Reactions of *N*-Sulphinylamines and Di-iminosulphur Derivatives with Acylketens

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The reactions of *N*-sulphinylmines with benzoylketen and with 2-carbonyl-1-tetralone (2b), generated *in situ via* thermolysis of the corresponding furandiones, gave [2 + 4] cycloadducts [1,2,3-oxathiazin-4(3*H*)-one 2-oxides (3)] in high yields. Similar treatment of di-iminosulphur derivatives with the keten (2b) led to 1-hydroxy-2-naphthamide derivatives as the main products.

N-SULPHINYLAMINES and di-iminosulphur derivatives are useful reagents for synthesizing heterocyclic compounds containing adjacent nitrogen and sulphur atoms.[1] We have recently shown that, in contrast to *N*-sulphinylamines,[2] the types of product from reactions of di-iminosulphur derivatives with ketens depend upon substituents on both reagents.[3] We now report the reactions of *N*-sulphinylamines (1) and di-iminosulphur derivatives (6) with acylketens (2).

The *N*-sulphinylaniline (1a) with benzoylketen (2a) generated *in situ* by pyrolysis of 5-phenylfuran-2,3-dione [4] in benzene at 70 °C, gave a [2 + 4] cycloadduct, 3,6-diphenyl-1,2,3-oxathiazin-4(3*H*)-one 2-oxide (3a), in 49% yield, together with benzoylacetanilide (4a) (37%). The i.r. spectrum of the cycloadduct (3a) exhibited C:O, C:C, and >S:O absorption at 1 655, 1 610, and 1 010 cm^{-1}, respectively. The n.m.r. spectrum ($CDCl_3$) displayed vinylic (1 H, s) and aromatic proton (10 H, m) signals at δ 6.40 and 7.15—7.85. Alkaline hydrolysis led to benzoylacetanilide (4a) in high yield.

The reactions of other *N*-sulphinylamines (1b—e) with (2a) similarly produced the corresponding oxathiazinone *S*-oxides (3b—e) (Table 1).

The yields were dependent upon the reaction temperature. Thus the reaction of (1a) with (2a) in refluxing benzene for 4 h gave 3-benzoyl-6-phenylpyran-2,4(3*H*)-dione (5a) (68%), formed *via* dimerization of (2a), in addition to the oxathiazinone (3a) (21%). Thus the cycloaddition of the *N*-sulphinylaniline (1a) to benzoylketen (2a) and the dimerization of (2a) must be in competition, since the cycloadduct (3a) is stable under the above conditions.

Similar treatment of the sulphinylaniline (1a) with 2-carbonyl-1-tetralone (2b), generated from 4,5-dihydronaphtho[1,2-*b*]furan-2,3-dione in refluxing benzene

TABLE 1

Reactions of *N*-sulphinylamines (1) with acylketens (2)

Starting materials		Reaction conditions		Product yields (%)		
		Temp.	Time			
(1)	(2)	(°C)	(h)	(3)	(4)	(5)
(1a)	(2a)	70	10.5	49	37	
(1a)	(2a)	80	4	21 [a]		68 [b]
(1b)	(2a)	70	6	47		
(1c)	(2a)	70	15	37	36	
(1d)	(2a)	70	7	51		
(1e)	(2a)	70	13	67	22	
(1a)	(2b)	80	9	74	7	
(1b)	(2b)	80	10	47	14	
(1c)	(2b)	80	15	70	21	
(1e)	(2b)	80	13	85		

[a] All reactions carried out in benzene. [b] Based on n.m.r. data.

led to a [2 + 4] cycloadduct, 5,6-dihydro-3-phenylnaphtho[2,1-*e*]-1,2,3-oxathiazin-4(3*H*)-one 2-oxide (3f), in 74% yield, showing n.m.r. signals ($CDCl_3$) at δ 2.90 (4 H, m, $[CH_2]_2$) and 7.15—7.75 (10 H, m, aromatic), and i.r. absorptions (Nujol) at 1 645 (C:O), 1 625 (C:C), and

[1] See, for example, (*a*) G. Kresze and W. Wucherpfennig, *Angew. Chem.*, 1967, **79**, 109; (*b*) H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes,' Academic Press, New York, London, 1967, p. 306.

[2] H. Beecken and F. Korte, *Tetrahedron*, 1962, **18**, 1527.

[3] (*a*) T. Minami, K. Yamataka, Y. Ohshiro, T. Agawa, N. Yasuoka, and N. Kasai, *J. Org. Chem.*, 1972, **37**, 3810; (*b*) T. Minami and T. Agawa, *ibid.*, 1974, **39**, 1210

[4] S. Murai, K. Hasegawa, and N. Sonoda, *Angew. Chem. Internat. Edn.*, 1975, **14**, 636.

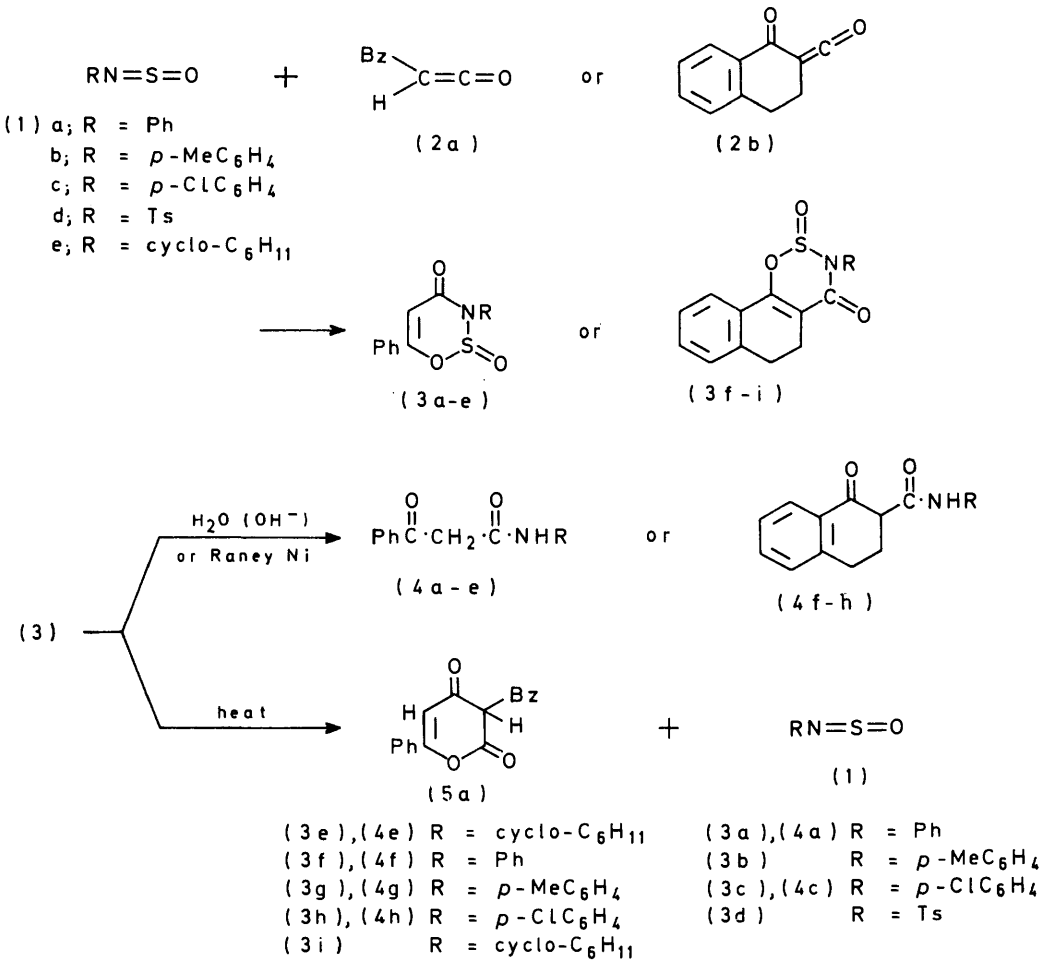
1 110 cm^{-1} (S:O), along with small amounts of 1,2,3,4-tetrahydro-1-oxo-2-naphthanilide (4f).

The results from other *N*-sulphinylamines (1b, c, and e) and (2b) are summarized in Table 1. The greater yields of cycloadducts (3) from reaction with (2b) than with (2a) may be due to the products (3f—i) being more stabled to hydrolysis during work-up than (3a—e), since overall yields are in both cases *ca.* 80%.

The reaction of bis-t-butyliminosulphur (6b) with the keten (2b) under similar conditions unexpectedly gave *N*-t-butyl-1-hydroxy-2-naphthamide (7b) in 29% yield; hydroxy-2-naphthamide (7c) in 22% yield. The corresponding reaction of bisphenyliminosulphur (6a) produced the corresponding naphthamide (7a) and small amounts of 3-anilino-1,2,3,4-tetrahydro-1-oxo-2-naphthanilide (8a).

However, similar treatment of the di-iminosulphur derivatives (6) with benzoylketen (2a) yielded only polymeric products, none of which was identified.

Recently we have shown that substituted ketens with a hydrogen atom on the α-carbon atom of substituent react with di-iminosulphur derivatives to give acyclic thiobis-amine derivatives.[3a] On the basis of this



SCHEME 1

no cycloadduct was obtained. The i.r. spectrum (Nujol) of the product (7b) showed characteristic bands at 3 400 and 1 610 cm^{-1} (NH and amide C:O). The n.m.r. spectrum ($CDCl_3$) contained methyl (9 H, s), NH (1 H, broad), aromatic (6 H, m), and OH proton (1 H, s) signals at δ 1.44, 6.12, 7.16—8.48, and 14.03, respectively, and no methylene proton resonance. The structure (7b) was confirmed by comparison (m.p. and i.r. data) with an authentic sample prepared from 1-hydroxy-2-naphthoyl chloride and t-butylamine.

The reaction of biscyclohexyliminosulphur (6c) with the keten (2b) similarly provided *N*-cyclohexyl-1-

observation, the reactions of the di-iminosulphur derivatives (6) with the acylketen (2b) may be accounted for in terms of the formation of an unstable [2 + 4] cycloadduct (9) as an initial intermediate, followed by rearrangement to an acyclic derivative (10), which would be easily hydrolysed to a 1-hydroxy-2-naphthamides (7) (Scheme 2). The mechanism of formation of (8a) is not clear at present.

Although the di-iminosulphur derivatives (6) gave notably different results from *N*-sulphinylamines (1) in reactions with the acylketens (2), both reactions presumably proceed *via* a [2 + 4] cycloadduct, as mentioned

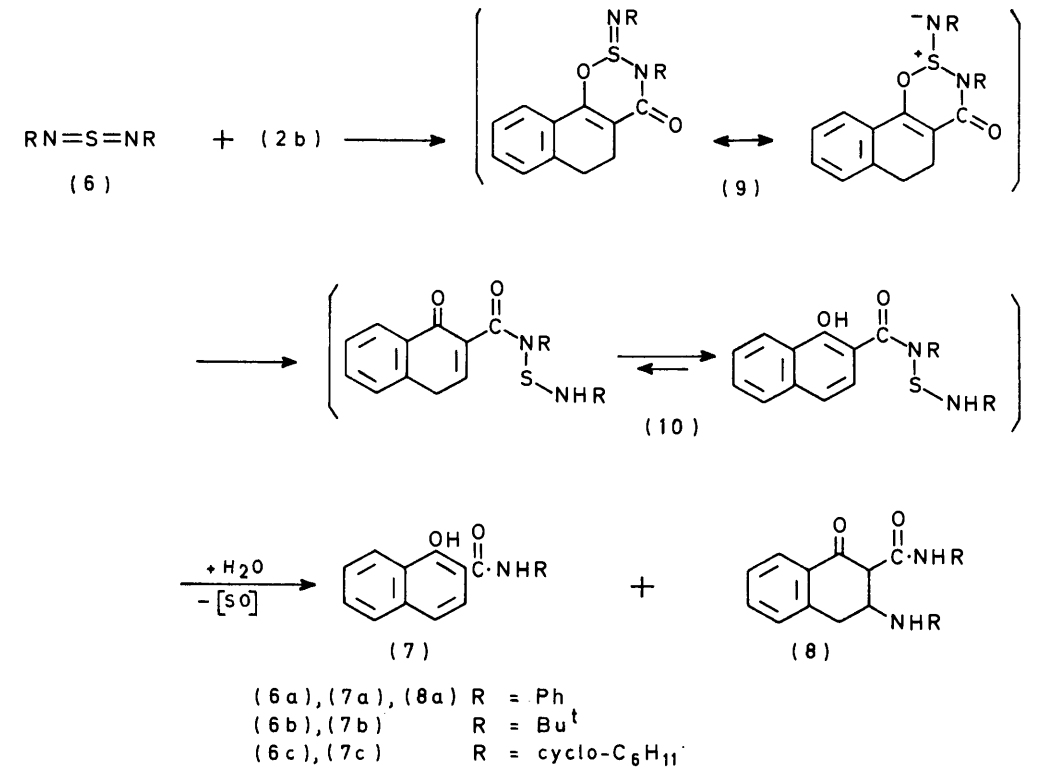
above. Hence the differences in properties between the S:N and S:O bonds of the cycloadducts might well control the final results.

EXPERIMENTAL

M.p.s were determined with a Yanagimoto micro-apparatus. ^{1}H N.m.r. spectra were recored with a JEOL JNM 3H-60 or JNM-PS-100 instrument for solutions in deuteriochloroform unless stated otherwise, i.r. spectra with a JASCO IR-E instrument for Nujol mulls, and mass spectra with a Hitachi RMU-6E instrument.

N-Sulphinylamines (1) [5] and bisphenyliminosulphur,[6] bis-t-butyliminosulphur,[7] and biscyclohexyliminosulphur [7] (6a—c) were prepared according to established procedures. 5-Phenylfuran-2,3-dione and 4,5-dihydronaphtho[1,2-*b*]furan-2,3-dione were synthesized according to reported procedures.[4]

Reaction of the N-*Sulphinylamines* (1a—e) *with Benzoylketen* (2b).—The general procedure was as follows. A stirred solution of the *N*-sulphinylamine (1) (0.02 mol) and 5-phenylfuran-2,3-dione (3.50 g, 0.02 mol) in dry benzene (80 ml) was heated at 70 °C under nitrogen until the i.r. spectrum showed no furandione carbonyl absorption at 1 710 cm^{-1} (6—15 h) (Table 1). The solvent was then evaporated off *in vacuo* and the residue set aside for several hours to crystallize. The resulting solid, 1 : 1 adduct (3), was filtered off and repeatedly recrystallized from benzene–hexane. The filtrate was chromatographed on silica gel (benzene–ethanol as eluant) to afford the crude benzoylacetamide derivative, which was recrystallized from ethanol. The *N*-sulphinylaniline (1a) (2.80 g, 0.02 mol; 10.5 h) gave



SCHEME 2

TABLE 2

Properties of 1,2,3-oxathiazine derivatives (3a—i)

Compd	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$(Nujol)/cm^{-1} C=O	C=C	S=O
(3a)	121—122	63.15	3.7	4.9	$C_{15}H_{11}NO_3S$	63.15	3.9	4.9	1 655	1 640	1 010
(3b)	152—153	64.25	4.3	4.55	$C_{16}H_{13}NO_3S$	64.2	4.4	4.7	1 660	1 615	1 020
(3c)	129—130	56.25	2.95	4.3	$C_{15}H_{10}ClNO_3S$	56.35	3.15	4.4	1 680	1 620	1 010
(3d)	118—121	53.0	3.5	3.85	$C_{16}H_{13}NO_5S_2$	52.9	3.6	3.85	1 670	1 615	990
(3e)	90—91	61.85	5.7	4.8	$C_{15}H_{17}NO_3S$	61.85	5.9	4.8	1 650	1 620	990
(3f)	156—158	65.55	4.15	4.5	$C_{17}H_{13}NO_3S$	65.6	4.2	4.5	1 645	1 625	1 110
(3g)	176—177	66.65	4.55	4.35	$C_{18}H_{15}NO_3S$	66.45	4.65	4.3	1 655	1 625	1 105
(3h)	153—154	59.3	3.4	3.95	$C_{17}H_{12}ClNO_3S$	59.05	3.5	4.05	1 655	1 625	1 105
(3i)	115—117	64.5	6.15	4.2	$C_{17}H_{19}NO_3S$	64.35	6.05	4.4	1 650	1 625	1 120

[5] See, for example, (*a*) D. Klamann, C. Sass, and M. Zelenka, *Chem. Ber.*, 1959, **92**, 1910; (*b*) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. Smalla, and A. Trede, *Angew. Chem.*, 1962, 74, 135.

[6] T. Minami, H. Miki, H. Matsumoto, Y. Ohshiro, and T. Agawa, *Tetrahedron Letters*, 1968, 3049.

[7] R. Appel and J. Kohnke, *Chem. Ber.*, 1970, **103**, 2152.

3,6-*diphenyl*-1,2,3-*oxathiazin*-4(3H)-*one* 2-*oxide* (3a) (2.80 g, 49%) and benzoylacetanilide (4a) (1.80 g, 37%). Other *N*-sulphinylamines (1b—e) gave similar results (Table 1). Spectral and analytical data are shown in Tables 2—4.

TABLE 3

N.m.r. data of 1,2,3-oxathiazines (3a—e)

Compd.	δ(CDCl$_3$) Aliphatic H	Olefinic H	Aromatic H
(3a)		6.40 (1 H, s)	7.15—7.85 (10 H, m)
(3b)	2.4 (3 H. s, CH_3)	6.40 (1 H, s)	7.15—8.15 (9 H, m)
(3c)		6.40 (1 H, s)	7.15—7.85 (9 H, m)
(3d)	2.4 (3 H, s, CH_3)	6.18 (1 H, s)	7.15—8.15 (9 H, m)
(3e)	1.0—2.4 (10 H, m, $[CH_2]_5$) 4.0—4.6 (1 H, m, N·CH)	6.35 (1 H, s)	7.20—7.80 (9 H, m)

Reaction of the N-*Sulphinylamines* (1) *with* 2-*Carbonyl*-1-*tetralone* (2b).—The reaction was carried out at 80 °C by the procedure described above, with the sulphinylamine (1) and 4,5-dihydronaphtho[1,2-*b*]furan-2,3-dione. The *N*-sulphinylaniline (1a) (1.40 g, 0.01 mol; 9 h) gave 5,6-*dihydro*-3-*phenylnaphtho*[2,1-e]-1,2,3-*oxathiazin*-4(3H)-*one* 2-*oxide* (3f) (2.30 g, 74%) and 1,2,3,4-tetrahydro-1-oxo-2-naphthanilide (4f) (0.20 g, 7%). Other *N*-sulphinylamines (1b—e) reacted analogously (Table 1). Spectral and analytical data are shown in Tables 2, 5, and 6.

Alkaline Hydrolysis of the Cycloadducts (3a *and* c).—A solution of the adduct (3a) (340 mg, 1.19 mmol) in 95% ethanol (10 ml) containing sodium hydroxide (0.3 g) was refluxed for 5 h. The solvent was evaporated off *in vacuo*, and water (30 ml) was added to the residual white powder. The solution was neutralized with hydrochloric acid and extracted with chloroform. The extract gave benzoylacetanilide (4a) (206 mg, 72%), identical with that obtained before. Similar treatment of (3c) (500 mg, 1.57 mmol; 11 h) afforded (324 mg, 76%) of *N*-*p*-chlorophenylbenzoylacetamide (4c), identical with that produced before.

TABLE 4

Properties of *N*-substituted benzoylacetamides (4a, c, and e)

Compd.	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$(Nujol)/cm^{-1} N–H	C=O	C=O
(4a)	106—107 [a]	75.35	5.2	5.9	$C_{15}H_{13}NO_2$	75.3	5.5	5.85	3 240	1 680	1 650
(4c)	146—149	65.5	4.15	5.2	$C_{15}H_{12}ClNO_2$	65.8	4.4	5.1	3 220	1 680	1 650
(4e)	113—115	73.3	7.85	5.7	$C_{15}H_{19}NO_2$	73.45	7.8	5.7	3 290	1 680	1 630

[a] Lit.,[8] 106—107 °C.

TABLE 5

N.m.r. data of 1,2,3-oxathiazines (3f—i)

Compd.	δ(CDCl$_3$) $[CH_2]_2$	Aromatic H	
(3f)	2.9br (4 H)	7.15—7.75 (9 H, m)	
(3g)	2.9br (4 H)	7.05—7.75 (8 H, m)	2.40 (3 H, s, CH_3)
(3h)	2.9br (4 H)	7.15—7,80 (8 H, m)	
(3i)	2.60—3.10 (4 H, m)	7.05—7.70 (4 H, m)	1.00—2.40 (10 H, m, $[CH_2]_5$) 4.00—4.70br (1 H, N·CH)

Thermolysis of the Adduct (3c).—A solution of the adduct (3c) (400 mg, 1.3 mmol) in dry toluene (15 ml) was refluxed for 3 h. The solvent was removed *in vacuo* and the residue was recrystallized from benzene–hexane to give 3-benzoyl-6-phenylpyran-2,4(3*H*)-dione (5a) (121 mg, 64%), m.p. 167—168°, identical with an authentic sample.[4] The filtrate was evaporated and the residue gave the sulphinylamine (1c) (0.15 g, 67%).

Reduction of the Adduct (3h).—A solution of the adduct (3h) (500 mg, 1.48 mmol) in tetrahydrofuran (70 ml) containing Raney nickel (1 g) was refluxed for 4 h. The organic layer was separated and concentrated. Recrystallization of the residue from benzene–hexane gave the amide (4h) (257 mg, 59%).

TABLE 6

Properties of 1-oxo-2-naphthamides (4f—h)

Compd.	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$(Nujol)/cm^{-1} N–H	C=O	C=O
(4f)	150—151	76.9	5.6	5.55	$C_{17}H_{15}NO_2$	76.95	5.7	5.3	3 220	1 665	1 640
(4g)	158—161	77.55	6.0	5.0	$C_{18}H_{17}NO_2$	77.4	6.14	5.0	3 240	1 670	1 650
(4h)	158—160	68.2	4.55	4.7	$C_{17}H_{14}ClNO_2$	68.1	4.7	4.65	3 200	1 670	1 640

TABLE 7

Analytical data of 1-hydroxy-2-naphthamides (7a—c)

Compound	Yield (%)	React. time (h)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(7a)	49	6	161—163	77.8	4.95	5.5	$C_{17}H_{13}NO_2$	77.55	5.0	5.3
(7b)	29	4	121—123	74.15	7.05	5.8	$C_{15}H_{17}NO_2$	74.05	7.05	5.75
(7c)	22	4	146—148	75.5	7.15	5.05	$C_{17}H_{19}NO_2$	75.8	7.1	5.2

The reaction of the sulphinylaniline (1a) (1.40 g, 0.01 mol) with benzoylketen (2a) (1.80 g, 0.01 mol) in refluxing benzene for 4 h afforded a mixture of (3a) (0.62 g, 21%) and 3-benzoyl-6-phenylpyran-2,4(3*H*)-dione [4] (5a) (0.98 g, 68%).

Reaction of the Di-iminosulphur Derivatives (6) *with*

2-*Carbonyl*-1-*tetralone* (2b).—The reaction was carried out at 80 °C (4—6 h) as above with the keten (2b) (2.0 g, 0.01 mol) and an equimolar amount of di-iminosulphur derivative (6). The solvent was removed and the residue chromatographed on silica gel (hexane and hexane–benzene as eluants). Bisphenyliminosulphur (6a) (2.20 g, 0.01 mol; δ [100 MHz; $(CD_3)_2SO$] 2.40—2.60 [1 H, m, C*H*(NHPh)], 2.68—2.84 [1 H, m, CO·C*H*(CONHPh)], 2.84—3.16 (2 H, m, CH_2), 6.24br (1 H, amino NH), 6.40—8.00 (14 H, m, aromatic), and 9.92 (1 H, s, amide NH); *m/e* (70 eV) 356 (M^+) and 237 (M^+ — PhNCO) (Found: C, 74.15; H, 7.05; N, 5.8. $C_{15}H_{17}NO_2$ requires C, 74.05; H, 7.05; N, 5.75%).

TABLE 8

Spectral data of 1-hydroxy-2-naphthamides (7a—c)

Compd.	δ				$\nu_{max.}$(Nujol)/cm^{-1}	
	Aliphatic H	Aromatic H	NH	OH	N–H	C=O
(7a) *		7.12—8.44 (11 H, m)	10.55br (1 H)	14.20 (1 H, s)	3 400	1 610
(7b)	1.44 (9 H, s, Bu^t)	7.16—8.48 (6 H, m)	6.12br (1 H)	14.03 (1 H, s)	3 400	1 610
(7c)	0.80—2.20 (10 H, m, $[CH_2]_5$) 3.80—4.20br (1 H, N·CH)	7.00—8.60 (6 H, m)	6.10br (1 H)	14.00 (1 H, s)	3 340	1 600

* In $(CD_3)_2SO$.

6 h) gave 1-hydroxy-2-naphthanilide (7a) (1.30 g, 49%) and 3-*anilino*-1,2,3,4-*tetrahydro*-1-*oxo*-2-*naphthanilide* (8a) (0.40 g, 11%). Other di-iminosulphur derivatives (6b and c) likewise gave 1-hydroxy-2-naphthamide derivatives (Table 7), but no products corresponding to (8a) were obtained. Spectral and analytical data for compounds (7a—c) are presented in Tables 7 and 8.

Compound (8a) had m.p. 214—216°; $\nu_{max.}$ (Nujol) 3 320 (NH), 1 680 (ring C:O), and 1 645 cm^{-1} (amide C:O); Authentic samples of compounds (7a and b), prepared from 1-hydroxy-2-naphthoyl chloride [9] and aniline or t-butylamine, were identical (m.p.s and i.r. spectra) with the foregoing products.

[6/1799 *Received*, 24*th September*, 1976]

[8] C. F. H. Allen and W. J. Humphlett, *Org. Synth.*, Coll. Vol. 4, 1963, p. 80.
[9] R. Anschütz, *Annalen*, 1906, **346**, 361.