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DIARYLDIACYLOXYSPIROSULFURANES—I

SYNTHESES FROM SULFIDES WITH HALOGENATING AGENTS

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Abstract—A series of diaryldiacyloxyspirosulfuranes has been prepared from bis(2-carboxyaryl) sulfides with different halogenating agents. In pyridine, sulfides with two electron-withdrawing nitro groups cannot be converted into spirosulfuranes, suggesting the participation of pyridine in Cl^+-transfer reactions. UV and IR spectroscopic data for spirosulfuranes are also reported and briefly discussed.

In a previous communication[1] we demonstrated the syntheses and the possible structure of bis-(2-carboxyphenyl)sulfur dihydroxide dilactone, (1,1'spirobi[3H-2,1-benzoxathiol]-3,3'-dione) (**1a**) which can be regarded as a representative of the diaryldiacyloxyspirosulfuranes of S(IV) [C,C,O,O] type (Scheme 1). At about the same time Martin *et al.*[2] reported on the synthesis of an acyclic diaryldialkoxysulfurane and later, among others, its spirocyclic analogue.[3,4] Spirocyclic sulfuranes and selenium-[5,6] as well as phosphorus[7a] analogues of the spirosulfurane **1a** show a relatively high stability toward heating and hydrolysis.

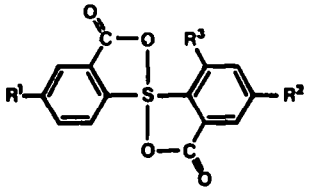
X-ray structure analyses for spirocyclic[1,8,9] and acyclic[10] sulfuranes as well as for selenurane[6] and phosphorane[7b] analogues have also been carried out. The spatial arrangement in these molecules exhibits a trigonal bipyramidal geometry about sulfur and selenium. The lone pair and the two phenyl groups are equatorial while the O atoms of high electronegativity occupy apical positions.

Our present study is centered on the scope and limitations of methods applicable to the preparation of spirocyclic sulfuranes derived from the compound **1a** and to that of the bis-spirosulfurane **3**. Using the sulfides **2a–2k** and **4**, a series of diaryldiacyloxyspirosulfuranes (**1a–1k**, **3**) was prepared and investigated for spectroscopic properties (Scheme 1).

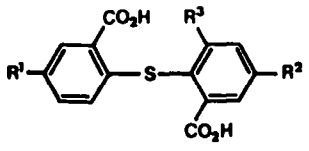
RESULTS AND DISCUSSION

Sulfuranes from bis(2-carboxyaryl) sulfides. The first syntheses of sulfuranes of S(IV) [C,C,O,O] type were carried out in inert solvents starting from sulfides and either chloramine-T[1] or chlorine[2] or bromine.[3] The spirosulfurane **1a** can also be generated by anodic oxidation from the sulfide **2a**.[11]

The applicability of other halogenating agents and

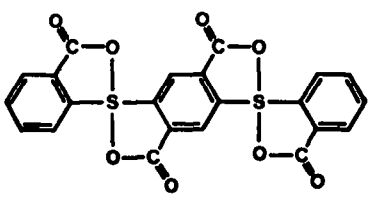


1a–1k



2a–2k

	a	b	c	d	e	f	g	h	i	j	k
R^1	H	NO_2	Cl	NHAc	OMe	NO_2	Cl	NHAc	OMe	H	H
R^2	H	H	H	H	H	NO_2	Cl	NHAc	OMe	Cl	NO_2
R^3	H	H	H	H	H	H	H	H	H	Cl	NO_2



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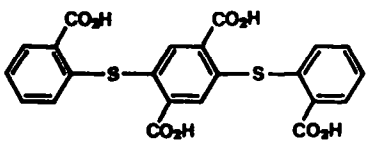

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Scheme 1.

different solvents were studied using 2,2'-thiodibenzoic acid (**2a**) as a model compound. The results are demonstrated in Table 1.

Data in Table 1 show that Methods B, C and D are the most suitable for the preparation of the compound **1a** from the sulfide **2a** (Experimental). An advantage of using pyridine is that in this solvent the solubility of the sulfide **2a** is excellent while that of the spirosulfurane **1a** is poor.

The formation of the spirosulfurane **1a** from 2,2'-thiodibenzoic acid (**2a**) and halogenating agents Q-X can be illustrated as shown in Scheme 2.

By investigating the kinetics of the reaction between organic sulfides and N-chloro-arenesulfonamides we found evidence earlier showing that a chlorosulfonium ion of type **5** is formed as a reactive intermediate[12] and that the reaction of sulfides having *ortho* carboxyl or *ortho* carboxylate group is anchimerically assisted owing to the electrostatic stabilization of the positive sulfonium centre by the negatively charged or polarized carbonyl O atom.[13] Due to the intramolecular nucleophilic attack of the *ortho* carboxyl group, a cyclic acyloxysulfonium ion (**7**) may be formed from the halosulfonium ion **5**, presumably through a monocyclic chlorosulfurane intermediate (**6**) (see Ref. 14). The intermediate **7** is stabilized by the nucleophilic addition of the second *ortho* carboxyl group leading to a spirocyclic sulfurane structure (**1a**). A similar mechanism may be postulated for the reaction of the sulfide **2a** with phenyl iodosoacetate (Scheme 2; X = I(OAc)Ph, Q = AcO).

In order to obtain some understanding as to how the electron-withdrawing or -donating substituents of the sulfides **2b–2k** influence the formation and the stability of the spirosulfuranes **1b–1k**, we studied their syntheses by methods suitable for the conversion of the compound **2a** into the spirosulfurane **1a**. Because of our interest in the stereochemistry of diaryldiacyloxysulfuranes, the bis-spirosulfurane **3** presumably existing both in racemic and meso forms, was also prepared. This compound is related to polymers with sulfurane structural units (Ref. 15). The results are shown in Table 2.

Regardless of the substituents of the aromatic rings, all spirosulfuranes **1b–1k** and **3** can be prepared from the sulfides **2b–2k** and **4** by using dichloramine-T, a highly efficient chlorinating agent,[12,13] in acetic acid (Method B). On the other hand, the sulfides **2f** and **2k** with two electron-withdrawing nitro groups cannot be converted in pyridine by dichloramine-T or *t*-butyl hypochlorite (Methods C and D) even at a higher reaction temperature. These facts suggest the formation of N-chloro pyridinium ion having presumably a lower chlorinating ability than dichloramine-T (see Ref. 16). This species may not be reactive enough to attack dinitro sulfides of extremely poor nucleophilicity, although these substrates have more efficient neighbouring groups in pyridine solvent (carboxylate) than in acetic acid (carboxyl) (Ref. 13).

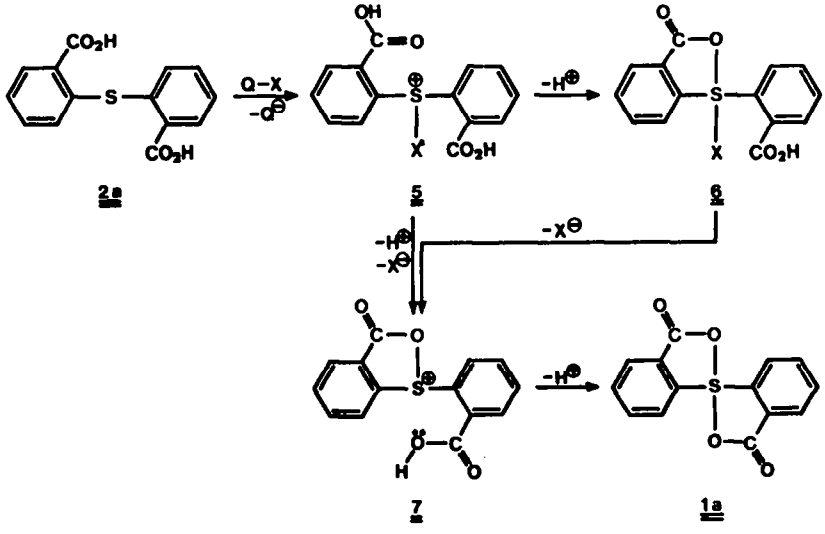
Table 1. Methods for the preparation of the spirosulfurane **1a** from the sulfide **2a** with halogenating agents

Method	Reactant/Solvent	Reaction Temp (°C)	Reaction Time (min)	Yield (%)
A	TsNClNa/dioxan	20	3 days	45
B	$TsNCl_2$/AcOH	30	10	85
C	$TsNCl_2$/pyridine	20	10	95
D	*t*-BuOCl[a]/pyridine	20	5	80
E	Cl_2/pyridine	20	10	77
F	$(CH_2CO)_2NBr$/pyridine	30	10	74
G	$C_6H_5I(OAc)_2$/AcOH	80	10	66

[a]This halogenating agent was introduced by Martin and Balthazor[14] for preparation of sulfuranes.

UV and IR spectra of spirosulfuranes. Data of the UV spectra of the spirosulfuranes **1a–1k** are collected in Table 2. The bands are tentatively assigned to the primary (^1L_a) and secondary (^1L_b) bands of the aromatic rings. The absorption due to the $n \rightarrow \pi^*$ transition of the lone pair of the S atom could not be detected.

In the sequence sulfoxide-sulfurane-sulfone, bathochromic shifts for the primary bands [λ_{max}/nm (log ϵ): 225sh (4.30), 232sh (4.26) and 236 (4.12)] and hypsochromic shifts for the secondary bands [λ_{max}/nm (log ϵ):



Scheme 2. (Q = TsNH, TsNCl, t-BuO, Cl, $(CH_2CO)_2N$; X = Cl, Br)

Table 2. Preparations of the spirosulfuranes **1b–1k** and **3** from the sulfides **2b–2k** and **4**; UV and IR data for spirosulfuranes

Spirosulfurane[a]	Reaction for preparation: Method (b)	Temp. (°C)	Time (min)	Yield (%)	M.p. (°C)	Analyses[d]	C(%)	H(%)	S(%)	UV spectra[e] λ_{max}/nm (log ε)	Characteristic IR bands[h] (cm^{-1}) ν(C=O)	ν(C–O)	ν(O–S–O)
1b	B	45	5	52	229–231		52.9	2.2	10.1	259 (4.06)	1746vs	1098s	819s, 692m
	C	20	120	22			53.0	2.2	10.1	335 sh (2.78)[f]	1720sh		
	D	20	60	28		for $C_{14}H_7NO_6S$					1710vs		
1c	B	45	5	60	253–254		54.9	2.4	10.7	237sh (4.31)	1738vs	1128s	828s, 696m
	C	20	80	64			54.8	2.3	10.5	284 (3.48)	1727vs		
	D	20	80	42		for $C_{14}H_7ClO_6S$					(1729vs)[f]		
1d	B	60	5	82	> 360		58.5	3.4	9.8	[g]	1740sh	1110m	810m, 693m
	C	20	100	58	(dec.)		58.4	3.4	9.7		1727sh		
	D	20	100	49		for $C_{16}H_{11}NO_5S$					1709vs		
1e	B	60	10	53	258–260		59.7	3.4	10.5	244sh (4.16)	1726vs	1109m	828 m, 695m
	C	20	60	58			59.6	3.3	10.6	284 (3.57)	(1723vs)[f]		
	D	20	60	30		for $C_{15}H_{10}O_5S$							
1f	B	80	5	86	263–265		46.5	1.8	9.0	257 (4.31)	1733vs		
	C	20	1 day	[c]	(dec.)		46.4	1.7	8.9	340sh (2.71)[f]	(1741vs)[f]	1131s	819s, 692m
	D	20	1 day	[c]		for $C_{14}H_6N_2O_8S$							
1g	B	60	5	70	305–308		49.4	2.0	9.7	242sh (4.35)	1748vs	1129m	837m, 690m
	C	20	40	74	(dec.)		49.3	1.8	9.4	287 (3.54)	1732sh		
	D	20	40	41		for $C_{14}H_6Cl_2O_4S$					(1739vs)[f]		
											(1728vs)[f]		
1h	B	80	60	93	> 360		56.0	3.8	8.4	[g]	1749vs	1109m	800s, 693m
	C	20	100	32	(dec.)		56.0	3.7	8.3		1709vs		
	D	20	100	36		for $C_{18}H_{14}N_2O_6S$							
1i	B	60	5	95	301–305		57.9	3.7	9.6	255 (4.24)	1731vs	1108m	790s, 700m
	C	20	40	69	(dec.)		57.8	3.6	9.7	295 (3.76)			
	D	20	40	80		for $C_{16}H_{12}O_6S$							
1j	B	70	30	80	279–281		49.5	1.9	9.3	248sh (4.13)	1745s	1110s	827s, 720m
	C	20	90	62	(dec.)		49.3	1.8	9.4	301sh (3.27)	1737s		
	D	30	5	76		for $C_{14}H_6Cl_2O_4S$					1712s		
1k	B	50	5	80	179–181		46.5	1.9	8.9	246 (4.25)	1730vs	1102s	817s, 719m
	C	20	1 day	[c]	(dec.)		46.4	1.7	8.9	308sh (3.42)[f]	(1741vs)[f]		
	D	20	1 day	[c]		for $C_{14}H_6N_2O_8S$							
3	B	70	5	77	310–313		57.0	2.3	13.6	[g]	1735vs	1102s	810s, 715m
	C	40	5	43	(dec.)		56.7	2.2	13.8				
	D	25	90	41		for $C_{22}H_{16}O_8S_2$							

[a] See Scheme 1. [b] $TsNCl_2$ in AcOH (B); $TsNCl_2$ in pyridine (C); *t*-BuOCl in pyridine (D). [c] No reaction. [d] Upper row "Found"; lower row "Required". [e] Solvent dioxan. Upper row "primary band"; lower row "secondary band" with vibrational structure. [f] $n \rightarrow \pi^*$ band of NO_2 group. [g] The spirosulfuranes **1d**, **1h** and **3** are practically insoluble in dioxan. [h] In KBr pellets. [i] In $CHCl_3$ solution.

281 (3.48), 276 (3.49) and 273 (3.52)] can be observed in dioxan for 2,2'-sulfinyldibenzoic acid (8), spirosulfurane 1a and 2,2'-sulfonyldibenzoic acid (9), respectively.

Since the UV absorption is influenced by the electronic interaction of the aromatic ring and of the S atom,[17] it may be assumed that the sulfuranyl substituent is a stronger electron-acceptor than the sulfinyl group in sulfoxides, but a weaker one than the sulfonyl group in sulfones. The same was concluded earlier from the interpretation of σ_R data.[18]

In the IR spectra of the spirosulfurane 1a the ν(C=O) band is found at 1731s cm^{-1} in KBr pellet and at 1724s cm^{-1} in $CHCl_3$.[19] The bands at 1111 s, 819s, 708m and 572m cm^{-1} show marked isotopic shifts ($\Delta\nu$ = 11, 10, 6 and 13 cm^{-1}, respectively) in the spectra of the spirosulfurane 1a containing one ^{18}O isotope in the C–O–S–O–C moiety (for the preparation see Ref. 20). The highest frequency band is assigned to the stretching vibration of the C–O bond. The absorption about 800 and 700 cm^{-1} may be due to the asymmetric and symmetric stretching vibrations of the almost linear O–S–O moiety (data for S–O single bonds in lit.[19,21]). The lowest frequency band may originate from a bending vibration of the C–O–S–O–C bonds. The IR bands characteristic of the spirosulfuranes 1b–1k and 3 are summarized in Table 2.

EXPERIMENTAL

Experimental conditions for the preparations of spirosulfuranes (solvent, reaction temp., reaction time, yield) as well as their characteristic data (m.p., analyses, UV, IR) are quoted only in case if they are not given in the main text (Tables 1 and 2). The compounds produced by different methods were identical.

Solvents were purified and dried by usual methods; pyridine and acetone by distillation over P_2O_5. Unless otherwise stated, evaporation was carried out under reduced pressure. Products obtained from mixtures or by crystallization were, after filtration and washing with cold solvent and ether, dried *in vacuo* over KOH pellets or P_2O_5 depending on the solvent used.

M.ps were determined with a "Boetius" m.p. apparatus. Microanalyses were carried out in the microanalytical laboratory of this Institute by Dr. H. Medzihradszky-Schweiger and Mrs. S. Kutassy. UV and IR spectra were recorded by Mrs. Zs. Petres and Miss K. Fehér with a Specord UV-VIS (Zeiss, Jena) and with a Specord IR 75 or an UR 10 (Zeiss, Jena) spectrometer, respectively.

Preparations for spirosulfuranes from bis-(2-carboxyaryl) sulfides (see also Tables 1 and 2)

Method A. To a soln of 2a (4.1 g, 15 mmol) in dry dioxan (150 ml) was added finely powdered, anhydrous chloramine-T[22] (98% of purity, 3.7 g, 16 mmol), and the mixture was allowed to stand at room temp. After evaporation of the solvent, 1a was extracted from the solid residue with boiling dry acetone (1200 ml). On cooling 1a separated in long, white, thin needles, m.p. 305–307° (Found: C, 61.8; H, 3.1; S, 12.0. $C_{14}H_8O_4S$ requires: C, 61.8; H, 3.0; S, 11.8%).

Methods B, C, D, F and G. To saturated solns of 10 mmol of 2a–2k and 4 were added halogenating agents [5.5 mmol of dichloramine-T for 2c–2e, 2g–2i, 11 mmol of it for 2b, 2f, 2j and 2k, 22 mmol of it for 4; 11 mmol of t-butyl hypochlorite, 22 mmol of it for 4; 20 mmol of N-bromosuccinimide dissolved in 30 ml of dry pyridine; 10 mmol of phenyl iodosoacetate, respectively]. After the time given in Tables, the mixtures were allowed to cool to room temp, and the crystals formed were isolated. Compound 1b did not crystallize from the mixture (Method B), therefore, after evaporation of the solvent, the residue was triturated with 60 ml of EtOAc, and the crystalline product 1b was isolated. A heterogenous reaction took place between 2h and dichloramine-T (Method B) even in 400 ml of dry AcOH solvent.

Method E. Into the cooled soln of 2a (2.74 g, 10 mmol) in dry pyridine (50 ml), dry Cl_2 was bubbled until the colour of the mixture turned red (*ca.* 10 min) and then crystalline 1a was isolated.

Preparations of sulfides.

2,2'-Thiodibenzoic acid (2a). This compound was prepared by a modification of a procedure reported in Ref. 23, in the following way. The mixture of 2-iodobenzoic acid (24.8 g, 0.1 mol), thiosalicylic acid (15.4 g, 0.1 mol), Cu(I) oxide (7.2 g, 0.05 mol) and pyridine (150 ml) was refluxed under N_2 until it became homogenous (*ca.* 2 hr). After cooling to room temp., ice (300 g) and conc. HCl aq (300 ml) were added to the mixture, then, over a period (1–2 hr), the crystals were filtered off, washed with water and redissolved in 5% NaOH aq (200 ml). After heating with charcoal (*ca.* 1 g) at 100° for 10 min, the soln was filtered and acidified with 20% HCl aq at 0°. The solid product was filtered off and recrystallized from AcOH to give 2a (19.2 g, 70%), m.p. 230–32°, lit.[24] m.p. 230–32°). When employing 2-chlorobenzoic acid and the solvent system as given in Ref. 23, the yield was 50% (reaction time 10 hr).

5-Nitro-2,2'-thiodibenzoic acid (2b). To a soln of NaOEt (0.5 mol; from 11.5 g of Na and 250 ml of abs EtOH) were added methyl thiosalicylate[25] (84.1 g, 0.5 mol) and subsequently methyl 2-chloro-5-nitrobenzoate[26] (108 g, 0.5 mol) at 50°. After the exothermic reaction had subsided, the mixture was refluxed for 5 hr under N_2 then KOH (56 g, 1 mol) dissolved in water (20 ml) and in EtOH (250 ml) was added with external cooling, and refluxed for an additional 0.5 hr. The formed salt was filtered off, washed with EtOH, dissolved in water (350 ml) and acidified with 20% HCl aq at 0°. The crude 2b was filtered off, washed with water, dried at 100° (150 g, 94%), m.p. 250–6°, and recrystallized from the mixture of AcOH (1500 ml) and water (90 ml) to give a pure product (130 g, 81%), m.p. 257–8° (Found: C, 52.7; H, 3.2; S, 10.5. $C_{14}H_9NO_6S$ requires: C, 52.7; H, 2.8; S, 10.0%).

5-Chloro-2,2'-thiodibenzoic acid (2c). The mixture of finely powdered 2b (25.6 g, 80 mmol), Fe dust (35 g), $FeCl_3$ (2 g) and water (300 ml) was heated and shaken frequently at 100° for 2 hr. Then EtOH (100 ml) was given to the thick, mud-like mixture and, after heating at 100° for 1 hr, conc. NH_4OH aq (80 ml) and charcoal (*ca.* 3 g) were added and heated for an additional 1 hr. The mixture was cooled to 0°, then filtered, and the ppt washed with conc. NH_4OH aq. The filtrate was evaporated and the residue was dissolved in water (100 ml) then acidified to *ca.* pH 3 with 20% HCl aq to give crude *5-amino-2,2'-thiodibenzoic acid* (10) which was filtered off, washed with water, and the pale yellow powder dried (16.7 g, 72%), m.p. 200–2°. This crude amino sulfide 10 is suitable for the preparation of 2c or 2d and can be converted by conc. HCl aq into its *hydrochloride* (10a) m.p. 245–55° (dec). (Found: C, 51.5; H, 3.6; Cl, 10.8; S, 10.0. $C_{14}H_{12}ClNO_4S$ requires: C, 51.6; H, 3.7; Cl, 10.9; S, 9.8%). Into a soln of the 10a (3.3 g, 10 mmol) and Cu(I) oxide (15 g, 105 mmol) in 150 ml of 15% HCl aq was dropped $NaNO_2$ (10 g, 145 mmol) dissolved in 40 ml of water, at 80–100°. After cooling, the crystals of 2c were filtered off, washed with water, dried at 100° (2.1 g, 69%), m.p. 240–5°, and recrystallized (twice) from AcOH–H_2O (7:1), m.p. 246–8° (Found: C, 54.0; H, 2.8; Cl, 11.6; S, 10.1. $C_{14}H_9ClO_4S$ requires: C, 54.5; H, 2.9; Cl, 11.5; S, 10.4%).

5-Acetylamino-2,2'-thiodibenzoic acid (2d). The mixture of the crude 10 (2.9 g, 10 mmol), Ac_2O (2 ml, 21 mmol), and AcOH (20 ml) was refluxed for 2 hr. After cooling the crystals of 2d were filtered off, washed with AcOH, and dried (3.1 g, 93%), m.p. 234° (Found: C, 57.8; H, 4.2; S, 9.5. $C_{16}H_{13}NO_5S$ requires: C, 58.0; H, 4.0; S, 9.7%).

5-Methoxy-2,2'-thiodibenzoic acid (2e). This compound was prepared from 2-bromo-5-methoxybenzoic acid[27] (23.1 g, 0.1 mol) and thiosalicylic acid (15.4 g, 0.1 mol) by the method given above for 2a, using the mixture of quinoline (90 ml) and pyridine (10 ml) as solvent instead of pyridine. The crude 2e was recrystallized from AcOH (17.7 g, 58%) m.p. 225–7° (Found: C, 59.4; H, 4.1; S, 10.7. $C_{15}H_{12}O_5S$ requires: C, 59.2; H, 4.0; S, 10.5%).

5,5'-Dinitro-2,2'-thiodibenzoic acid (2f). The mixture of methyl 2-chloro-5-nitrobenzoate[26] (130 g, 0.6 mol), potassium ethyl xanthate (96.7 g, 0.6 mol) and EtOH (270 ml) was refluxed for 8 hr. After cooling the crystals were filtered off, washed with cold EtOH (3 × 50 ml) and hot water (4 × 150 ml) then recrystallized

from AcOH. A mixture of methyl and ethyl esters of **2f** was obtained (104 g). This product (10 g), mixed with a soln of KOH (4.5 g) in water (90 ml) and with pyridine (10 ml), was heated and shaken frequently at 100° for 4 hr. To the homogenous soln conc. HCl aq (15 ml) was added and allowed to cool to room temp. The yellowish red crystals of **2f** obtained were filtered off and dried (7.7 g, 85%), m.p. 300–4°. For analysis a sample of this product was recrystallized from 1-pentanol, m.p. 303–6° (Found: C, 40.4; H, 2.5; S, 8.6. $C_{14}H_8N_2O_8S$ requires: C, 46.2; H, 2.2; S, 8.8%).

5,5'-Dichloro-2,2'-thiodibenzoic acid (**2g**). 14.6 g (40 mmol) of **2f** was reduced to *5,5'-diamino-2,2'-thiodibenzoic acid* (**11**) by the method given above for the preparation of **10**, using the same quantities of reactants and solvents. The crude **11** (9.4 g, 77%), m.p. 240–50°, can be converted by conc. HCl aq into its *dihydrochloride* (**11a**), m.p. 245–55° (dec). (Found: C, 42.3; H, 4.2; Cl, 17.9; S, 8.2. $C_{14}H_{14}Cl_2N_2O_4S \cdot H_2O$ requires: C, 42.5; H, 4.1; Cl, 18.0; S, 8.1%). **2g** was prepared from **11a** (3.8 g, 10 mmol) by the procedure given above for **2c**. The crude **2g** (3.0 g, 87%) m.p. 260–5°, was recrystallized from AcOH–H_2O (7:1), m.p. 268–70° (Found: C, 49.0; H, 2.6; Cl, 20.7; S, 9.1. $C_{14}H_8Cl_2O_4S$ requires: C, 49.0; H, 2.4; Cl, 20.7; S, 9.3%).

5,5'-Diacetylamino-2,2'-thiodibenzoic acid (**2h**). The mixture of the crude **11** (3.2 g, 10 mmol), Ac_2O (8 ml, 85 mmol) and AcOH (20 ml) was refluxed for 4 hr. After cooling the heterogenous mixture to 20°, the crystals of **2h** were filtered off, washed with AcOH and dried (3.8 g, 98%), m.p. >360°. (Found: C, 55.6; H, 4.3; N, 7.1; S, 8.2. $C_{18}H_{16}N_2O_6S$ requires: C, 55.7; H, 4.2; N, 7.2; S, 8.3%).

5,5'-Dimethoxy-2,2'-thiodibenzoic acid (**2i**). To a soln of NaOH (9.6 g, 0.24 mol in 150 ml of water) were added 5-methoxyanthranilic acid hydrochloride[28] (24.4 g, 0.12 mol), and subsequently $NaNO_2$ (8.3 g, 0.12 mol), then it was added dropwise to the mixture of conc. HCl aq (34 ml) and ice (44 g) at 0–5°. The cold soln of the diazonium salt obtained was neutralized with NaOAc and added dropwise to the soln of potassium ethyl xanthate (55.4 g, 0.35 mol) in 150 ml of water at 75–80°. After the evolution of N_2 had subsided, the mixture was cooled to 0°, and acidified with conc. HCl aq. The mud-like material collected by decantation was heated with a soln of NaOH (10 g in 100 ml of water) at 100° (2 hr), then the homogenous soln was cooled to 0° and acidified with 20% HCl aq to give *5,5'-dimethoxy-2,2'-dithiodibenzoic acid* (**12**), a yellow ppt which was filtered off and dried (19.6 g, 83%), m.p. 258–62°. The soln of the crude **12** in AcOH (200 ml) together with Zn dust (20 g) was refluxed for 4 hr. After cooling, the ppt was collected by centrifugation and added to 10% NaOH aq (120 ml) then boiled under N_2 for 20 min, cooled and filtered. The clear filtrate was acidified with conc. HCl aq to give the crystals of *5-methoxythiosalicylic acid* (**13**) which were filtered off and dried (14.4 g, 78%), m.p. 166–8°. For analysis a sample of the crude **13** was recrystallized from EtOH–H_2O, m.p. 168–71° (lit.[29] m.p. 300–1°, 170–3°). (Found: C, 51.9; H, 4.5; S, 17.1; SH, 17.6. $C_8H_8O_3S$ requires: C, 52.2; H, 4.4; S, 17.4; SH, 18.0%). To prepare **2i**, the method given above for the preparation of **2e** was applied starting from 2-bromo-5-methoxybenzoic acid[27] (2.3 g, 10 mmol) and from **13** (1.84 g, 10 mmol). The **2i**, obtained as a crude product (2.32 g, 69%), was recrystallized from AcOH, m.p. 210–2°. (Found: C, 57.8; H, 4.4; S, 9.6. $C_{16}H_{14}O_6S$ requires: C, 57.5; H, 4.2; S, 9.6%).

3,5-Dichloro-2,2'-thiodibenzoic acid (**2j**). In a soln of NaOH (6.0 g, 0.15 mol in 350 ml of water) were dissolved 3,5-dichloro-2-aminobenzoic acid[30] (25 g, 0.15 mol) and subsequently $NaNO_2$ (10 g, 0.15 mol). After cooling to 10°, this soln was added dropwise into stirred 15% HCl aq (150 ml) at 10°. To the cold soln of the obtained diazonium salt decolorizing carbon was added, then it was filtered and dropped into a soln of KI (50 g in 100 ml of water) at 60–80°. After cooling the white crystals of 3,5-dichloro-2-iodobenzoic acid (**14**) were filtered off (25 g, 66%, m.p. 165–70°) and recrystallized from AcOH–H_2O (2:1), m.p. 170–1° (lit.[31] m.p. 171–2°). To prepare **2j**, the method given above for the preparation of **2a** was applied, starting from **14** (15.8 g, 0.05 mol) and from thiosalicylic acid (7.7 g, 0.05 mol). The **2j** obtained as a crude product (13.5 g, 79%) was recrystallized from AcOH–H_2O (9:1), m.p. 278–80° (Found: C, 48.8; H, 2.5; Cl, 20.4; S, 9.3. $C_{14}H_8Cl_2O_4S$ requires: C, 49.0; H, 2.4; Cl, 20.7; S, 9.3%).

3,5-Dinitro-2,2'-thiodibenzoic acid (**2k**). The mixture of thiosalicylic acid (30.8 g, 0.2 mol) 3,5-dinitro-2-chlorobenzoic acid[32] (49.3 g, 0.2 mol) and Na_2CO_3 (35 g, 0.33 mol) in water (650 ml) was heated under N_2 at 100° for 2 hr, then cooled and acidified with 20% HCl aq. The yellow crystals formed were filtered off, washed with water and dried at 100°. The crude **2k** (7.2 g, 99%), m.p. 225–30°, was obtained, suitable for the preparation of **1k** by halogenating agents. For analysis a sample was recrystallized from EtOH several times, m.p. 243–5° (Found: C, 46.0; H, 2.5; S, 9.0. $C_{14}H_8N_2O_8S$ requires: C, 46.2; H, 2.2; S, 8.8%).

2,5 - Bis(2 - carboxyphenylthio) - 1,4 - benzenedicarboxylic acid (**4**). To the mixture of $KMnO_4$ (265 g, 1.68 mol) and K_2CO_3 (25 g) in water (3000 ml) was added 2,5-dibromo-*p*-xylene[33] (76 g, 0.29 mol) then it was stirred and refluxed until the colour of $KMnO_4$ disappeared (*ca.* 20 hr). The ppt (MnO_2) was filtered off and washed with hot water. The cold filtrates were combined and acidified with conc. HCl aq to get *2,5-dibromoterephthalic acid* (**15**) which was filtered off and dried (25 g, 27%) m.p. 318–20° (lit.[34] m.p. 318–20°). To prepare **4**, the method given above for the preparation of **2a** was applied using **15** (6.3 g, 20 mmol) and thiosalicylic acid (6.2 g, 40 mmol) as starting materials, and a mixture of quinoline (30 ml) and pyridine (3 ml) as solvent. Work up gave 7.6 g (81%) of **4**, m.p. 315–25° (dec) (Found: C, 56.4; H, 3.2; S, 13.3. $C_{22}H_{14}O_8S_2$ requires: C, 56.2; H, 3.0; S, 13.6%).

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