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CHIRAL SULFOXIDES FROM (*R*)-α-DIMETHYLAMINOETHYLFERROCENE

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Abstract—Chiral sulfoxides and sulfones of potential interest in organic synthesis are prepared by the reaction of 2-lithio-1-(dimethylaminoethyl)-ferrocene with disulfides, followed by oxidation of the sulfides thus obtained with sodium metaperiodate on alumina or with 3-chloroperbenzoic acid. Most of the reactions, in particular oxidations of the sulfides to form the sulfoxides, proceed with high diastereoselectivity. The sulfoxides and sulfones can be isolated as pure enantiomers. Assignment of absolute configurations is based on independent synthesis together with ^{1}H- and ^{13}C-NMR data and ORD measurements.

Chiral sulfoxides are of great interest as intermediates in the synthesis of chiral compounds, e.g. pheromones[1] and steroids.[2] This is due to their ability to transfer chirality from sulfur to carbon[3] and the reductive cleavability of the alkyl sulfoxide bond. Their application as chiral dipolarophiles has recently been reported.[4]

Sulfoxides can be prepared by a variety of methods.[5] Most important for the preparation of chiral sulfoxides are the reaction of chiral sulfinic acid derivatives with carbanions[6] and the asymmetric oxidation of sulfides.[7] Generally, these methods suffer from poor yields and/or lack of enantiomeric purity of the products. Recently, however, Andersen's procedure has been modified to give much better results.[8]

We now wish to report a new type of chiral sulfoxide derived from ferrocene. These are of potential interest for organic synthesis, since they can be prepared quite conveniently with satisfactory stereoselectivity. A sulfoxide with a ferrocene moiety directly attached to sulfur has already been reported,[9] but no attempts have been made to prepare such sulfoxides in chiral form.

RESULTS

(*R*)-α-Dimethylaminoethylferrocene[10] is lithiated stereoselectively to form the (*R*,*R*) and (*R*,*S*) diastereoisomers of 2-lithio-1-dimethyl-aminoethylferrocene **2** in the ratio 96:4.[11] The lithiated compounds react readily with disulfides to yield the chiral sulfides **3**–**7** (Scheme 1) which can be obtained free from isomers by crystallisation. The yields and properties are shown in Table 1.

Oxidation of the sulfides can be achieved by sodium metaperiodate or 3-chloroperbenzoic acid. The outcome depends strongly on the reactants (Table 2). 3-Chloroperbenzoic acid shows remarkable diastereoselectivity; at low temperature with only a small excess, it oxidises sulfides **3**–**6** to form the (*S*,*R*,*S*)-sulfoxides† **8a**, **9a**, **10a** and **11a**, accompanied only by relatively small amounts of the (*R*,*R*,*S*)-diastereoisomers. However, $NaIO_4$ on alumina does not always show such stereoselectivity. Sulfoxides **8**, **9** and **12** are formed as 1 : 1 mixtures of the two diastereoisomers, while oxidation of the sulfides **5** and **6** yields only the (*R*,*R*,*S*)-sulfoxides **10b** and **11b**. The results are presumably due to conformational effects. Diastereoselectivity in oxidation of sulfides with 3-chloroperbenzoic acid and t-butyl hypochlorite has also been observed in other systems of comparable conformational rigidity.[12]

Thus, with suitable reagents and favourable reaction conditions not only the chiral sulfoxides **8**–**12**, but also the chiral sulfones **13**–**16** (Table 3 and Scheme 1) can be prepared from the corresponding sulfides.

DISCUSSION

Configurational assignment of the sulfoxides was achieved by independent synthesis of **11a** and the enantiomer of **11b** by the Andersen method,[6] from reaction of (−)-menthyl-4-toluenesulfinate (with an (*S*)-configuration at the sulfur atom) with (*R*,*R*)- and (*S*,*S*)-2-lithio-1-dimethylaminoethylferrocene, respectively. The nucleophilic substitution occurs with inversion of the configuration at the sulfur centre,[6] and thus leads to the (*S*,*R*,*S*)- and (*S*,*S*,*R*)-sulfoxides, respectively. The (*S*,*R*,*S*)-diastereoisomer is identical with compound **11a**, while the (*S*,*S*,*R*)-diastereoisomer has properties of the enantiomer of **11b** (Scheme 2).

The configuration of the other sulfoxides can be assigned by comparison of their NMR spectra with those of the unequivocally established compounds **11a** and **11b**. In ^{1}H-NMR spectra, a higher deshielding of the CH-protons 6, the Me protons of the dimethylamino group 8 and the aliphatic part of the substituent *R* is found for the (*S*,*R*,*S*)-diastereoisomers (Table 4 and Scheme 3). In ^{13}C-NMR spectra, the (*S*,*R*,*S*)-sulfoxides show higher shielding for the two substituted C-atoms 1 and 2 of the ferrocene ring while the unsubstituted C-atoms of the same ring are more deshielded. Higher shielding is also observed for the CH-carbon 6 and usually for the aliphatic C-atoms of the substituent *R*. In contrast, the Me-carbon 7 and the carbons of the dimethylamino group are more deshielded in the (*S*,*R*,*S*)-series (Table 5 and Scheme 3).

The NMR results seem plausible on the basis of the probably preferred conformation of the diastereomeric sulfoxides shown in Scheme 1. Thus, the lone pair of the sulfur is always directed towards the Fe-atom and the unsubstituted ring ('*endo*'), and the oxygen of the

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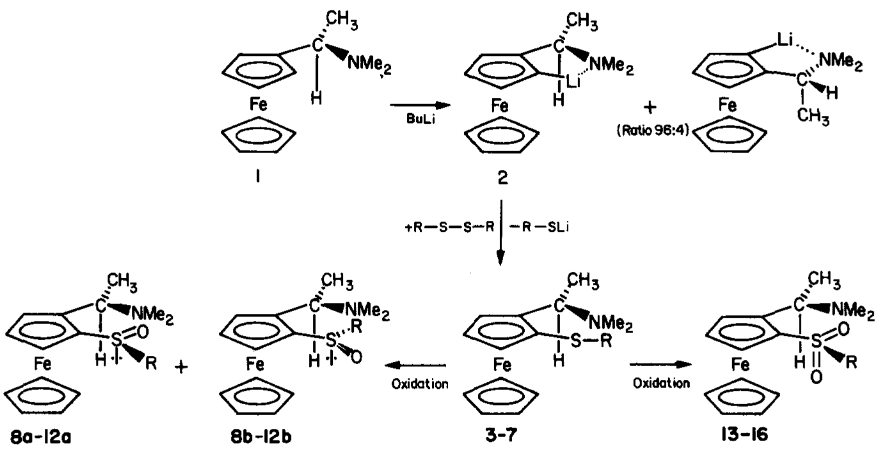
† In a descriptor like (*S*,*R*,*S*), the first letter indicates the chirality at sulfur, the second the central chirality at carbon and the last the planar chirality of the ferrocene system.



Scheme 1.

sulfoxides is directed to the amino side chain in the (*S*,*R*,*S*)-diastereoisomer, while the substituent *R* comes close to the dimethylamino group in the (*R*,*R*,*S*)-sulfoxide. The greater steric bulk of the substituent *R*, relative to the oxygen, may therefore account for the lower electron density at hydrogens 6 and 8 and carbons 3,4,5,7 and 8, as well as for the higher electron density at carbons 1,2 and 6 in the (*S*,*R*,*S*)-diastereoisomer, by polarising the bonds in the two side chains.

The close relationship between the sulfoxides of the (*S*,*R*,*S*)-series on the one hand *vs* the (*R*,*R*,*S*)-series on the other is also observed in their macroscopic properties. Thus, for example the (*S*,*R*,*S*)-sulfoxides have a higher tendency to crystallise from apolar solvents like hexane, while the (*R*,*R*,*S*)-sulfoxides uniformly have higher R_f-values (silica gel; CH_2Cl_2–MeOH, 5:1).

The chiroptic behaviour of the sulfoxides is not easy to understand. According to an empirical rule suggested by Schlögl[13] for 1,2-disubstituted ferrocene derivatives, the sign of $[\alpha]_D$ can be related to conformation and configuration. Assuming that the side chain with the asymmetric C-atom is the ligand of lower symmetry, Schlögl's rule predicts negative signs for the $[\alpha]_D$ of the (*R*,*S*)-sulfides and sulfones, as observed (Table 3). The (*R*,*R*,*S*)-sulfoxides also show generally high values of $[\alpha]_D$ of negative sign, but in the (*S*,*R*,*S*)-sulfoxides, no such generalisation can be made. We therefore measured their ORD curves which,

Table 2. Oxidation of sulfides 3–7

Sulfide	Procedure[a]	Products	(yield %)
3	A	**8a** (47)	**8b** (10)
3	B	**8a** (28)	**8b** (30)
3	A	**13** (45)	
4	A	**9a** (40)	**9b** (5)
4	B	**9a** (26)	**9b** (26)
4	A	**14** (49)	
5	A	**10a** (25)	—
5	B	**10a** (5)	**10b** (43)
5	A	**15** (20)	
6	A	**11a** (28)	Traces
6	B	Traces	**11b** (38)
6	A	**16** (76)	
7	A	**12a** (20)	**12b** (41)

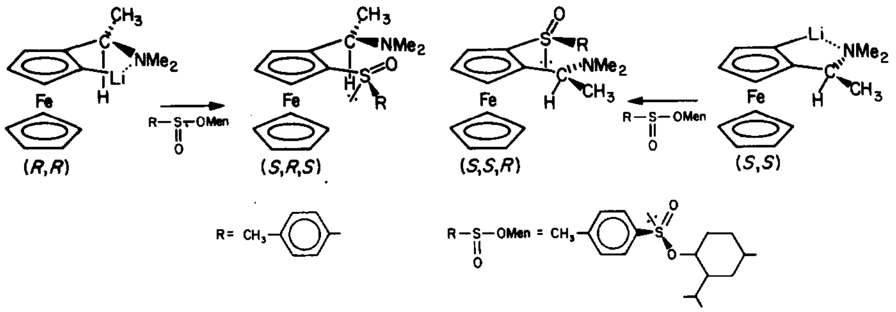
[a] See Experimental for detailed procedures.

Table 1. Properties of (*R*,*S*)-sulfides 3–7

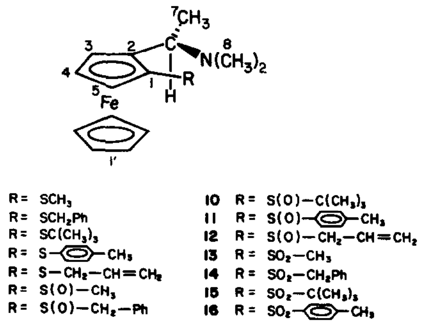
Sulfide	R	Yield (%)	M.p. (°)	IR (cm^{-1})	$[\alpha]_D^{20}$ (ethanol)	MS
3	CH_3	65	77–78	810 s	−186.9	303 (m^+) 288 (m-CH_3) 259 (m-NMe_2)
4	CH_2Ph	70	79–80	700 vs 820 vs	−73.5	379 (m^+) 334 (m-$HNMe_2$) 301 (m-C_6H_6)
5	$C(CH_3)_3$	48	57.5–59	815 s	−167.4	345 (m^+) 330 (m-CH_3) 300 (m-$HNMe_2$)
6	4-CH_3—C_6H_4	75	68–69	810 s	−207.5	379 (m^+) 364 (m-CH_3) 355 (m-NMe_2)
7	CH_2—CH=CH_2	65	Oil	735 vs 820 vs	−102.6	329 (m^+) 314 (m-CH_3) 284 (m-$HNMe_2$)

Table 3. Properties of sulfoxides **8**–**12** and sulfones **13**–**16**

Compound No.	R	M.p. (°)	IR (cm^{-1})	$[\alpha]_D^{20}$ (ethanol)	Configuration	MS
8a	CH_3	124–125	1050 vs	−53.5	*S,R,S*	319 (m^+) 302 (m-OH)
8b	CH_3	85–86	1035 vs	−290.2	*R,R,S*	259 (m-$HNMe_2$)
9a	CH_2Ph	87–88.5	1050 vs	+101.0	*S,R,S*	395 (m^+) 378 (m-OH)
9b	CH_2Ph	125.5–126.5	1040 vs	−121.2	*R,R,S*	304 (m-CH_2Ph)
10a	$C(CH_3)_3$	105.5–107	1050 vs	+104.3	*S,R,S*	361 (m^+) 344 (m-OH)
10b	$C(CH_3)_3$	115–116	1050 vs	−360.7	*R,R,S*	305 (m-C_4H_8)
11a	4-CH_3—C_6H_4	Oil	1045 vs	−112.2	*S,R,S*	395 (m^+) 378 (m-OH)
11b	4-CH_3—C_6H_4	Oil	1040 vs	−374.0	*R,R,S*	335 (m-CH_3-$HNMe_2$)
12a	CH_2—CH=CH_2	36–38	1040 vs	+93.0	*S,R,S*	345 (m^+) 328 (m-OH)
12b	CH_2—CH=CH_2	Oil	1045 s	−148.3	*R,R,S*	284 (m-OH-NMe_2)
13	CH_3	117–118	1125 s 1295 vs	−73.7	*R,S*	335 (m^+) 320 (m-CH_3) 291 (m-NMe_2)
14	CH_2Ph	79.5–81	1115 s 1310 vs	−53.5	*R,S*	411 (m^+) 396 (m-CH_3) 366 (m-$HNMe_2$)
15	$C(CH_3)_3$	118–119	1120 s 1295 vs	−110.9	*R,S*	377 (m^+) 362 (m-CH_3) 333 (m-CH_3-NMe_2)
16	4-CH_3—C_6H_4	165.5–166	1145 s 1305 s 1315 s	−57.5	*R,S*	411 (m^+) 396 (m-CH_3) 367 (m-NMe_2)



Scheme 2.



Scheme 3.

however, do not give a clear picture either (Figs. 1 and 2).

It has been reported[14] that 'averaging' the ORD curves of epimeric 1,2-disubstituted ferrocenes serves to separate the contributions of central and planar chirality. To our surprise, this is also apparently valid for pairs of these diastereoisomeric sulfoxides, even though the chirality of the sulfoxide moiety might have been expected to introduce further complications. Thus, forming the average between the ORD curves of the (*R,R,S*)- and the (*R,S,R*)-sulfoxides (the latter being the mirror images of the experimentally obtained (*S,R,S*) curves) should eliminate the influences of the planar chirality and the central chirality at carbon. The

Table 4. ^{1}H-NMR data of compounds 3–16

Compound No.	Proton No.					R
	1'[a]	3–5	6[b]	7[c]	8[d]	
3	4.11	4.15 (m, 2H); 4.32 (m, 1H)	3.94	1.40 (J = 6.8 Hz)	2.13	2.29 (s, 3H)
4	4.07	4.05 (m, 1H); 4.11 (m, 1H) 4.22 (m, 1H)	4.11	1.35 (J = 7.0 Hz)	2.21	3.86 (d, 1H); 4.00 (d, 1H); J = 12.0 Hz; 7.22 (m, 5H)
5	4.10	4.22 (m, 1H); 4.25 (m, 2H)	3.86	1.31 (J = 6.6 Hz)	2.13	1.25 (s, 9H)
6	4.16	4.30 (m, 2H); 4.48 (tr, 1H)	3.87	1.46 (J = 7.2 Hz)	1.93	2.23 (s, 3H); 6.95 (d, 2H); 7.09 (d, 2H); J = 8.6 Hz
7	4.09	4.16 (tr, 1H); 4.20 (tr, 1H) 4.30 (tr, 1H)	4.01	1.34 (J = 6.8 Hz)	2.13	3.24 (m, 1H); 3.49 (m, 1H); 4.93 (m, 1H); 4.97 (m, 1H); 5.85 (m, 1H)
8a	4.29	4.37 (m, 2H); 4.49 (m, 1H)	4.35	1.29 (J = 6.6 Hz)	2.16	3.02 (s, 3H)
8b	4.30	4.30 (m, 2H); 4.74 (m, 1H)	3.99	1.23 (J = 6.8 Hz)	2.04	2.73 (s, 3H)
9a	4.31	3.94 (m, 1H); 4.15 (tr, 1H) 4.37 (m, 1H)	4.60	1.28 (J = 7.2 Hz)	2.27	4.63 (d, 1H); 4.82 (d, 1H); J = 11.6 Hz 7.07 (m, 2H); 7.25 (m, 3H)
9b	4.26	4.24 (m, 1H); 4.33 (m, 2H)	4.06	1.27 (J = 6.8 Hz)	2.17	3.89 (d, 1H); 4.30 (d, 1H); J = 12.4 Hz 7.16 (m, 2H); 7.28 (m, 3H)
10a	4.34	4.31 (m, 2H); 4.39 (m, 1H)	—[e]	1.30 (J = 6.8 Hz)	2.13	1.24 (s, 9H)
10b	4.34	4.37 (m, 2H); 4.67 (m, 1H)	3.98	1.31 (J = 6.8 Hz)	2.05	1.20 (s, 9H)
11a	4.17	4.32 (m, 2H); 4.38 (m, 1H)	—[e]	1.38 (J = 6.6 Hz)	1.99	2.40 (s, 3H); 7.28 (d, 2H); 7.67 (d, 2H); J = 8.2 Hz
11b	4.38	4.28 (m, 2H); 4.56 (m, 1H)	4.20	1.28 (J = 6.8 Hz)	1.97	2.33 (s, 3H); 7.17 (d, 2H); 7.62 (d, 2H); J = 7.7 Hz
12a	4.34	4.37 (m, 1H); 4.27 (tr, 1H) 4.34 (m, 1H)	4.46	1.25 (J = 6.7 Hz)	2.16	4.14 (m, 2H); 5.17 (m, 1H); 5.22 (m, 1H); 5.63 (m, 1H)
12b	4.29	4.30 (m, 2H); 4.69 (m, 1H)	4.60	1.23 (J = 6.7 Hz)	2.05	3.48 (m, 1H); 3.70 (m, 1H) 5.19 (m, 1H); 5.32 (m, 1H) 5.87 (m, 1H)
13	4.37	4.39 (m, 2H); 4.68 (m, 1H)	4.34	1.23 (J = 6.8 Hz)	2.11	3.18 (s, 3H)
14	4.34	4.21 (m, 2H); 4.40 (m, 1H)	—[e]	1.26 (J = 7.0 Hz)	2.25	4.49 (d, 1H); 4.77 (d, 1H); J = 13.4 Hz; 7.15 (m, 2H); 7.26 (m, 3H)
15	4.39	4.43 (m, 2H); 4.58 (tr, 1H)	4.27	1.29 (J = 6.8 Hz)	2.10	1.35 (s, 9H)
16	4.44	4.36 (m, 2H); 4.74 (tr, 1H)	4.43	1.23 (J = 7.2 Hz)	1.86	2.35 (s, 3H); 7.17 (d, 2H); 7.85 (d, 2H); J = 8.6 Hz

Spectra recorded in $CDCl_3$ at 200 MHz, with TMS as internal standard.
[a] s, 5H. [b] qua, 1H. [c] d, 3H. [d] s, 6H.
[e] Signal could not be detected due to overlap.

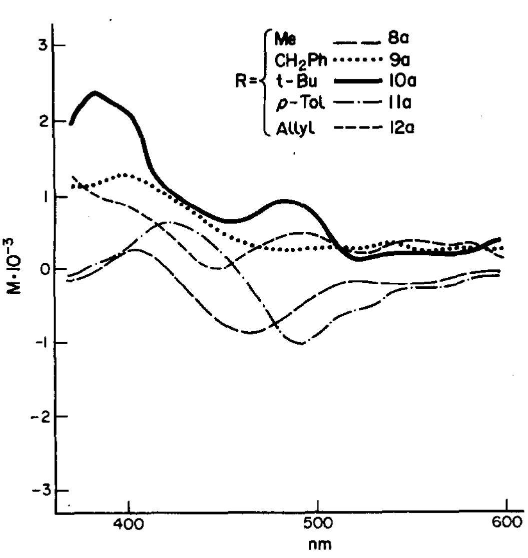


Fig. 1. ORD curves of the (*S*,*R*,*S*)-sulfoxides **8a–12a**.

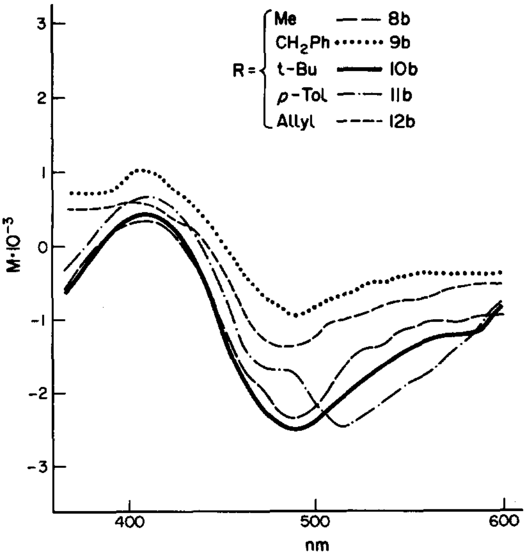


Fig. 2. ORD curves of the (*R*,*R*,*S*)-sulfoxides **8b–12b**.

Table 5. ^{13}C-NMR spectra of compounds **3**–**16**

Compound	Carbon No.						
No.	1′	1,2	3–5	6	7	8	*R*
3	69.88	92.10 83.23	71.02 67.17 66.42	56.01	12.89	40.41	19.81
4	69.87	94.15 78.83	74.61 67.92 66.68	56.10	10.19	39.93	41.42; 126.49; 128.11 129.02; 138.88
5	70.19	94.34 76.68	76.68 68.11 67.40	55.58	10.84	40.00	31.36; 46.03
6	70.19	98.52 76.88	75.19 67.92	55.58	15.65	40.65	20.84; 127.00; 128.82; 134.34; 136.48
7	69.87	93.95 78.96	74.48 67.72 66.68	55.91	10.72	39.93	39.93; 116.49; 134.93
8a	70.27	91.17 90.50	69.19 67.90 67.66	55.13	9.49	39.59	40.52
8b	70.43	93.44 91.68	68.41 67.24 63.61	56.99	7.31	38.97	43.67
9a	70.32	90.71 86.88	70.84 69.28 67.33	54.61	7.86	39.48	60.19; 127.46; 128.24; 130.38; 131.87
9b	70.45	91.90 90.35	68.57 67.14 65.06	57.12	7.09	39.15	62.01; 127.57; 128.13; 130.41; 131.79
10a	70.86	93.14 82.22	70.33 69.24 68.25	53.76	9.95	39.79	23.83; 56.24
10b	70.78	95.27 89.12	68.55 67.79 65.47	56.22	8.13	39.08	23.82; 56.78
11a	70.51	91.42 91.23	69.28 68.63 68.37	55.65	12.73	40.00	21.30; 125.12; 128.88; 140.31; 148.86
11b	70.62	94.54 93.11	68.22 67.60 64.62	56.77	7.99	38.85	21.26; 124.99; 129.03 140.04; 144.06
12a	70.38	90.84 87.66	70.51 69.28 67.40	54.61	8.05	39.28	58.31; 121.87; 128.20
12b	70.42	91.85 90.26	68.51 67.11 65.03	56.95	7.11	38.88	59.73; 121.88; 127.57
13	71.02	91.52 87.11	71.44 70.17 67.85	54.73	7.31	39.13	43.93
14	70.94	91.59 84.32	72.82 70.12 67.84	54.66	7.23	39.41	61.16; 128.09; 129.47; 130.97
15	71.53	93.90 82.48	73.11 70.06 68.63	53.79	9.16	39.47	24.01; 60.23
16	71.29	91.82 88.27	71.53 70.15 68.42	54.60	8.75	38.97	21.46; 127.27; 128.51; 140.60; 142.35

Spectra recorded in $CDCl_3$ at 22.53 MHz, with TMS as internal standard.

Table 6. Analytical data of the new compounds 3–16

Compound No.	Molecular formula	Molecular weight	Elemental analysis					
			Calculated (%)			Found (%)		
			C	H	N	C	H	N
3	$C_{15}H_{21}FeNS$	303.26	59.41	6.98	4.62	59.38	7.24	4.70
4	$C_{21}H_{25}FeNS$	379.36	66.49	6.64	3.69	66.47	6.75	3.63
5	$C_{18}H_{27}FeNS$	345.34	62.61	7.88	4.06	62.66	7.78	4.04
6	$C_{21}H_{25}FeNS$	379.36	66.49	6.64	3.69	66.35	6.66	3.71
7	$C_{17}H_{23}FeNS$	329.30	62.01	7.04	4.25	62.29	6.86	4.01
8a	$C_{15}H_{21}FeNOS$	319.25	56.44	6.63	4.39	56.34	6.62	4.40
8b	$C_{15}H_{21}FeNOS$	319.25	56.44	6.63	4.39	56.42	6.60	4.25
9a	$C_{21}H_{25}FeNOS$	395.35	63.80	6.37	3.54	63.72	6.28	3.56
9b	$C_{21}H_{25}FeNOS$	395.35	63.80	6.37	3.54	63.65	6.50	3.71
10a	$C_{18}H_{27}FeNOS$	361.33	59.84	7.53	3.88	59.60	7.60	3.65
10b	$C_{18}H_{27}FeNOS$	361.33	59.84	7.53	3.88	59.60	7.38	3.99
11a	$C_{21}H_{25}FeNOS$	395.35	63.80	6.37	3.54	64.05	6.21	3.70
11b	$C_{21}H_{25}FeNOS$	395.35	63.80	6.37	3.54	63.75	6.42	3.60
12a	$C_{17}H_{23}FeNOS$	345.29	59.14	6.71	4.06	58.99	6.95	4.16
12b	$C_{17}H_{23}FeNOS$	345.29	59.14	6.71	4.06	59.08	6.88	4.01
13	$C_{15}H_{21}FeNO_2S$	335.25	53.74	6.31	4.18	53.51	6.33	4.04
14	$C_{21}H_{25}FeNO_2S$	411.35	61.32	6.13	3.41	61.50	6.02	3.11
15	$C_{18}H_{27}FeNO_2S$	377.33	57.30	7.21	3.71	57.28	7.44	3.61
16	$C_{21}H_{25}FeNO_2S$	411.35	61.32	6.13	3.41	61.03	5.91	3.37

remaining curve (Fig. 3) should then indicate the contribution of the sulfoxide moiety. The close similarity between the curves is obvious, each showing a strong negative Cotton effect in the range of the 'ferrocene chromophore' (455–465 nm). In the tolyl sulfoxides this is slightly perturbed by the superposition of an additional Cotton effect near 470 nm. The same signs of this 'ferrocenyl sulfoxide' Cotton effect confirm our conclusions from the NMR measurements about the chirality at sulfur.

EXPERIMENTAL

^{1}H-NMR spectra were measured with a Bruker WP 200, ^{13}C-NMR spectra with a Jeol JNM-FX 60, IR spectra with a Perkin–Elmer 257 spectrometer and mass spectra with a Varian CH 4 spectrometer. The ORD curves were taken with a Perkin–Elmer 141 M spectrometer.

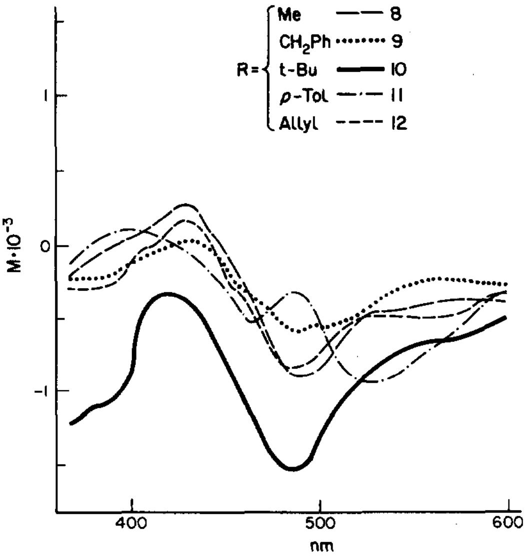


Fig. 3. Average of the ORD curves of the (*R,R,S*)- and the (*R,S,R*)-sulfoxides **8–12**.

Sulfides 3–7

A soln of 10 mmol (2.57 g) of (*R*)-dimethylaminoethylferrocene ($[\alpha]_D^{22} = +14.8$; $c = 1$, EtOH)[10] in 20 ml of dry Et_2O was treated with a hexane soln of n-BuLi (11 mmol). After 3 hr at reflux, 12 mmol of the respective disulfide was added. The mixture was refluxed for 20 hr. Water was added, the layers were separated, and the organic layer was extracted with water and with 10% H_3PO_4, which was washed with ether and then neutralised with NaOH aq. The sulfides were dissolved in ether, dried with Na_2SO_4 and the solvent was evaporated. The crude sulfides can be purified by crystallisation from hexane or by chromatography (silica gel; CH_2Cl_2). Yields and properties are listed in Table 1.

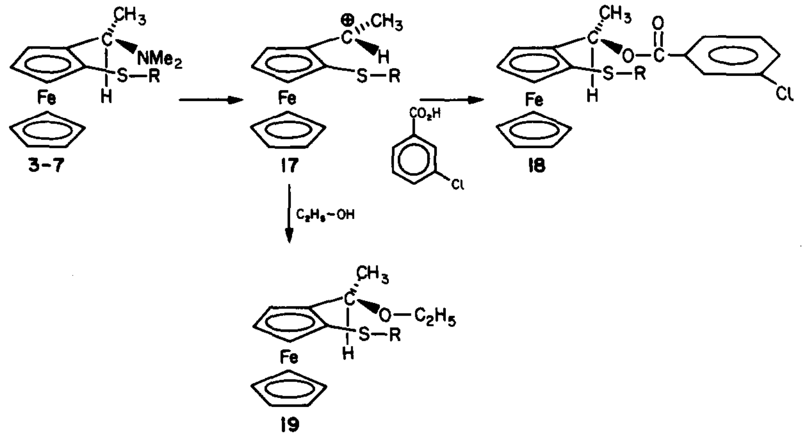
(S,R,S)-2-*Dimethylaminoethyl*-1-(4-*methylphenyl-sulfinyl*)-*ferrocene* 11a *and its* (S,S,R)-*diastereoisomer*

These compounds were prepared from (*R*)-dimethylaminoethylferrocene (or the (*S*)-enantiomer, respectively, lithiated as above, by reaction with (−)-menthyl toluenesulfinate according to a known procedure,[8] and purified as described below (yield 17%).

Oxidation of the sulfides 3–7

A. *With* 3-*chloroperbenzoic acid*. A soln of 10 mmol of the sulfide in 60 ml of CH_2Cl_2 was cooled to −60°, and a soln of 3-$ClPhCO_3H$ (20 mmol in order to obtain the sulfoxides, 60 mmol for obtaining the sulfones) in CH_2Cl_2 was added dropwise. The mixture was stirred at −60° for 2 hr and then allowed to come to room temp. The excess 3-$ClPhCO_3H$ was destroyed with $NaHSO_3$ aq. The organic layer was washed with 10% NaOH aq and then with water. After being dried with $MgSO_4$, the solvent was evaporated and the residue purified by chromatography (silica gel; CH_2Cl_2–MeOH, 5 : 1). The (*R,R,S*)-sulfoxides have higher R_f-values. Recrystallisation from ether affords the pure products. Yields and properties are listed in Tables 2 and 3. Low yields are often due to formation of the 3-chlorobenzoates **18**, presumably through intermediacy of **17** (Scheme 4).

B. *With* $NaIO_4$ *on alumina*. The procedure is identical to that reported by Liu and Tong,[15] with product isolation as above. When the oxidant had deteriorated during prolonged



Scheme 4. Side reactions in the oxidation of the sulfides 3–7.

storage (2–3 months), the ethyl ethers (Scheme 4) were the main products.

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