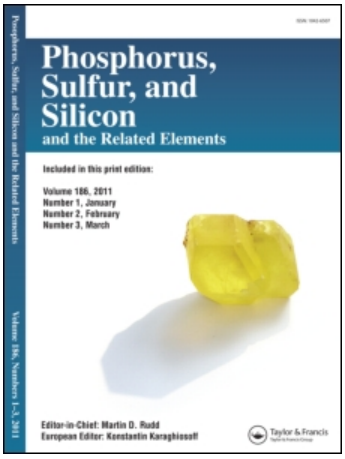

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THERMAL FISSION OF HYDROXYLAMINE DERIVATIVES WITH NEIGHBOURING-GROUP-PARTICIPATION BY THIOETHER FUNCTIONS: PREPARATION OF 1,2-BENZISOTHIAZOLES

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THERMAL FISSION OF HYDROXYLAMINE DERIVATIVES WITH NEIGHBOURING-GROUP-PARTICIPATION BY THIOETHER FUNCTIONS: PREPARATION OF 1,2-BENZISOTHIAZOLES

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Some of the factors influencing the preparation of 1,2-benzisothiazoles from 2-(alkylthio)phenyl-substituted oximes are discussed. Good yields of 3-aryl-1,2-benzisothiazoles **4** may be obtained from readily available precursors. Reaction takes place under particularly mild conditions when a *t*-butylthio function is situated *anti* to the leaving group at oxime-nitrogen and S—N overlap is not restricted by ring-strain in the transition-state.

The corresponding *N*-methyl-hydroxamic acid derivatives **2** give good yields of 2-methyl-1,2-benzisothiazol-3(2H)-one **13** only when a *t*-butylthio substituent is present, e.g. in **2f**. The ethylthio- and *i*-propylthio-analogues **2d** and **2e** give the vinylthioethers **12**, while the methylthio derivatives **2a–c** undergo a novel rearrangement to "Pummerer" esters **11**. The preparation of the polycyclic compounds fluoreno-[9,9a,1-cd]-1,2-thiazole **7** and 2,2'-bi(2H-fluoreno[9,9a,1-de]-1,3-thiazine) **8** is described.

INTRODUCTION

The previous paper[1] describes a simple method for the preparation of *ortho*-(alkylthio)-benzoic acids, -imines and -benzophenones. Further hydroxylamine derivatives of these compounds are thus readily available and this paper describes the thermal reactions of oxime and hydroxamic acid species (e.g. **1** and **2**) in an attempt to involve the sulphide sulphur atom in N—O fission reactions, in analogy to those already described for perbenzoates.[2]

The present report is confined to preparative aspects of these reactions; the complex question of ion-pair and/or radical-pair intermediates will be discussed elsewhere.[3]

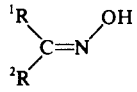
RESULTS AND DISCUSSION

New oximes and hydroxamic acids used in this paper are listed in Tables I and II respectively. These were converted to the corresponding derivatives **1**, **2** and **3**, listed in Tables III and IV.

Thus a total of 17 closely related compounds were prepared for study. The thermal fission reactions of this series resulted in a variety of products, depending on the substituent at sulphur, the nature of the hydroxylamine derivative (oxime or hydroxamic acid), the leaving-group, the solvent, temperature, and the extent of sulphur-nitrogen interaction in the transition-state, which may be affected by physical restraint (fluorenones, geometrical isomerism). In almost every case, however, the presence of the thioether function exerts a decisive influence on the nature of the major product obtained.

TABLE I

Analyses, yields and melting points for oximes of the structure



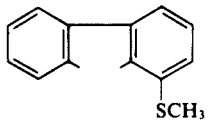
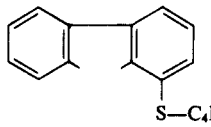
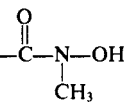
^1R	^2R	calculated C	H	N	found C	H	N	yield %	m.p. °C
C_6H_5	2-t-$C_4H_9SC_6H_4$	71.56	6.71	4.91	71.34	6.85	4.92	25	163–5
2-t-$C_4H_9SC_6H_4$	C_6H_5	71.56	6.71	4.91	71.33	6.86	4.94	44	125–6
2-i-$C_3H_7SC_6H_4$	C_6H_5	70.83	6.32	5.16	70.61	6.37	5.20	70	96
2-t-$C_4H_9SC_6H_4$	2-C_5H_4N	67.12	6.34	9.78	67.05	6.34	9.75	55	178
		69.70	4.59	5.81	69.85	4.75	5.78	83	228 (dec)
		72.07	6.05	4.94	71.80	6.21	5.05	47	240 (dec)

TABLE II

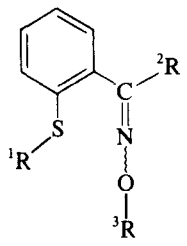
Analyses, yields and melting points for hydroxamic acids of the structure 

R	calculated C	H	N	found C	H	N	yield %	m.p. °C
2-$CH_3SC_6H_4$	54.80	5.62	7.10	54.98	5.71	6.98	68	155–6
2-$C_2H_5SC_6H_4$	56.86	6.20	6.63	56.77	6.23	6.63	33	107–8
2-i-$C_3H_7SC_6H_4$	58.65	6.71	6.22	58.36	6.56	6.31	64	84–5
2-t-$C_6H_4SC_6H_4$	60.24	7.16	5.85	60.57	7.25	5.67	61	122–3

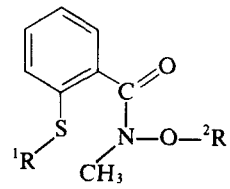
TABLE III

Analyses, yields and melting points for O-Acyl oxime derivatives **1** and **3**

Config.	C	calculated H	N	C	found H	N	yield %	m.p. °C
1a E	68.99	6.11	4.47	68.92	6.00	4.43	80	84–6 (dec)
b E	74.02	5.95	3.60	74.26	6.03	3.81	70	74–5
c Z	74.02	5.95	3.60	73.82	6.00	3.64	72	168–9
d E	70.75	5.68	7.18	70.54	5.68	7.22	90	167–9
e Z	73.58	5.64	3.73	73.88	5.65	3.84	89	105–6
f E	64.50	6.50	7.52	64.24	6.44	7.55	27	64 (dec)
g Z	64.50	6.50	7.52	64.88	6.33	7.52	55	111 (dec)
3a E	72.06	4.54	4.20	72.03	4.51	4.14	72	142 (dec)
b E	74.40	5.46	3.62	74.15	5.41	3.57	53	100–1 (dec)
c E	62.19	4.91	8.53	62.45	5.11	8.61	74	100 (dec)



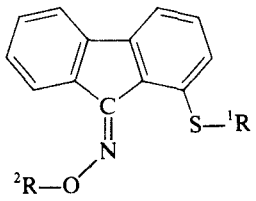
1



2

	E/Z	^1R	^2R	^3R
a	E	t-C_4H_9	H	C_6H_5CO
b	E	t-C_4H_9	C_6H_5	C_6H_5CO
c	Z	t-C_4H_9	C_6H_5	C_6H_5CO
d	E	t-C_4H_9	2-C_5H_4N	C_6H_5CO
e	Z	i-C_3H_7	C_6H_5	C_6H_5CO
f	E	t-C_4H_9	C_6H_5	$(CH_3)_2NCS$
g	Z	t-C_4H_9	C_6H_5	$(CH_3)_2NCS$

	^1R	^2R
a	CH_3	C_6H_5CO
b	CH_3	4-$CH_3OC_6H_4CO$
c	CH_3	4-$NO_2C_6H_4CO$
d	C_2H_5	C_6H_5CO
e	i-C_3H_7	C_6H_5CO
f	t-C_4H_9	C_6H_5CO
g	t-C_4H_9	$(CH_3)_2NCS$



3

	^1R	^2R
a	CH_3	C_6H_5CO
b	t-C_4H_9	C_6H_5CO
c	CH_3	$(CH_3)_2NCS$

TABLE IV

Analyses, yields and melting points for *O*-Acyl hydroxamic acids **2**

	calculated			found			yield	m.p.
2	C	H	N	C	H	N	%	°C
a	63.77	5.02	4.65	63.63	4.81	4.63	80	63–4
b	61.63	5.14	4.23	61.62	5.13	4.08	49	106–7
c	55.49	4.05	8.09	55.32	4.06	8.11	91	146–8
d	64.76	5.39	4.44	64.01	5.32	4.27	81	oil
e	65.65	5.77	4.25	65.49	5.59	3.97	88	oil
f	66.47	6.12	4.08	66.34	6.18	3.97	71	86–8
g	55.20	6.80	8.58	55.19	6.89	8.73	67	107–9 (dec)

O-Acyl Oximes **1** *and* **3**

Some previous work[4-7] has described the thermal reactions of oxime derivatives closely related to those of the present study. No very clear picture emerges, since fragmentation to nitriles[5] (from aldoximes), Beckmann rearrangement to amides[5] and benzothiazoles[6] have all been reported, in addition to the more interesting ring-closure to 1,2-benzisothiazoles.[4,6,7] An easy synthesis of 3-aryl-1,2-benzisothiazoles **4** (R = Ar) was desired in the present work, since this class of compounds is not readily available.[8,9]

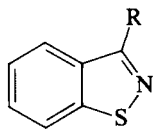
The few data already reported[5-7] can be interpreted to imply that a benzoate leaving-group in **1** would be superior to tosyloxy or acid catalysis on the oxime itself. Similarly, a *t*-butyl function at sulphur[4] could be superior to methyl, since in the latter case fragmentation to nitriles appears[5] to be the main reaction. The influence of oxime configuration has not been investigated. To clarify these points, the (E)-aldoxime derivative **1a** was chosen first for study.

Methanol solutions of **1a** were heated under reflux for one hour. On work-up, 80–90% 1,2-benzisothiazole **4a** was isolated, along with *t*-but-OCH_3 (55%), isobutene (27%), benzoic acid (82%) and the imide **5** (3–5%). No trace of nitriles could be detected in the crude product and the benzisothiazole was easily separated from the imide by distillation, after the removal of benzoic acid with dilute alkali. This reaction is clearly the method of choice for the preparation of **4a**, since extremely mild conditions of reaction and work-up are involved. Since no chromatography is involved (c.f. Ref. 4), large quantities of **4a** may be prepared in a highly pure state. 1,2-Benzisothiazole has been variously described as yellowish[9] and pink,[10] and reported melting points range from oil to 41°C. Samples obtained in the present work were water-clear, weakly fluorescent, and melted at 35–36°C. The use of solvents other than alcohols slows the reaction appreciably and *t*-butyl benzoate appears as a side product which is difficult to remove efficiently.

Extension to the derivative **1b** also resulted in a high yield of the benzisothiazole **4b**, (see Table V). The (Z)-isomer **1c**, however, would not react under these conditions, and a higher-boiling solvent (*o*-dichlorobenzene, DCB) was used with success. Examination of Table V shows that the configuration of the oxime clearly dictates how readily the *O*-benzoyl oximes react. Unfortunately, the major oxime isolated on oximation of *ortho*-substituted benzophenones is always the isomer with OH *syn* to the ring bearing the bulky *ortho*-substituent.[11] For this reason, 3-aryl-1,2-benzisothiazoles are best prepared in a high-boiling solvent such as DCB at 160°C. The oximes used need not be diastereomerically pure, and 3-heteroaryl-1,2-benzisothiazoles (e.g. **4c**) may be likewise obtained. The use of ^1R = *t*-butyl simplifies the purification, although ^1R = *i*-propyl may also be used. ^1R = methyl and ethyl were not tested in this series, since these derivatives are not so easily obtained by the reaction described in the previous paper,[1] and presumably offer no preparative advantages.

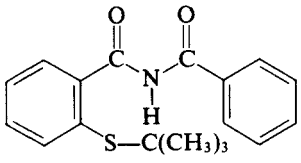
The use of thiocarbamoyl leaving groups (e.g. **1f,g**) results in a quicker reaction, *also* for the (Z)-isomer. This opens up the possibility of a preparation of 3-aryl-1,2-benzisothiazoles at temperatures only slightly above room-temperature, ***independent*** of the configuration of the ketoxime used. One disadvantage, however, lies in the thio-oxime[12] side-product (e.g. **6**) and thiocarbamoyl decomposition products, which may be difficult to remove in some cases.

The fluorenone derivatives **3** illustrate that not only the oxime configuration is important, but also the effect of ring-strain on the N—S overlap in the transition-



4

	R
a	H
b	C_6H_5
c	2-C_5H_4N



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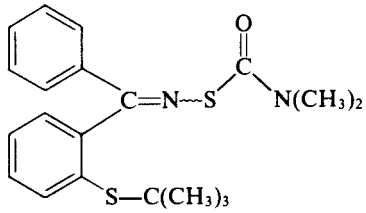


6

state. Thus the compounds **3a,b** possess the favorable (E)-configuration, but react very much slower than the corresponding compound **1b**, since the fluorenylidene structure "ties back" the sulphur atom. Thus **3b** was recovered essentially unchanged from methanol after 12 hours at 65°C. Reaction to the desired fluoreno-[9,9a,1-cd]-1,2-thiazole **7** was however achieved in DCB at 160°C (see Scheme I). The S-methyl counterpart **3a** did not react cleanly to **7** under these conditions, but gave instead the blue-black insoluble dimer **8** in 30% isolated yield, while the thiocarbamoyl derivative **3c** gave **9** in ca. 90% yield on standing in chloroform at room-temperature overnight. These examples illustrate the necessity for the correct choice of substituent, leaving group and solvent if the desired product is to be obtained in good yield.

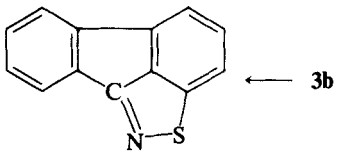
It should be noted that ring-closure to 3-aryl-1,2-benzisothiazoles may be achieved from derivatives other than oximes: Scheme II shows the result of one preliminary experiment, in which the method of the previous paper[1] was applied in a *one-pot* procedure, whereby the reagents were added sequentially. An overall yield of ca. 30% **4b** was obtained after work-up, when chlorine was used as oxidant, (non-optimized yield). The use of bromine resulted in the formation of the azine **10** in 20–25% yield.

TABLE V

Conditions for the preparation of 1,2-Benzisothiazoles **4** and **7** from *O*-Acyl oximes

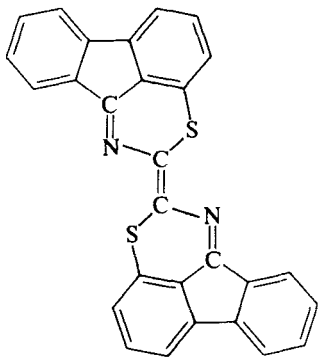
Precursor	solvent	h	t°C	Product	yield	other products
1a	CH_3OH	1	65	**4a**	80–90	See text
1a	DCB[a]	0.1	160	**4a**	75	Isobutene, t-BuOC(=O)C_6H_5 (8%)
1b	CH_3OH	10	65	**4b**	82	Similar to **1a** in CH_3OH
1c	DCB	15	160	**4b**	65	Similar to **1a** in DCB
1d	DCB	20	160	**4c**	66	Similar to **1c**
1e	DCB	12	160	**4b**	61	i-C_3H_7OC(=O)C_6H_5 (53%)
1f	CH_3OH	3	41	**4b**	60–70	**6** (~20%)
1g	CH_3OH	20	41	**4b**	60–70	**6** (~20%)
3b	DCB	2	160	**7**	55	Similar to **1c**

[a] DCB = *o*-Dichlorobenzene



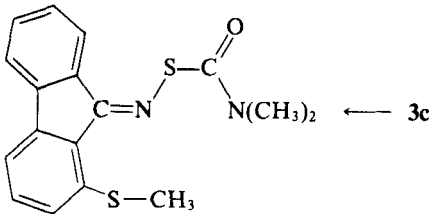
3b

7



3a

8



3c

9

SCHEME I

Major products from the solution thermolysis of the fluorenone derivatives **3**. Conditions—**3a**, **3b**: DCB, 160°C; **3c**: $CHCl_3$, 20°C.

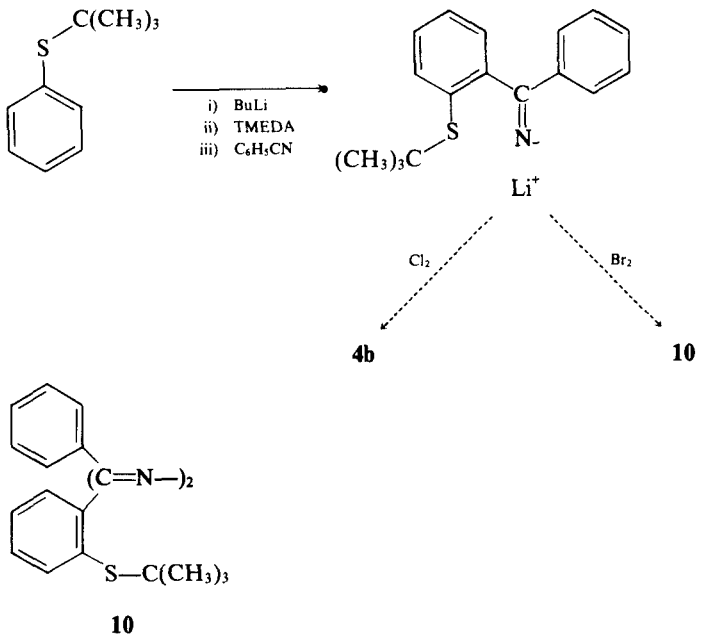
These results may be summarized as follows for the preparation of 1,2-benzisothiazoles from thermolysis of **1**:

1) ^1R should ideally be *t*-butyl.

2) ^2R may be H, aryl, heteroaryl or part of fluorenylidene structure, provided ^1R is *t*-butyl.

3) *o*-Dichlorobenzene at 160°C (6–20 hours) gives acceptable yields in all cases where ^1R is *t*-butyl, irrespective of the configuration of the oxime used.

4) $^3R = (CH_3)_2NCS$ may be used in special cases where the *syn* oxime predominates and high temperatures must be avoided. In this case methanol should be used as solvent.



SCHEME II

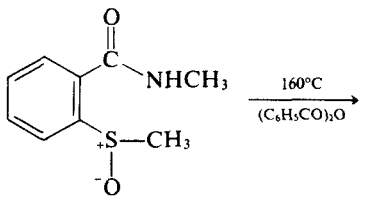
One-pot preparation of 3-phenyl-1,2-benzisothiazole **4b**. Conditions—see Ref. 1 and experimental section.

O-Acyl-N-methyl-hydroxamic acid derivatives **2**

N-Alkyl-hydroxamic acids do not undergo Lossen arrangement, although other thermal transformations may be observed.[13] The corresponding *O*-acyl-derivatives are thermally fairly stable.

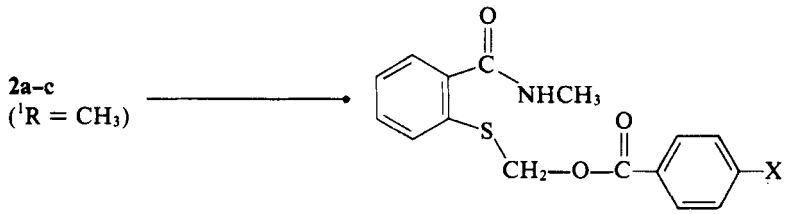
The present series **2a–f**, on heating in DCB at 160°C, showed a greater sensitivity to the nature of the alkyl group ^{1}R at sulphur than did the oxime derivatives described above. Three different types of major product were isolated, depending on whether ^{1}R possessed hydrogens α to the point of attachment (i.e. methyl), *α and β* (^{1}R = ethyl, *i*-propyl) or β-hydrogens alone (R = *t*-butyl). Scheme III summarizes the results:

1) Thermal reactions of **2a–c**. Table VI lists the yields of the esters **11** isolated after work-up. The structure of the rearrangement product **11** was confirmed by an independent synthesis using a Pummerer reaction:[14,15]



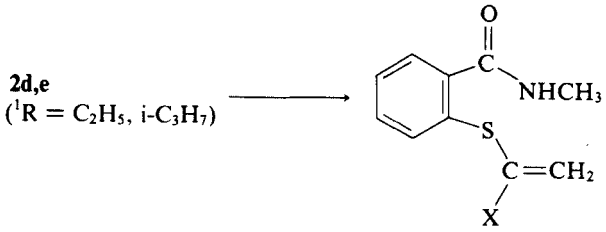
11a

2) The ethyl and *i*-propyl derivatives **2d,e** gave vinyl sulphides **12** in acceptable yields. Analytical data are listed in Table VI.



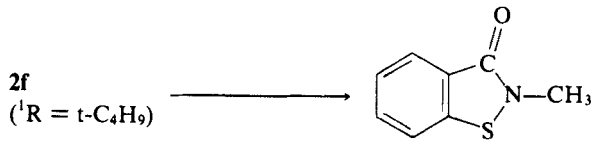
11

X = (a) H; (b) CH_3O; (c) NO_2.



12

X = (a) H; (b) CH_3.



13

SCHEME III

Major products from the thermolysis of *O*-benzoyl hydroxamic acids **2a–f** in DCB at 160°C.

3) The *t*-butyl derivative **2f** gave 2-methyl-1,2-benzisothiazol-3(2H)-one **13** in good yield, along with isobutene and benzoic acid. The heterocycle **13** has also been prepared by other procedures[9] and has interesting biological properties.[9,16]

These reactions of **2a–f** may thus be classified as "pseudo-Pummerer" in nature, since Pummerer-type products are obtained, without however at any time requiring a sulphoxide intermediate.[14,15,17,18] The use of thiocarbamoyl leaving groups[3] is here disadvantageous, since **13** is formed from **2g** in lower yield (55%), along with side-products including an amide and sulphenamide[19] which are difficult to remove efficiently.

EXPERIMENTAL

Ketones

1-(Methylthio)fluoren-9-one was prepared by methylation of 1-mercaptofluoren-9-one[20] with dimethyl sulphate in aqueous alkali. Yield 65%, m.p. 168–9°C. *Anal.* Calcd. for $C_{14}H_{10}OS$: C, 74.33; H, 4.46. Found: C, 74.48; H, 4.21.

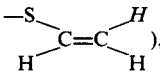
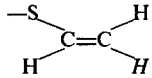
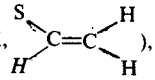
TABLE VI

Heating times, m.p., yields and analyses for the products **11–13** obtained on thermolysis of **2** in DCB at 160°C. See Scheme III.

Precursor	Product	h	yield[a] %	m.p. °C	required C	required H	required N	found C	found H	found N
2a	**11a**[b]	12	35	105–7	63.77	5.02	4.65	63.47	5.11	4.60
2b	**11b**	40	30	138–9	61.63	5.14	4.23	61.82	5.12	4.19
2c	**11c**	6	70	143–5	55.49	4.05	8.09	55.61	3.89	7.98
2d	**12a**[c]	12	45	101–2	62.17	5.74	7.25	61.91	5.77	7.18
2e	**12b**	12	60	93–4	63.75	6.32	6.76	63.94	6.41	7.01
2f	**13**[d]	6	78	51–2	(lit.[9] 51–2)		—	—	—	—

[a] isolated yields. Spectrometric yields were higher.

[b] ^{1}H-NMR ($CDCl_3$): δ = 2.92 (d, J = 5 Hz; 3H,NHCH_3), 5.64 (s; 2H,S—CH_2), 6.3 (s; 1H,NH), 7.2–8.1 (m; 9H,aromatic—H). IR(CCL_4): 1733,1678 cm.

[c] ^{1}H-NMR ($CDCl_3$), δ = 2.86 (d, J = 4.8 Hz; 3H,NHCH_3), 5.40 (d, J = 16.7 Hz; 1H, ), 5.41 (d, J = 9.2 Hz; 1H, ), 6.46 (dd, J = 16.7, 9.2 Hz; 1H, ), 6.9 (s; 1H,NH), 7.1–7.7 (m; 4H,aromatic—H).

[d] ^{1}H-NMR ($CDCl_3$): δ = 3.45 (s; 3H,NCH_3), 7.3–7.7 (m; 3H,aromatic—H), 8.0–8.2 (m; 1H,aromatic—H).

1-(t-Butylthio)fluoren-9-one was prepared from the same thiol by treatment with *t*-butanol in 70% H_2SO_4 at 10°C for two hours. Yield 10%, m.p. 117–8°C. *Anal.* Calcd. for $C_{17}H_{16}OS$: C, 76.10; H, 6.01. Found: C, 76.33; H, 5.89.

Oximes: Substituted benzophenone oximes were prepared by heating ethanolic solutions of the corresponding imine[1] in the presence of hydroxylamine hydrochloride and acetic acid.

General Procedure: The imine[1] (50 mmol) was dissolved in ethanol (100 ml) and hydroxylamine hydrochloride (140 mmol) added. Glacial acetic acid (8 ml) was added dropwise and the resultant mixture heated under reflux for 20 h then poured onto ice (500 g). (For the 2-pyridyl derivative the aqueous mixture was rendered alkaline with sodium carbonate.) The resultant powder was isolated and crystallized from ethanol. Separation of pure geometrical isomers could be carried out by careful recrystallization from ethanol.

Fluorenone oximes were prepared under alkaline conditions from the parent ketone.[21] See Table I.

(E)-2-(*t*-butylthio)benzaldoxime was prepared by a reported procedure.[4]

Hydroxamic acids were prepared from the corresponding benzoic acids[1] using standard procedures. See Table II.

O-Benzoyl-oximes and O-benzoyl-hydroxamic acids were prepared by dropwise addition of equimolar amounts of benzoyl chloride to the corresponding oxime or hydroxamic acid in THF at 10°C in the presence of a twofold excess of triethylamine. The resultant mixture was stirred for 4 h at room temperature then poured onto ice. Solid benzoates were collected by filtration and recrystallized from benzene/petrol. The compounds **2d,e** are oils and were purified as follows: the aqueous mixture was extracted with ether, the organic phase washed with dilute alkali and water, dried, and the solvent evaporated. The resultant oil was taken up in the minimum of dry ether, filtered and the solvent re-evaporated. See Tables III and IV.

O-(N,N-Dimethylthiocarbamoyl)-oximes and -hydroxamic acids

1f,g 2g and **3c** were prepared following standard procedures.[12,19] For the isolation of the (E)-isomer **1f**, it is essential that the oxime sodium salt be isolated and added portionwise to the stirred solution of the

thiocarbamoyl chloride in DMF at −10°C. On no account should the sodium salt be first dissolved in DMF, as this results in partial isomerization to the sodium salt of the (Z)-oxime. See Tables III and IV.

Thermolysis Reactions

The following procedures i–iii were used, under consideration of the heating times indicated by Tables V and VI, Schemes I and III.

Typical Procedures

(*i*) *1,2-Benzisothiazole* **4a** A solution of 15 g (47.9 mmol) (E)-O-benzoyl-2-(*t*-butylthio)benzaldoxime **1a** in 34 g methanol was heated under reflux for 60 min. Isobutene (0.6 g, 22%) was evolved. Fractional distillation of the solvent gave *t*-butyl-methyl ether (1.8 g, 42%) (NMR-55%). The residue was dissolved in ether and washed with saturated aqueous sodium carbonate until no further benzoic acid was isolated from the acidified aqueous portions. The ether layer was dried, evaporated and the residue distilled under reduced pressure (20 mm). The distillate (5.8 g, 90%) was recrystallized from hexane to yield 1,2-benzisothiazole **4a** (4.8 g, 74%), m.p. 35–36°C (lit.[4] 35–6°C). The pot-residue gave:

N-benzoyl-N-[2-(t-butylthio)benzoyl] amine **5** (0.5 g, 3%), m.p. 100°C. *Anal.* Calcd. for $C_{18}H_{19}NO_2S$: C, 68.99; H, 6.11; N, 4.47. Found: C, 69.02; H, 6.12; N, 4.51. ^{1}H-NMR ($CDCl_3$): δ = 1.3 (s; 9H, S—C(CH_3)$_3$), 6.0 (s; 1H, N*H*), 7.3–8.2 (m; 9H, aromatic-H).

(*ii*) *3-Phenyl-1,2-benzisothiazole* **4b** Methanol solutions of the (E)-benzoate **1b** were heated under reflux for 10 h and worked up as in (i), except that the product was not subjected to distillation. Recrystallized from aqueous alcohol; yield 82%, m.p. 71°C (lit.[8] 71°C). Pure 3-phenyl-1,2-benzisothiazole is colorless.

(*iii*) *3-(2-Pyridyl)-1,2-benzisothiazole* **4c** A solution of **1d** (7 g, 17.9 mmol) in **10g** *o*-dichlorobenzene was heated at 160°C for 20 h. The dark solution was taken up in ether (100 ml), washed successively with saturated aqueous sodium carbonate (2 × 100 ml) and water (50 ml), dried and the ether evaporated. The *o*-dichlorobenzene was removed i.v. and the residual oil taken up in boiling hexane (30 ml). Active alumina (**1g**, neutral) was added and the hot solution was filtered. The hexane was reduced to ca. 5 ml and allowed to cool. The resultant crystals were isolated by filtration. Yield 2.5g, 66%, m.p. 62°C. *Anal.* Calcd. for $C_{12}H_8N_2S$: C, 67.92; H, 3.80; N, 13.20. Found: C, 68.12; H, 3.77; N, 13.45.

Similarly prepared:

Fluoreno[9,9a,1-cd]-1,2-thiazole **7** (Scheme I). Yield 55%, m.p. 80–81°C. *Anal.* Calcd. for $C_{13}H_7NS$: C, 74.63; H, 3.37; N, 6.70. Found: C, 74.43; H, 3.33; N, 6.65. MS (70 eV): m/e = 209 (100%, M^+).

Modifications to Procedure iii:

Thermolysis of **1e**: *i*-Propyl benzoate was distilled off with the *o*-dichlorobenzene during work-up.

Thermolysis of **3a**: (Scheme I). After 1 h the reaction solution was cooled to O°C and filtered. The blue-black crystals so obtained were washed with ether until the ether remained colorless.

2,2'-Bi(2H-fluoreno[9,9a,1-de]-1,3-thiazine) **8** is virtually insoluble in all common solvents. Yield 30%, m.p. > 360°C. *Anal.* Calcd. for $C_{28}H_{14}N_2S_2$: C, 76.01; H, 3.19; N, 6.33. Found: C, 75.81; H, 3.09; N, 6.48. MS (70 eV): m/e = 442 (100%, M^+), 221 (40%, M^{2+}). IR (KBr)—no alkyl C—H.

From O-Benzoyl-hydroxamic acids by procedure iii:

Benzoic acid -[2-(methylaminocarbonyl)phenylthiomethyl] esters **11**. See Table VI. Column chromatography was used to purify[22] **11a**. The compounds **11b,c** were purified by recrystallization from benzene/petrol.

S-[2-(Methylaminocarbonyl)phenyl]alkene-thiols **12**. See Table VI and Scheme III.

2-Methyl-1,2-benzisothiazol-3(2H)-one **13**. This compound crystallized on long storage of the crude oil at 5°C. Yield 78%, m.p. 51–2°C, in all respects identical to the literature sample.[9,23]

Pummerer Reaction

A solution of 1.0 g (5.08 mmol) *N*-methyl-2-(methylsulphinyl)-benzamide[15] and 1.15 g (5.09 mmol) benzoic anhydride in *o*-dichlorobenzene (10 ml) was heated at 160°C for 4 h. Column chromatography[22] gave **11a** (0.88 g, 58%), m.p. 107°C, identical in all respects to the compound described in Table VI. Mixed m.p. 106–7°.

One-Pot Procedures See Scheme II.

A suspension of the lithium salt of 2-(*t*-butylthio)benzophenone imine in hexane was prepared as described in the previous paper.[1] The suspension was cooled to −40°C under vigorous stirring and chlorine gas (equimolar amount) was introduced at such a rate that the temperature remained constant. The reaction mixture was carefully brought up to room-temperature and finally heated to reflux for 30 min. The mixture was then cooled, poured carefully onto ice and worked up in the usual manner.

In the analogous reaction using bromine as oxidant, one equivalent of liquid bromine was added dropwise to the cooled (−14°) stirred suspension of the lithium salt, and the final period of reflux was extended to 2 hours. Work-up gave a dark red viscous oil and a great deal of insoluble residue. Treatment of both fractions with boiling acetone yielded orange crystals of *2-(t-butylthio)benzophenone azine* **10** (20–25%), m.p. 202–3° (acetone). *Anal.* Calcd. for $C_{34}H_{36}N_2S_2$: C, 76.09; H, 6.76; N, 5.22. Found: C, 75.96; H, 6.64; N, 5.38.

Thiono-thiolo Rearrangement[12]

Reaction was carried out at room temperature or slightly above.

From **3c** in chloroform: *S-[1-(methylthio)fluorenylidenamino]-N,N-dimethyl-thiocarbamate* **9**, yield 90%, m.p. 215°. *Anal.* Calcd. for $C_{17}H_{16}N_2OS_2$: C, 62.19; H, 4.91; N, 8.53. Found: C, 61.68; H, 5.15; N, 8.21.

From **1f** or **1g** in methanol: **4b** (60–70%) and the S-(methyleneamino)-thiocarbamate **6** (10–20%), m.p. 158–9°C. *Anal.* Calcd. for $C_{20}H_{24}N_2OS_2$: C, 64.50; H, 6.50; N, 7.52. Found: C, 64.73; H, 6.69; N, 7.56.

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