**).

16a: M.p. 60–61° ([19]: 58–60°). Spectral data: identical with those in [19].

16b: M.p. 47–48° ([20]: 46–48°). Spectral data: identical with those in [14].

Thermolysis of **19**. The products of the thermolysis were rinsed from the cold finger with $CHCl_3$. Evaporation and CC (SiO_2, hexane/AcOEt 99:1) followed by bulb-to-bulb distillation at $50°/5 \cdot 10^{-2}$ Torr gave 224 mg (54%) of *3-benzylidene-4-methyl-3*H-*1,2-dithiole* **(20)**. Colorless oil. IR (neat): 3082*w*, 3060*m*, 2970*w*, 2947*w*, 2921*m*, 2863*w*, 1598*m*, 1497*s*, 1452*m*, 1430*w*, 1380*w*, 1333*w*, 1203*m*, 1073*m*, 1032*w*, 922*w*, 916*w*, 855*m*, 838*m*, 759*s*, 690*m*. ^{1}H-NMR: 2.28 (br. *s*, 3 H); 6.84 (br. *s*, 1 H); 7.12 (br. *s*, 1 H); 7.17–7.40 (*m*, 3 H); 7.53–7.63 (*m*, 2 H).^{13}C-NMR: major isomer: 144.2, 138.7, 134.7 (3 C); 128.9, 127.4, 125.8, 125.6, 120.3 (5 CH); 16.0 (Me); minor isomer: 143.3, 137.2, 136.3 (3 C); 128.7, 128.4, 127.1, 123.1, 122.1 (5 CH); 15.7 (Me). MS (isomer mixture): 206 (11, M^+), 205 (20), 204 (100), 190 (23), 174 (41), 173 (29), 128 (11), 115 (17), 1021 (13), 89 (13). Anal. calc. for $C_{11}H_{10}S_2$ (206.32): C 64.03, H 4.89, S 31.08; found: C 64.00, H 4.81, S 30.88.

Thermolysis of **21**. The products of the thermolysis were rinsed from the cold finger with $CHCl_3$. Evaporation and CC (silica gel, hexane/AcOEt) gave 84 mg (70%) of **22**, after recrystallization from hexane/$CHCl_3$, 77 mg (42%) of **23**, after recrystallization from hexane/CH_2Cl_2, and 40 mg (9%) of **24**, after further purification by TLC (SiO_2, hexane/AcOEt 9:1).

*Phenanthro[9,10-*c*]-1,2-dithiete* (**22**): Orange solid. M.p. 213–215° (hexane/CH_2Cl_2). IR (KBr): 3070*w*, 3051*w*, 1456*w*, 1437*s*, 1336*s*, 1297*m*, 1254*m*, 1127*w*, 1059*w*, 1015*w*, 952*w*, 742v*s*, 723*s*. ^{1}H-NMR: 7.10–7.50 (*m*, 3 H); 7.70–7.80 (*m*, 1 H). ^{13}C-NMR: 142.3, 133.4, 133.1 (3 C); 125.0, 124.9, 124.0, 121.6 (4 CH). MS: 240 (100, M^+). Anal. calc. for $C_{14}H_8S_2$ (240.35): C 69.96, H 3.35, S 26.68; found: C 69.99, H 3.28, S 26.51.

*3*H-*1,2-Benzodithiole-3-thione* (**23**): Yellow solid. M.p. 95–97° ([21]: 98°). Spectral data: identical with those in [21].

N-*(3*H-*1,2-Benzodithiol-3-ylidene)prop-1-en-2-amine* (**24**): Oil. IR (neat): 3091*w*, 3062*w*, 2976*w*, 2953*w*, 2921*w*, 2850*w*, 1632*m* (C=N), 1589*m*, 1469*s*, 1456*s*, 1447*m*, 1362*m*, 1322*m*, 1221*s*, 1165*m*, 1076*m*, 908*m*, 809*m*, 783*m*, 742v*s*. ^{1}H-NMR: 2.25–2.32 (*m*, 3 H); 5.53–5.68 (*m*, 2 H); 7.33–7.55 (*m*, 2

H); 7.80–7.96 (*m*, 1 H); 8.10–8.25 (*m*, 1 H). ^{13}C-NMR: 22.3 (Me); 117.8 (=CH_2); 119.7, 124.7, 124.9, 127.2 (4 C); 133.5, 139.7, 153.1 (3 C); 165.3 (C=N). MS: 207(3, M^+), 175 (57), 153 (34), 149 (41), 136 (38), 89 (54), 77 (100).

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