

Synthesis of β -Imino-sulphones. Reaction of the β -Imino-sulphones with Carbon Disulphide

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A series of β -imino-sulphones were synthesised by the reaction of alkyl- and aryl-sulphonyl carbanions with nitriles. The β -imino-sulphones, on treatment with carbon disulphide and sodium t-pentyl oxide at room temperature, gave three types of compounds, 1,3-thiazine-2,6-dithiones, 1,2-dithiole-3-thiones, and 1,3-thiazole-2-thiones. In some cases, the formation of 1,3-thiazine-2,6-dithiones were accompanied by the formation of 2-thioxo-1,3-thiazine-6-ones. Ethyl 2-imino-1-methyl-2-phenylethyl sulphone, in this reaction, gave bis-(1,3-dithiol-4-yl) disulphide.

THE only 2-imino-sulphone known so far seems to be 2-iminopropyl phenyl sulphone, which is obtained by the reaction of phenylsulphonylacetophenone with aqueous ammonia.¹

Our unsuccessful attempt to synthesise 2-imino-2-phenylethyl methyl sulphone by the ammonolysis of α -methylsulphonylacetophenone led us to develop a novel route to β -imino-sulphones. The synthesis consists in the reaction of alkyl- and aryl-sulphonyl carbanions with nitriles; the carbanions, prepared by Corey's method,² used were those of dimethyl, ethyl methyl, diethyl, methyl phenyl, and methyl *p*-tolyl sulphones.

The β -imino-sulphones obtained were stable enough to be isolated from their lithium salts by hydrolysis under

basic conditions. Aceto- and phenyl-acetonitriles were reluctant to undergo this reaction and the dimers of the nitriles were obtained as the major product as the result of an anion exchange between sulphonyl carbanion and the nitrile to give the nitrile anion.

It is obvious from n.m.r. spectra that the imino-sulphones (9)—(15) have an ethyl group.

The 2-imino-sulphones [(1)—(33)] were obtained in both ketimine and enamine form, and easily hydrolysed to 2-alkyl- or 2-aryl-sulphonyl ketones under the acidic conditions. The experimental data are shown in Table 1.

We now describe the reaction of the 2-imino-sulphones with carbon disulphide. We have previously shown^{3,4}

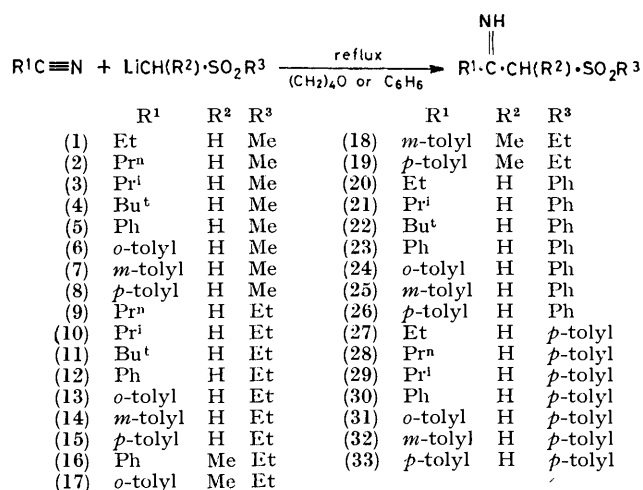
³ M. Muraoka, T. Yamamoto, and T. Takeshima, *Bull. Chem. Soc. Japan*, 1975, **48**, 2462.

⁴ M. Muraoka, T. Yamamoto, S. Yamaguchi, F. Tonosaki, T. Takeshima, and N. Fukada, *J.C.S. Perkin I*, 1977, 1273.

¹ R. Otto and W. Otto, *J. prakt. Chem.*, 1887, [2] **36**, 407.

² E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1345.

that cyclohexanones, phloroglucinol, glutazines, β -imino-nitriles and esters, in the presence of ammonia, react with carbon disulphide to give 1,3-thiazine-2,4-dithiones, 3-imino-dithiocarboxylic acids, and other compounds. Mayer and Jentzsch⁵ first synthesised 3-(*N*-alkyl)imino-dithiocarboxylic acids by the reaction of *N*-substituted ketimines and carbon disulphide. Gompper and his co-workers⁶ have also reported that *NN*-dialkylenamines react with carbon disulphide to afford 3-(*NN*-dialkyl-imino)-dithiocarboxylate dipoles, which react further with phenyl isothiocyanate to yield 1,3-thiazine-2,4-dithiones. Takeshima and his co-workers^{7,8} synthesised 2-iminocyclopentanedithiocarboxylic acids by the reaction of unstable and unisolable cyclopentanone imides with carbon disulphide. They^{7,9,10} also synthesised 1,3-thiazine-4-thiones by the reaction of a variety of unisolable ketimines with carbon disulphide. Papini



SCHEME 1

and his co-workers¹¹ have reported that 3-amino-5-pyrazolone reacts with carbon disulphide to give pyrazolo[3,4-*d*][1,3]thiazine-2,4-dithione.

The present investigation was undertaken to extend the reaction of carbon disulphide and β -imino-sulphones. The reaction mode, however, was different from those of ketimines, glutazines, and β -imino-nitriles and esters.

β -Iminosulphones gave three types of compounds, 1,3-thiazine-2,6-dithiones [(34)—(53)], 1,2-dithiole-3-thiones [(54)—(74)], and 1,3-thiazole-2-thiones [(77)—(79)] (see Scheme 2). The 1,2-dithiole-3-thiones were obtained in poor yields. Vigorous evolution of ammonia was observed during the separation of these compounds from the reaction mixture. Further, when the reaction mixture, after acidification, was quickly extracted with ether, the extract was exceedingly sensitive to Ni^{II} giving a royal purple complex. It is probable, on the basis of these facts, that 1,2-dithiole-3-thiones were

⁵ R. Mayer and J. Jentzsch, *J. prakt. Chem.*, 1964, [4] **23**, 83.

⁶ R. Gompper, B. Wetzel, and E. Wolfgang, *Tetrahedron Letters*, 1968, 5519.

⁷ T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *J. Org. Chem.*, 1969, **34**, 730.

⁸ T. Takeshima, T. Miyauchi, N. Fukada, S. Koshizawa, and M. Muraoka, *J.C.S. Perkin I*, 1973, 1009.

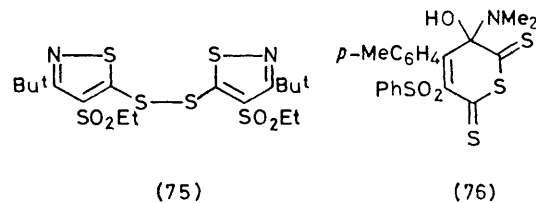
produced from 3-imino-dithiocarboxylic acids *via* β -thio-dithiocarboxylic acids.

The 1,3-thiazole-2-thiones were formed by the intramolecular nucleophilic substitution of *N*-[2-(alkyl- or aryl-sulphonyl)]vinylidithiocarbamic acids. The reaction was markedly influenced by the R¹ substituent. Thus when R¹ was an alkyl or *o*-tolyl substituent, the thiazole-2-thiones could not be obtained whilst with an aryl substituent present, the dithioles were obtained in good yields (Table 4).

In some cases, 1,3-thiazine-2,6-dithiones were accompanied by 2-thio-1,3-thiazin-6-ones [(80)—(82)]. The latter, in contrast with the former, were stable under basic conditions and thus could be separated from the former by treatment with aqueous morpholine. The i.r. spectrum of compound (82) had a carbonyl band at 1 689 cm⁻¹ corresponding to thioacetic *S*-acid and its esters. The mass spectrum showed the fragmentation which is in good agreement with 2-thio-1,3-thiazin-6-one (Scheme 3).

The thiazine-2,6-dithiones, especially the ones having an arylsulphonyl group, in contrast with known 1,3-thiazine-2,4-dithiones, were exceedingly unstable to bases.

The imino-sulphones which have a *t*-butyl group at the β -position or a methyl group at the α -position were reluctant to react with carbon disulphide or, if they reacted, the reaction products were different from those expected. Thus, 2-imino-3,3-dimethylbutyl ethyl sulphone, when treated with carbon disulphide in the presence of sodium *t*-pentyl oxide, gave 4-ethylsulphonyl-1,2-dithiole-3-thione (74) whose *t*-butyl group had been removed. In addition, bis-(4-ethylsulphonyl-3-*t*-butylisothiazol-5-yl) disulphide (75) was obtained. The mass spectrum of compound (75) had the most intense peak at *m/e* 264. The i.r. spectrum showed no absorption bands



above 1 500 cm⁻¹ except for the bands at 2 880—2 960 cm⁻¹. A medium absorption band at 1 485 cm⁻¹ may be due to the isothiazole ring. 2,5-Disubstituted thiazoles also show ring-stretching bands in the same region.¹² Ethyl 2-imino-1-methyl-2-phenylethyl sulphone, in this reaction, gave bis-(5-methyl-2-thio-2*H*-1,3-dithiol-4-yl) disulphide (83).

Only 2-imino-2-(*p*-tolyl)ethyl phenyl sulphone gave a compound C₂₀H₁₉NO₃S₄ (76) in addition to compounds

⁹ T. Takeshima, T. Hayashi, M. Muraoka, and T. Matsuoka, *J. Org. Chem.*, 1967, **32**, 980.

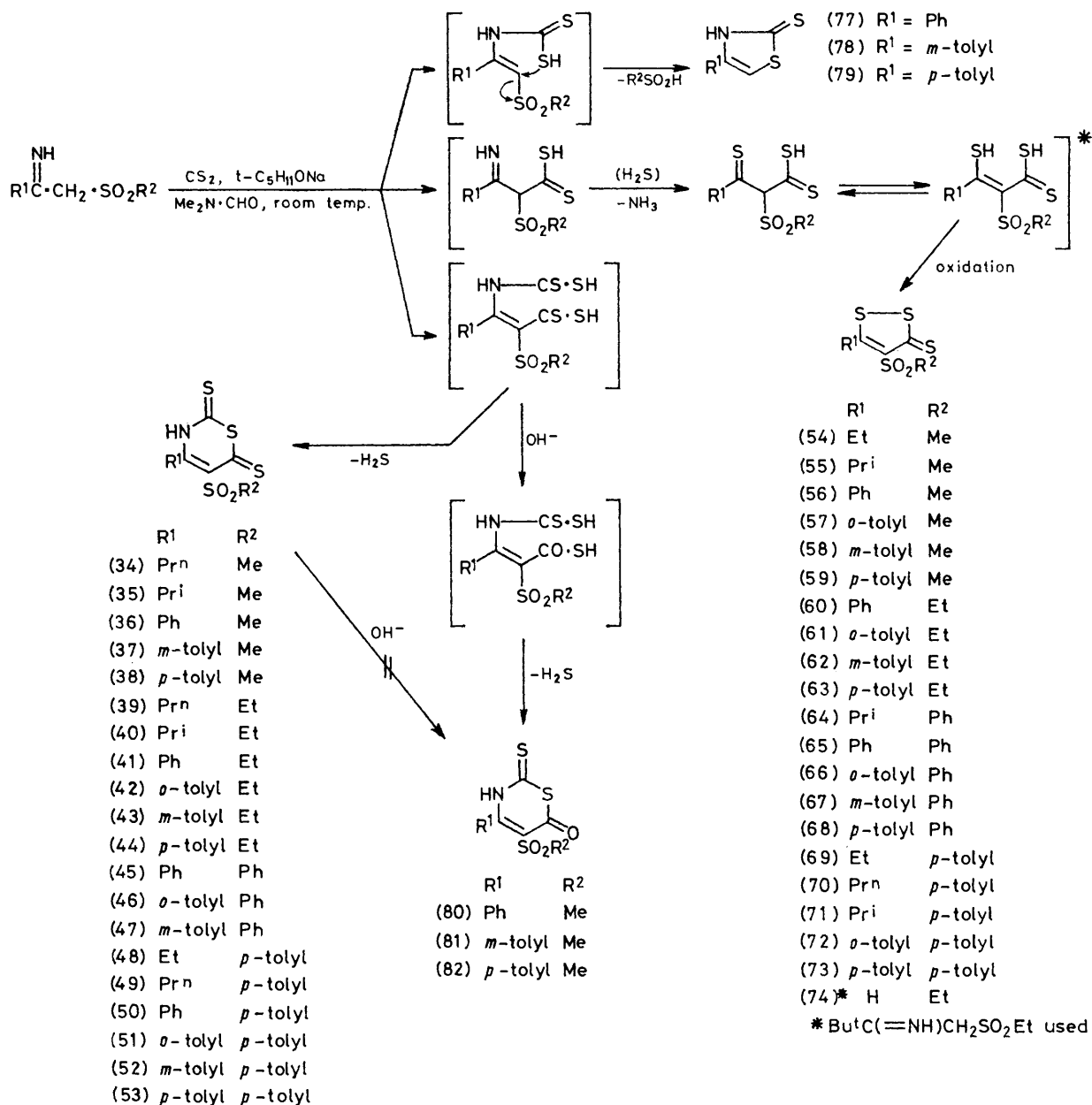
¹⁰ T. Takeshima, T. Imamoto, M. Yokoyama, K. Yamamoto, and M. Akano, *J. Org. Chem.*, 1968, **33**, 2877.

¹¹ P. Papini and G. Auzzi, *Gazzetta*, 1966, **96**, 125.

¹² P. Brookes, A. T. Fuller, and J. Walker, *J. Chem. Soc.*, 1957, 689.

(68) and (79). Both i.r. and n.m.r. spectra of compound (76) showed absorptions arising from hydroxy- and dimethylamino-groups. From these facts together with

reflux condenser. Dimethyl sulphone (9.4 g, 0.10 mol), dissolved in tetrahydrofuran (200 ml), was added dropwise with stirring and cooling in an ice-bath.² The stirring was con-



SCHEME 2 * Suggested mechanism

u.v. and mass spectra, 5-(*NN*-dimethylamino)-5-hydroxy-3-phenylsulphonyl-4-(*p*-tolyl)thiio-2,6-dithione was tentatively assigned structure (76).

EXPERIMENTAL

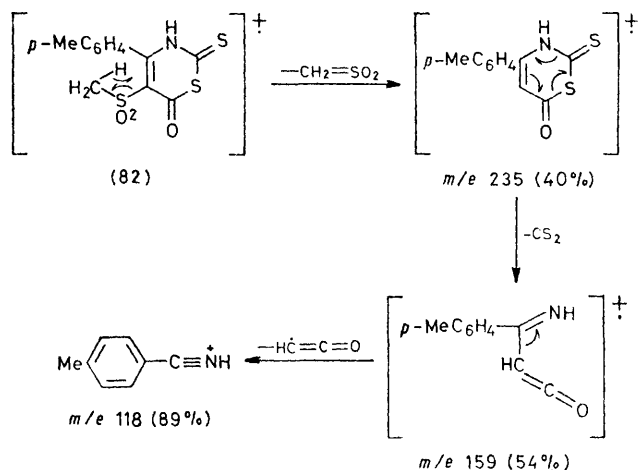
Preparation of β-Imino-sulphones (1)–(33).—Two examples are described.

2-Iminobutyl methyl sulphone (1). A solution of butyllithium (6.4 g, 0.10 mol) in hexane (65 ml) was placed in a three-necked flask fitted with a mechanical stirrer and a

continued for an additional 15 min, and propionitrile (5.5 g, 0.10 mol) was added to this within 30 min at room temperature; the mixture was then refluxed for 18 h. After the reaction mixture had cooled, water (150 ml) was added to the mixture. The water layer was extracted twice with benzene, and the tetrahydrofuran layer and benzene extracts were combined, washed once with water and once with saturated salt solution and then dried (MgSO₄) and evaporated to give an oil; this was fractionated. The fraction with b.p. 138–140 °C at 0.5 Torr was collected; yield 3.7 g (25%). The distillate solidified after 7 days: m.p. 62–64

$^{\circ}\text{C}$; ν_{max} (KBr) 3 460s (NH_2), 3 355s (NH_2), 3 250m ($=\text{NH}$), 1 622s and 1 580s (conj. C=C, C=N, and NH_2), 1 271vs (SO_2), and 1 100vs cm^{-1} (SO_2); τ (CDCl_3) 4.25br (ca. 1.7 H, NH_2 and $=\text{NH}$), 5.08 (ca. 0.9 H, s, $=\text{CH}-$), 6.89 [ca. 0.1 H, s, $\text{C}(=\text{NH})\text{CH}_2\text{SO}_2$], 7.02 (3 H, s, SO_2Me), 7.79 (2 H, q, CH_2Me), and 8.82 (3 H, t, CH_2Me).

Ethyl 2-imino-2-(p-tolyl)ethyl sulphone (15). The preparation of the suspension of ethylsulphonylmethyl-lithium in benzene was similar to the preparation for methylsulphonyl



SCHEME 3

methyl-lithium. *p*-Toluenitrile (11.7 g, 0.10 mol) was added within 30 min at room temperature and the mixture was refluxed for 5 h. The solid was collected, washed with benzene, dissolved in 90% methanol (120 ml), and then water (400 ml) was added to the solution. The resulting crystalline solid was collected, washed with water, dried, and recrystallised from benzene-hexane (1 : 1) to give white crystals (15.3 g, 68%), m.p. 100–101 $^{\circ}\text{C}$; τ (CDCl_3) 2.57 (4 H, q, C_6H_4), 4.08br (ca. 1.8 H, NH_2 and $=\text{NH}-$), 5.03 (0.9 H, s, $=\text{CH}-$), 6.89 (2 H, q, CH_2Me), 7.55 (3 H, s, PhMe), 8.28 [ca. 0.2 H, s, $\text{C}(=\text{NH})\text{CH}_2$], and 8.57 (3 H, t, CH_2Me).

Conditions, yields, m.p.s and b.p.s, and elemental analyses of the β -imino-sulphones are shown in Table 1. I.r. and n.m.r. spectra also agreed with the proposed structures.

TABLE I
 β -Imino-sulphones (1)–(33) *

Compound	Reflux time (h) ^a	Yield (%)	M.p. and b.p. ($t/^{\circ}\text{C}$) ^b
(1)	18	25	62–64
	(THF) ^c		138–140/0.5
(2) ^c	18	44	135–140/0.5
	(THF)		
(3)	20	25	35–36
	(THF)		135–140/0.1
(4)	16.5	52	134–136
	(THF)		(C_6H_6 – C_6H_{14})
(5)	20	79	62–63
	(THF)		(C_6H_6 – C_6H_{14})
(6)	20	41	118–119
	(THF)		(C_6H_6 – C_6H_{14})
(7)	20	73	67–68
	(THF)		(C_6H_6 – C_6H_{14})
(8)	20	64	102–103
	(THF)		(C_6H_6 – C_6H_{14})
(9) ^c	19	36	140–141/0.65
	(C_6H_6)		
(10) ^c	23	36	124–126/0.15
	(C_6H_6)		

Compound	Reflux time (h) ^a	Yield (%)	M.p. and b.p. ($t/^{\circ}\text{C}$) ^b
(11)	22	50	117–118
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(12)	5	69	88–89
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(13)	5	68	76–77
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(14)	8	70	59–60
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(15)	8	68	100–101
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(16)	5	54	106–107
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(17)	22.5	50	106–107
	(C_6H_6)		(hot C_6H_6)
(18) ^d	5	66	59–60
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(19)	19.5	44	90–91
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(20)	16.5	68	77–78
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(21)	22.5	36	173–178/0.33
	(C_6H_6)		
(22)	14	20	126–127
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(23)	5	69	120–121
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(24)	5	60	101
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(25)	4.5	69	75–76
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(26)	4	69	85
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(27)	12	42	93–95
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(28)	17.5	47	80–81
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(29)	12	38	103–104
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(30)	21.5	60	115–116
	(C_6H_6)		(C_6H_6 – C_6H_{14})
(31) ^e	24	72 ^e	
	(C_6H_6)		
(32)	6.5	72 ^f	58–59
	(C_6H_6)		
(33)	6.5	64	107–108
	(C_6H_6)		(C_6H_6 – C_6H_{14})

* All the compounds had satisfactory microanalyses and these are deposited as a Supplementary publication (SUP No. 22275, 8 pp.). For details of the Supplementary publications scheme see Notice to Authors No. 7, *J.C.S. Perkin I*, 1977, Index issue.

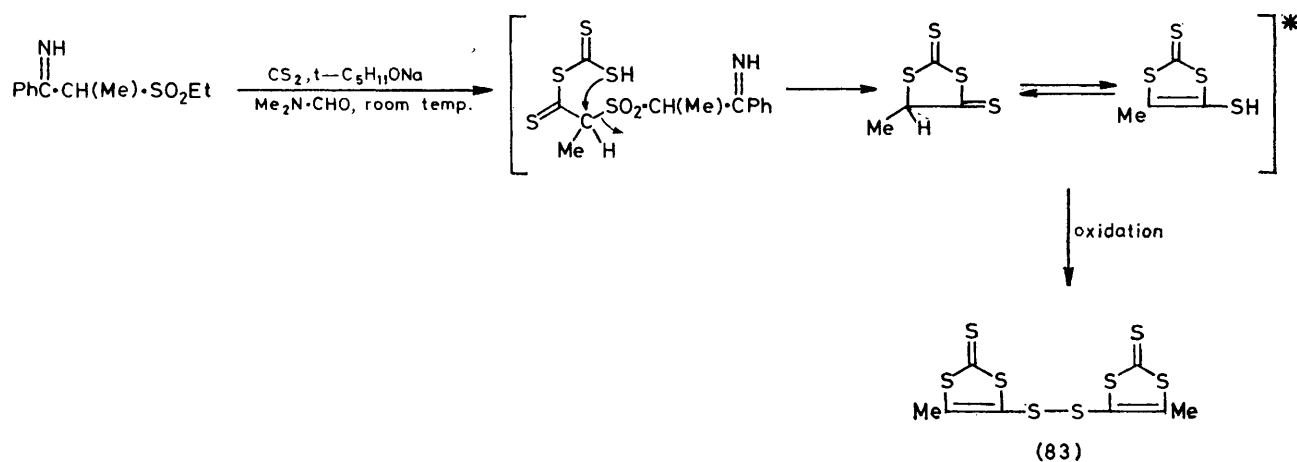
^a Solvent in parentheses. ^b Solvent for recrystallisation in parentheses. ^c These compounds were analysed as 2,4-dinitrophenylhydrazones of the corresponding ketones; methylsulphonylmethyl propyl ketone 2,4-dinitrophenylhydrazone, m.p. 157–158 $^{\circ}\text{C}$; ethylsulphonylmethyl propyl ketone 2,4-dinitrophenylhydrazone, m.p. 190–191 $^{\circ}\text{C}$; ethylsulphonylmethyl isopropyl ketone 2,4-dinitrophenylhydrazone, m.p. 138–139 $^{\circ}\text{C}$; 2-*p*-tolylsulphonylmethylacetophenone 2,4-dinitrophenylhydrazone, m.p. 169–170 $^{\circ}\text{C}$. ^d Unstable in light. ^e Yield treated at 130 $^{\circ}\text{C}$ for 6 h under diminished pressure (0.5 Torr). ^f Yield treated at 130 $^{\circ}\text{C}$ for 6 h under diminished pressure (0.5 Torr). This imino-sulphone solidified after a few days but could not be recrystallised by any solvents because of the tend to form an oil. ^g THF = tetrahydrofuran.

Reaction of 2-Imino-2-(p-tolyl)ethyl Methyl Sulphone with Carbon Disulphide.—5-Methylsulphonyl-4-(*p*-tolyl)-1,3-thiazine-2,6(3H)-dithione (38). To a mixture of 2-imino-2-(*p*-tolyl)ethyl methyl sulphone (2 g, 0.0095 mol), sodium *t*-pentyl oxide (2.8 g, 0.026 mol), and dimethylformamide (20 ml), carbon disulphide (2 g, 0.026 mol) was added dropwise and the mixture was shaken at room temperature for 24 h. Water (25 ml) was added; the aqueous 6M-acetic

acid (6 ml) was added to the solution below 0 °C. The acidified solution was washed with ether (100 ml) and the aqueous solution, after any remaining ether had been removed under reduced pressure, was acidified further with 2M-hydrochloric acid (15 ml). The solid which separated

n.m.r., and mass spectra agreed with the proposed structures.

4-Methylsulphonyl-5-(p-tolyl)-1,2-dithiole-3-thione (59). The ether extract was washed twice with aqueous 2% sodium hydroxide and twice with water after which it was



SCHEME 4 * Suggested mechanism

was collected, washed with water, and dried; yield 0.75 g (25%). Recrystallisation from acetone-water gave brown crystals; ν_{\max} (KBr) 3 147m (NH), 3 095m (ArCH), 1 564s (conj. C=C), 1 443vs (hetero ring), 1 320vs (SO₂), 1 202s

immediately evaporated to dryness. The residue was washed with ethanol and dried; yield 0.24 g (6%). Recrystallisation from hot ethanol gave red crystals; ν_{\max} (KBr) 1 603m (Ph), 1 460s (hetero ring), 1 306vs (SO₂), 1 142vs (SO₂), and 1 041 cm⁻¹ (C=S); λ_{\max} (EtOH) 236 (log ϵ 4.41), 283 (4.04), 322 (4.01), and 415 nm (3.95). The molecular ion was absent in the mass spectrum, as it was for other dithiole-3-thiones, instead a $M^+ - 64$ ion was observed in all cases. Yields, m.p.s, colours, and elemental analyses of

TABLE 2

1,3-Thiazine-2,6-dithiones (34)—(53) *

Compound	Yield (%)	M.p. (t/°C) ^a	Colour
(34) ^b	17	190—191	Red
(35) ^{b,c}	18	177—178	Brownish orange
(36) ^{b,c}	20	184—185	Light brown
(37) ^{b,c}	25.5	187	Light brown
(38) ^{b,c}	25	194—194.5	Light brown
(39) ^b	3	175—176	Light brown
(40) ^{b,c}	22	156.5—157	Brownish orange
(41) ^b	17	189	Brown
(42) ^b	4	197—198	Reddish brown
(43) ^b	22	190—191	Light brown
(44) ^b	15	190.5	Brown
(45) ^{c,d}	23	188—189	Reddish brown
(46) ^d	12	198—199	Brown
(47) ^{c,d}	27	185—186	Reddish brown
(48) ^d	5	193	Brown
(49) ^d	11	201.5	Yellowish brown
(50) ^d	36	180—180.5	Yellowish brown
(51) ^d	16.5	211—212	Dark brown
(52) ^d	15	184	Yellowish brown
(53) ^d	34	187—188	Brown

* For microanalyses see footnote to Table 1.

^a With decomposition; recrystallised from acetone-water.

^b Obtained on acidification with 6M-acetic acid. ^c I.r. spectrum of crude material had a weak carbonyl band near 1 690 cm⁻¹ due to the 2-thioxo-1,3-thiazin-6-one, but the band disappeared on purification. ^d Obtained on acidification with 6M-acetic acid. The crude solid washed with ether repeatedly.

(C=S), and 1 155vs cm⁻¹ (SO₂); λ_{\max} (EtOH) 236sh (log ϵ 4.00), 316 (4.43), 372 (3.63), 442sh (3.91), and 460 nm (4.01); τ (C₅D₅N) 2.18 (4 H, q, C₆H₄), 2.43br (ca. 0.7 H, s, NH), 6.22 (3 H, s, SO₂Me), 7.78 (3 H, s, PhMe), and 7.95 (ca. 0.3 H, s, tautomeric SH); m/e 329 (M^+).

Yields, m.p.s, colours, and elemental analyses of the 1,3-thiazine-2,6-dithiones are shown in Table 2. I.r., u.v.,

TABLE 3

1,2-Dithiole-3-thiones (54)—(73) *

Compound	Yield (%)	M.p. (t/°C) ^a	Colour
(54) ^b	1	108—109 (EtOH)	Yellow
(55) ^b	3	68 (PrOH)	Yellow
(56) ^b	6	181—181.5 (EtOH)	Red
(57) ^b	11	190—191 (EtOH)	Orange
(58) ^b	8	147—148 (EtOH)	Red
(59) ^b	6	156—157 (EtOH)	Red
(60) ^b	6.5	193—194 (EtOH)	Orange
(61) ^b	1	173—174 (EtOH)	Orange
(62) ^b	4	166.5—167 (EtOH)	Yellow
(63) ^b	6	137—138 (EtOH)	Yellow
(64) ^c	5	130—131 (EtOH)	Golden yellow
(65) ^c	8	168—169 (MeOH)	Red
(66) ^c	3	172—173 (MeOH)	Yellow
(67) ^c	6	168—169 (MeOH)	Dark red
(68) ^c	2	169—170 (MeOH)	Dark red
(69) ^c	11	158 (EtOH)	Orange
(70) ^c	10	149—149.5 (PrOH)	Orange-red
(71) ^c	6	154—155 (EtOH)	Orange
(72) ^c	1	148—150 (EtOH)	Yellowish orange
(73) ^c	2.5	205—205.5 (EtOH)	Reddish brown

* For analyses see footnote to Table 1.

^a Solvent in parentheses. ^b Separation similar to that of compound (59). ^c Obtained from the combined ether washings of the crude 1,3-thiazine-2,6-dithiones.

the dithioles are shown in Table 3. I.r. and u.v. spectra agreed with the proposed structures.

4-(p-Tolyl)-1,3-thiazole-2(3H)-thione (79). Ether was removed from the above combined alkaline aqueous washings

under reduced pressure; the solution was then acidified with 6*M*-acetic acid (15 ml) below 0 °C. The solid which separated was collected, washed with water, and dried; yield 0.42 g (25%). Recrystallisation from acetone-water gave yellow crystals, m.p. 190—191 °C; ν_{\max} (KBr) 3 080br (NH), 1 595m (Ar C=C), 1 500m (Ar C=C), 1 442s (hetero ring), 1 336m (hetero ring), and 1 055vs cm^{-1} (C=S); λ_{\max} (EtOH) 242 (log ϵ 4.22), 292sh (4.02), and 322 nm (4.17); $\tau[(\text{CD}_3)_2\text{SO}]$ —3.68br (1 H, s, NH), 2.42 (4 H, q, C_6H_4), 2.68 (1 H, s, 5-H), and 7.62 (3 H, s, Me) (Found: C, 58.0; H, 4.35; N, 6.65; S, 30.7%; M^+ , 207. $\text{C}_{10}\text{H}_9\text{NS}_2$ requires C, 57.9; H, 4.4; N, 6.8; S, 30.9%; M , 207).

5-Methylsulphonyl-2-thioxo-4-(*p*-tolyl)-1,3-thiazine-6(3H)-one (82). The mother liquor from which compound (38) was isolated was set aside for 24 h. The resulting solid material was collected, washed with aqueous 20% morpholine and then with water, dried (*ca.* 0.1 g, 3%), and recrystallised from hot ethanol to give red crystals, m.p. 184—185 °C (decomp.); ν_{\max} (KBr) 3 100br (NH), 1 689vs (C=O), 1 530m (conj. C=C), 1 448vs (hetero ring), 1 313vs (SO_2), 1 190s (C=S), and 1 136vs cm^{-1} (SO_2); λ_{\max} (EtOH) 241 (log ϵ 4.08), 309 (4.30), 394 (3.96), and 460 nm (3.62); $\tau[(\text{CD}_3)_2\text{SO}]$ 2.56 (4 H, q, C_6H_4), 5.20 (*ca.* 0.7 H, s, NH), 6.63 (3 H, s, SO_2Me), 7.60 (3 H, s, PhMe), and 7.91 (*ca.* 0.2 H, s, tautomeric SH) (Found: C, 46.2; H, 3.65; N, 4.2; S, 31.0%; M^+ , 313. $\text{C}_{12}\text{H}_{11}\text{NO}_3\text{S}_3$ requires C, 46.0; H, 3.5; N, 4.5; S, 30.7%; M , 313). Compound (82) formed mixed crystals with compound (38) which contained 3 mol. equiv. of the former and 1 mol. equiv. of the latter.

4-Ethylsulphonyl-1,2-dithiole-3-thione (74).—The preparation was similar to that for the preparation of compound (59). Recrystallisation from hot propanol gave orange crystals (8%), m.p. 172—173 °C; ν_{\max} (KBr) 3 070m (olefinic CH), 1 458vs (hetero ring), 1 305vs (SO_2), 1 130vs (SO_2), and 1 020s cm^{-1} (C=S); λ_{\max} (EtOH) 232 (log ϵ 4.01), 263 (3.65), 276 (3.61), 323 (3.53), and 415 nm (3.88) (Found: C, 26.8; H, 2.75; S, 56.5%; M^+ , 226. $\text{C}_5\text{H}_6\text{O}_2\text{S}_4$ requires C, 26.5; H, 2.7; S, 56.7%; M , 226).

Bis-(4-ethylsulphonyl-3-*t*-butylisothiazole-5-yl) Disulphide (75).—The molar ratio of ethyl 2-imino-3,3-dimethylbutyl sulphone and carbon disulphide, conditions, and work-up procedure were similar to those for the preparation of compound (38). The crude grey solid was recrystallised from acetone-water to give grey crystals (14%), m.p. 245—246 °C; ν_{\max} (KBr) 2 960m, 2 880w, 1 485m, 1 448s, 1 365m, 1 336s, 1 312vs, 1 194s, and 1 140vs; $\tau(\text{C}_5\text{D}_5\text{N})$ 6.39 (4 H, q, $2 \times \text{CH}_2$), 8.40 (18 H, s, $2 \times \text{Bu}^t$), and 8.53 (6 H, t, $2 \times \text{Me}$); m/e 528 (M^+ , 19%), 264 ($M^+/2$, 100), 250 (38.5), 218 (18), 204 (12), 158 (10.5), 156 (14), and 131 (64) (Found: C, 41.3; H, 5.0; N, 5.3; S, 36.6. $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_6$ requires C, 40.9; H, 5.3; N, 5.3; S, 36.4%).

5-(*NN*-Dimethylamino)-5-hydroxy-3-phenylsulphonyl-4-(*p*-tolyl)thiin-2,6-dithione (76).—The molar ratio of 2-imino-2-(*p*-tolyl)ethyl phenyl sulphone and carbon disulphide, conditions, and work-up procedure were similar to those for the preparation of compound (38). The crude solid was obtained on addition of 6*M*-acetic acid. Recrystallisation from acetone-water gave brown crystals (25%), m.p. 184—188 °C (decomp.); ν_{\max} (KBr) *ca.* 3 500br (OH), 1 562s

(conj. C=C), 1 460vs (hetero ring), 1 442vs (hetero ring), 1 322vs (SO_2), 1 198vs (C=S), and 1 151s (SO_2); λ_{\max} (EtOH) 239sh (log ϵ 4.12), 314 (4.45), 380 (3.67), and 463 nm (4.01); $\tau[(\text{CD}_3)_2\text{SO}]$ 2.0—2.7 (9 H, m, Ph and C_6H_4), 4.90br (1 H, s, OH), 6.40 (6 H, s, NMe_2), and 7.58 (3 H, s, PhMe); $\tau(\text{C}_5\text{D}_5\text{N})$ —0.60 (1 H, s, OH) (Found: C, 53.4; H, 3.8; N, 3.2; S, 28.65. $\text{C}_{20}\text{H}_{19}\text{NO}_3\text{S}_4$ requires C, 53.4; H, 4.3; N, 3.1; S, 28.5%).

1,3-Thiazole-2(3H)-thiones (77) and (78).—The preparation of these compounds was similar to that of compound (79). **4-Phenyl-1,3-thiazole-2(3H)-thione (77);** yellow crystals, m.p. 168—170 °C (Found: C, 55.8; H, 3.5; N, 7.1. $\text{C}_9\text{H}_7\text{NS}_2$ requires C, 55.9; H, 3.65; N, 7.25%). **4-(*m*-Tolyl)-1,3-thiazole-2(3H)-thione (78);** m.p. 161—162 °C (Found: C, 57.8; H, 4.5; N, 6.6; S, 30.95. $\text{C}_{10}\text{H}_9\text{NS}_2$ requires C, 57.9; H, 4.4; N, 6.8; S, 30.9%). Spectroscopic data of compounds (77) and (78) were similar to those of compound (79). Yields of compounds (77)—(79) are shown in Table 4.

TABLE 4
Yields of 1,3-thiazole-2-thiones (77)—(79)

Reactant	Product	Yield (%)
(5)	(77)	17
(7)	(78)	26.5
(8)	(79)	25
(12)	(77)	29
(14)	(78)	32
(15)	(79)	33
(23)	(77)	17
(25)	(78)	30
(26)	(79)	25
(30)	(77)	29
(33)	(79)	24

2-Thioxo-1,3-thiazine-6(3H)-ones (80) and (81).—The preparation of these compounds was similar to that of compound (82). **5-Methylsulphonyl-4-phenyl-2-thioxo-1,3-thiazin-6(3H)-one (80);** red crystals (*ca.* 0.5%), m.p. 203—204 °C (Found: C, 43.9; H, 3.0; N, 4.5; S, 32.1%; M^+ , 299. $\text{C}_{11}\text{H}_9\text{NO}_3\text{S}_3$ requires C, 44.1; H, 3.0; N, 4.7; S, 32.1%; M , 299). **5-Methylsulphonyl-2-thioxo-4-(*m*-tolyl)-1,3-thiazin-6(3H)-one (81);** red crystals (3%), m.p. 197 °C (Found: C, 46.2; H, 3.65; N, 4.2; S, 30.5%; M^+ , 313. $\text{C}_{12}\text{H}_{11}\text{NO}_3\text{S}_3$ requires C, 46.0; H, 3.5; N, 4.5; S, 30.7%; M , 313).

Bis-(5-methyl-2-thioxo-1,3-dithiole-4-yl) Disulphide (83).—The molar ratio of ethyl 2-imino-1-methyl-2-phenylethyl sulphone, carbon disulphide, and sodium *t*-pentyl oxide, conditions, and work-up procedure were similar to those for the preparation of compound (38). Recrystallisation from hot dimethylformamide gave golden yellow crystals (33%), m.p. 154—155 °C; ν_{\max} (KBr) 1 424w, 1 379w, 1 059vs, 1 018w, 930w, and 873w cm^{-1} ; λ_{\max} ($\text{C}_5\text{H}_5\text{N}$) 369 (log ϵ 4.51) and 375 nm (4.51); $\tau(\text{C}_5\text{D}_5\text{N})$ 6.85 (6 H, s, $2 \times \text{Me}$); m/e 358 (M^+ , 41.5%), 180 ($M^+ - M/2 + \text{H}$, 73), 179 ($M^+/2$, 28), 103 (179 — CS_2 , 76), and 59 (100) (Found: C, 27.1; H, 1.7; S, 71.7. $\text{C}_8\text{H}_6\text{S}_8$ requires C, 26.8; H, 1.7; S, 71.5%).

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