Arylsulfanes—Synthesis and Nuclear Magnetic Resonance Spectra

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The synthesis of a series of variously substituted arylsulfanes of the general formula $RC_6H_4S_xH$ is described. The proton n.m.r. spectra of the members of the series are reported and discussed in terms of intramolecular electronic effects, conformational factors, and hydrogen bonding.

On décrit la synthèse d'une série d'arylsulfanes de formule générale $RC_6H_4S_xH$. Les spectres r.m.n. de ces composés sont décrits et discutés en termes d'effets électroniques intramoléculaires, de facteurs conformationnels et de ponts hydrogène. [Traduit par le journal]

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Introduction

The preparation, isolation, and characterization of asymmetrical sulfanes having the general formula ArS_xH has presented a considerable synthetic challenge to many workers. Disproportionation, rearrangement, and the general instability of longer sulfur chains under the preparative reaction conditions have been the major problem areas. Fehér's work (1) on the preparation and isolation of the hydrogen polysulfides or sulfanes (HS_xH) is a classic illustration of such rearrangement and disproportionation. Tsurugi and co-workers (2) have refined the original method of Böhme and Zinner (3) for the preparation of aryldisulfanes using acylchlorosulfanes followed by alcoholysis, thus building up the sulfane chain one atom at a time. In this work an extension of Fehér's original technique using dichloromonosulfane (SCl_2) or dichlorodisulfane (S_2Cl_2) followed by "thiohydrolysis" with liquid hydrogen sulfide has permitted the synthesis of the higher members of the homologous series of substituted arylsulfanes by adding sulfur atoms in steps of two or three at each stage (see Scheme 1).

N.m.r. has been shown to be a useful analytical tool for simultaneously identifying and quantitatively estimating the individual sulfane members in complicated mixtures (4). In a mixture of sulfanes the exchange rate of protons between individual —SH species takes place sufficiently slowly that the n.m.r. spectrum is characterized by separate distinct signals for the sulfhydryl protons. By using the ratios of the respective peak areas a quantitative analysis of the mixture is possible. This analytical method was used successfully to study the formation of sulfanes in the sulfur–H_2S system, and in the kinetic study of the thiol–sulfur reaction (5).

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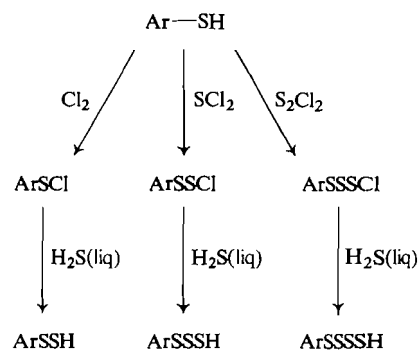
Synthesis

The general procedure for arylsulfane chain lengthening commencing with the appropriate thiol is summarized in Scheme 1. It is important to note that because of the extreme difficulty of separation and purification of higher members of the sulfane series the n.m.r. shift values reported for some tri-, tetra-, and higher homologues are taken from mixtures of the sulfanes. These cases where actual isolation was not performed are clearly identified in the data compilations.



SCHEME 1

Reaction of arylchlorosulfanes (ArS_xCl) with mercaptans rather than H_2S to yield disubstituted sulfanes ($R_1S_xR_2$) has been previously reported (6).

Arylchloromonosulfane, the precursor of the

TABLE 1. Summary of analytical data for arylsulfanes[a]

Sulfane	Formula	Yield[c] %	Iodometric titration[b] Calcd.	Found	% (by n.m.r.)[c] —S_4H	—S_3H	—S_2H
Phenyldisulfane	C_6H_5SSH	95	17.45	16.96		8	92
p-Methylphenyldisulfane	$CH_3C_6H_4SSH$	98	15.12	14.75		12	88
p-Chlorophenyldisulfane	ClC_6H_4SSH	98	11.49	11.40		1.6	98.4
p-Nitrophenyldisulfane	$NO_2C_6H_4SSH$	94	15.23	15.11			>99
o-Nitrophenyldisulfane	$NO_2C_6H_4SSH$	79	16.36	16.49			>99
Phenyltrisulfane	$C_6H_5S_3H$	90	15.34	15.98		82.2	17.8
p-Methylphenyltrisulfane	$CH_3C_6H_4S_3H$	96	13.84	14.32		84.1	15.9
Phenyltetrasulfane	$C_6H_5S_4H$	73	12.31	13.24	60	40	
p-Methylphenyltetrasulfane	$CH_3C_6H_4S_4H$	80	8.91	9.41	59	41	

[a]See Experimental for details.
[b]Milliliters of 0.1 *N* I_2 solution.
[c]Total yield of sulfane products; distribution indicated by n.m.r.

respective sulfane was synthesized by treatment of an aromatic thiol with chlorine, *i.e.*

$$Ar—SH + Cl_2 \rightarrow Ar—SCl + HCl$$

The arylchlorodisulfane was prepared in good yield and with satisfactory purity by careful, slow addition of the thiol in CS_2 solution to a very large excess of SCl_2 at -70 °C.

$$Ar—SH + SCl_2 \rightarrow Ar—SSCl + HCl$$

The solvent and excess of SCl_2 must be distilled off *in vacuo* at low temperature. Under similar conditions the reaction of excess S_2Cl_2 with ArSH yields ArS_3Cl.

Under rigorous exclusion of moisture an excess of liquid H_2S reacted with the arylchlorosulfanes at -70 °C to yield the corresponding monosubstituted sulfanes according to

$$Ar—S_xCl + H_2S \rightarrow Ar—S_{x+1}H + HCl$$

The reaction proceeds smoothly and it is unnecessary to isolate the intermediate ArS_xCl. The products were obtained in nearly quantitative yields and were yellow viscous liquids at room temperature, soluble in CS_2 and characterized by a less unpleasant odor than the corresponding thiols. They are relatively stable and may be stored for some weeks when kept near 0 °C and under anhydrous conditions. The products were analyzed by iodometric titration and n.m.r. The results are summarized in Table 1.

The absence of sulfur analysis data as a criterion in Table 1 deserves comment. Sulfur analyses, while certainly informative, suffer from the difficulty that with a homologous series such as the sulfanes, a mixture of disproportionated members of the series, *e.g.* penta- and trisulfane can give a sulfur analysis which would correspond to a pure tetrasulfane. Therefore, *in situ* identification by n.m.r., which reflects the specific molecular integrity of the species, was preferred in combination with iodometric titration of the terminal —SH function. Table 1 also shows the percentages of other sulfanes present in the various samples as obtained from n.m.r. analysis.

Following the synthesis of the sulfanes ArS_xH, a number of experiments were carried out mainly in order to support the structure assignments which were initially based on spectroscopic data, by conversion of these compounds into known sulfane derivatives.

Aryldisulfane was oxidized with iodine;

$$2\ ArS_2H + I_2 \rightarrow ArS_4Ar + 2\ HI$$

or was converted to the trisulfane by treatment with ArSCl.

$$ArS_2H + ArSCl \rightarrow ArS_3Ar + HCl$$

Reaction of aryltrisulfane with arylchloromonosulfane yielded diaryltetrasulfane;

$$ArS_3H + ArSCl \rightarrow ArS_4Ar + HCl$$

the end products were characterized (m.p. and mixed m.p.) by comparison with an authentic sample prepared by an independent synthesis.

Several variables must be considered when planning the synthesis of a particular sulfane. These variables are (1) the molar ratio of the thiol to chlorosulfane or of the arylchlorosulfane to hydrogen sulfide, (2) the reaction temperature, and (3) the reaction time, *i.e.* controlled rate of

TABLE 2. Characteristic chemical shifts[a] of aromatic thiols and of arylsulfanes

	Formula	—SH (τ p.p.m.)	Ring protons[b] (τ p.p.m.)
Thiols			
Benzenethiol	C_6H_5SH	6.71	2.90
p-Methylbenzenethiol	$CH_3C_6H_4SH$	6.79	3.00
p-Chlorobenzenethiol	ClC_6H_4SH	6.63	2.91
p-Nitrobenzenethiol	$NO_2C_6H_4SH$	6.12	2.39
o-Nitrobenzenethiol	$NO_2C_6H_4SH$	5.98	2.34
Sulfanes			
Phenyldisulfane	$C_6H_5S_2H$	6.62	2.68
p-Methylphenyldisulfane	$CH_3C_6H_4S_2H$	6.61	2.83
p-Chlorophenyldisulfane	$ClC_6H_4S_2H$	6.53	2.69
p-Nitrophenyldisulfane	$NO_2C_6H_4S_2H$	6.42	2.02
o-Nitrophenyldisulfane	$NO_2C_6H_4S_2H$	6.81	2.25
Phenyltrisulfane	$C_6H_5S_3H$	6.11	2.74
p-Methylphenyltrisulfane	$CH_3C_6H_4S_3H$	6.18	2.82
p-Chlorophenyltrisulfane	$ClC_6H_4S_3H$	6.05[c]	
Phenyltetrasulfane	$C_6H_5S_4H$	6.02	2.62
p-Methylphenyltetrasulfane	$CH_3C_6H_4S_4H$	6.07	2.85
p-Chlorophenyltetrasulfane	$ClC_6H_4S_4H$	5.86[c]	
Phenylpentasulfane	$C_6H_5S_5H$	5.93[c]	
Phenylhexasulfane	$C_6H_5S_6H$	5.90[c]	
Phenylheptasulfane	$C_6H_5S_7H$	5.88[c]	

[a]TMS internal reference in CS_2 solution, (concentration 1.0 mol l^{-1})
[b]Taken in the center of the multiplet.
[c]The signal positions are estimated and are taken from the sulfane mixture.

addition of reactant. In general, increasing the number of sulfur atoms in the sulfane requires more careful control of these conditions for optimum results.

An interesting observation was made in attempts to catalyze the synthesis of arylsulfanes (ArS_xH) by means of HCl. The reaction was performed both with liquid H_2S saturated with HCl before addition of the arylchlorosulfanes and without addition of HCl. No difference could be observed. This is interesting since Muller and Hyne found (7) in the preparation of HS_3H and HS_4H that satisfactory results were obtained only with H_2S saturated with HCl.

Higher Homologues by Disproportionation and Decomposition

On prolonged standing at room temperature and during distillation, sulfanes were found to decompose into diarylpolysulfanes, thiol, hydrogen sulfide, and sulfur. Attention was focussed in this work on the unsubstituted parent phenylsulfanes. The principal end products of the decomposition of phenyldisulfane, for instance, were sulfur, diphenyldisulfane and tetrasulfane, benzenethiol, and hydrogen sulfide;

$$3ArSSH \rightarrow ArS_xAr + ArSH + H_2S + S$$

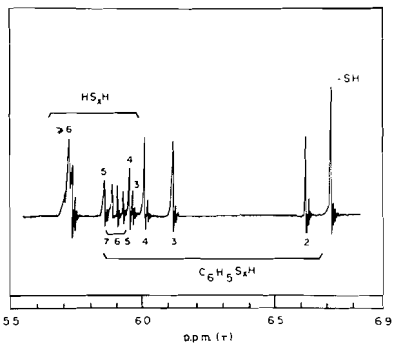


FIG. 1. Expanded n.m.r. spectrum of polysulfane region with assignments. Numbers indicate value of x.

By examining the reaction mixture by n.m.r. during and after distillation it was found that the sulfanes do not decompose directly into the final products Ar—S_xAr, Ar—SH, H_2S, and S but do so through the formation of a number of higher sulfanes of both the ArS_xH and HS_xH type. A typical spectrum of such a polysulfanes mixture showing the presence of the ArS_xH, HS_xH, and parent thiol is shown in Fig. 1. The n.m.r. chemical shifts for the phenylsulfanes are listed in Table 2. In the spectrum the —SH resonance signals are clearly assignable as

indicated by the superscript numbers indicating the length of the sulfur chain. The n.m.r. signals resulting from HS_xH species in the spectrum were assigned according to Hyne *et al.* (5). Inspection of Fig. 1 shows that arylsulfanes up to a sulfur chain length of seven may be identified by clearly separated signals. With increasing sulfur chain length chemical shifts of the sulfhydryl protons are shifted downfield. Assignments were made accordingly and confirmed by adding samples of known sulfane composition to the reaction mixture and observing an increase in the area of the appropriate signals.

The reactions involved in the decomposition of arylsulfanes are evidently complex as evidenced by the production of a large number of intermediates and end products. There is a considerable body of results on the thermal decomposition of sulfanes (8–11) and, for the most part, the evidence indicates that a radical mechanism predominates. Analogies between arylsulfane disproportionation and previous studies on the thermal decomposition of HS_xH (11) suggest a primary homolytic dissociation of the S—S bond into free radicals.

$$ArSSH \rightarrow ArS\cdot + \cdot SH$$

Hydrogen abstraction reactions between primary radical products and the parent sulfane must follow the dissociation step above.

$$ArSSH + ArS\cdot \rightarrow ArSH + ArSS\cdot$$

$$ArSSH + HS\cdot \rightarrow H_2S + ArSS\cdot$$

Subsequent reactions may involve radical–radical recombination of the type

$$ArSS\cdot + HS\cdot \rightarrow ArS_3H$$

$$ArSS\cdot + ArSS\cdot \rightarrow ArS_4Ar$$

$$ArS\cdot + ArS\cdot \rightarrow ArS_2Ar$$

Thermal decomposition of the higher sulfanes ArS_3H and ArS_4H would then proceed by a similar initial homolysis;

$$ArS_3H \rightarrow \begin{cases} ArS. + .S_2H \\ ArS_2. + .SH \end{cases}$$

$$ArS_4H \rightarrow \begin{cases} ArS. + .S_3H \\ ArS_2. + .S_2H \\ ArS_3. + .SH \end{cases}$$

The primary radicals again abstract hydrogen from the parent sulfane which is present in relatively large excess. The occurrence of higher sulfanes of the type ArS_xH and HS_xH with $x \geqslant 6$ indicates that further disproportionation reactions take place and result in chain propagation and chain termination by similar radical–radical recombinations.

While this investigation represents only a cursory examination of the decomposition of arylsulfanes ArS_xH, the results indicate that the decomposition is a complex reaction involving disproportionation into polysulfanes HS_xH and higher and lower members of the series ArS_xH.

Nuclear Magnetic Resonance Spectra

The availability of a range of variously substituted arylsulfanes of the general formula $RC_6H_4S_xH$ has permitted the determination of the proton n.m.r. behavior of the series of compounds and hence the examination of intramolecular electronic transmission effects. Variation of the R substituent through CH_3, H, Cl, and NO_2 provides both electron donating and withdrawing influences on the aromatic ring. Values of x, the sulfur chain length, from 1 to 4 permit examination of the influence of this factor on the transmission of electronic effects from the aromatic ring to the terminal sulfane proton. The pertinent n.m.r. data are reported in Table 2. Marcus and Miller (12) and Tsurugi and co-workers (2) have reported n.m.r. data on substituted thiols ($x = 1$) and disulfanes ($x = 2$) and have commented on the need to extrapolate to zero concentration because of the possibility of intermolecular hydrogen bonding effects. In the substituted arylsulfanes examined in this work the dependence of S—H proton shift on concentration was found to be small in all but the nitro case. All determinations were therefore made at the same dilution (1.0 *M* in CS_2). While these values may differ slightly from infinite dilution values (C_6H_5SSH 6.62 τ, this work; 6.61 τ, ref. 2) the values for the series are internally consistent. Van Wazer and Grant (13) have reported the dependence of methyl proton n.m.r. shift on sulfur chain length for the series of dimethylsulfanes, $CH_3S_xCH_3$. Schmidbaur *et al.* (4) and Muller and Hyne (14) have provided corresponding data for the simple sulfane series, HS_xH. All of these results show a downfield

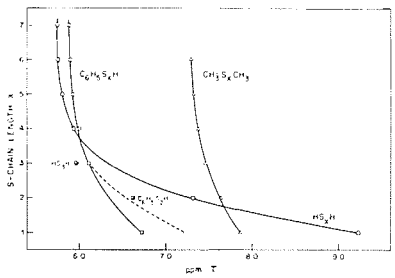


FIG. 2. Dependence of the sulfane proton signal positions on the sulfur chain length. ○ HS_xH: TMS internal reference in CS_2 solution (concentration: 1.0 mol^{-1}); values from reference 14. □ $C_6H_5S_xH$: TMS internal reference in CS_2 solution (concentration: 1.0 mol^{-1}). △ $CH_3S_xCH_3$: TMS internal reference in $(CH_3)_2S$ solution; Values from ref. 13.

shift or deshielding effect on the terminal protons as the sulfane chain length is increased. As illustrated in Fig. 2 the arylsulfanes are no exception to this rule. There is a clear indication, however, that the aryldisulfane is somewhat anomalous as has been noted for the trisulfane in the HS_xH series.

This anomalous behavior in the disulfanes is clearly established by the data for the variously substituted sulfanes plotted in Fig. 3. The *p*-CH_3 and *p*-Cl series both show precisely similar deviations from the smooth curve behavior as is noted for the unsubstituted parent phenylsulfane. Tsurugi and co-workers (2) in their examination of the effect of varying ring substitution on SH proton shift for the RC_6H_4-SSH series concluded that the S—S bond in the disulfane does not transmit conjugation and

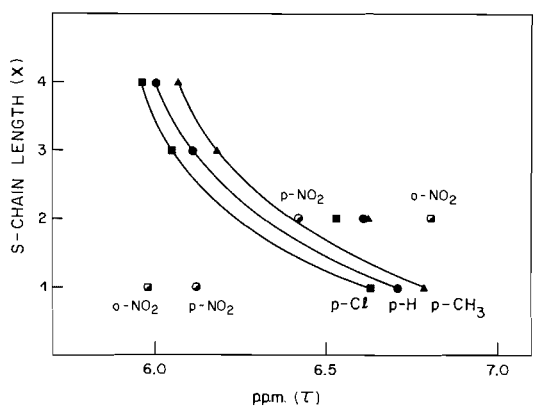


FIG. 3. Sulfhydryl proton signal position of substituted arylsulfanes as a function of sulfur chain length.

permits only very little inductive effect transmission. This might be considered as an explanation for the anomalous behavior of the disulfanes illustrated in Fig. 2 if the phenomenon persisted at higher sulfur chain lengths. Clearly, however, this is not so and it is therefore difficult to accept that by simply extending the sulfur chain the transmission effect is restored.

Downfield shifts from expected values as observed in the case of H_2S_3 are generally attributed to decreased proton shielding resulting from intra- or intermolecular hydrogen bonding. Schmidbaur *et al.* (4) first suggested this explanation for the anomalous n.m.r. signal in H_2S_3 and self association in both thiols and sulfanes has been subsequently demonstrated by i.r. and Raman spectroscopy (31, 32). In the case of phenyldisulfane and the corresponding *p*-methyl and *p*-chloro species, however, the observed anomalous shift of the terminal S—H proton is *upfield* implying increased rather than decreased proton shielding relative to that experienced by other members of the homologous sulfane series. The fact that a change from electron donating to electron withdrawing ring substituents does not significantly affect the anomalous n.m.r. response suggests that the source of the anomaly in the disulfane is not likely inductive or electromeric. While there is a very noticeable concentration effect on n.m.r. shifts in the nitrophenylsulfanes as discussed below the signal position for the other phenylsulfanes is not markedly concentration dependant. This argues against the source of the anomaly being intermolecular association between the —SH proton of one sulfane and the shielding (diamagnetic) basal plane of the aromatic ring of a second phenylsulfane molecule. One possible rationalization of the anomalous shift observation is that the —SH proton in the phenyldisulfane is, by virtue of the C—S—SH bond angle, constrained to move on or close to the "zero effect" surface between the paramagnetic (deshielding) and diamagnetic (shielding) regions associated with the aromatic ring (see Fig. 4). Compared with thiophenol, therefore, the —SH proton in the disulfane would be subject to much less deshielding. In the higher sulfanes the increasing number of rotamer conformations and distance of the terminal SH from the ring will markedly reduce any anomalous shift influence. In a sense, the

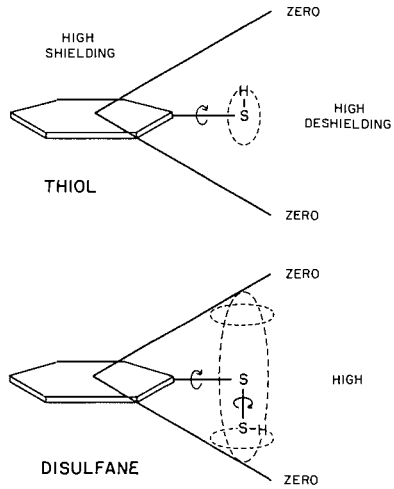


FIG. 4. Anisotropy effects.

apparently anomalous n.m.r. response for the phenyldisulfane is really more a manifestation of "anomalous" deshielding in the parent thiol. The dotted line shown in Fig. 2 represents a graphical interpretation of this suggestion.

In a very recent paper Tsurugi (33) reports the n.m.r. shifts for various benzyl, benzhydryl, and triphenylmethyl sulfanes. The anomalous shift associated with the disulfane is not observed as might be expected due to the insertion of the $-CH_2-$ or $-CH-$ group between the sulfur chain and the ring. The markedly different behavior of the triphenylmethyl sulfane shifts as a function of sulfur chain length is, however, suggested by Tsurugi to be the result of anisotropic factors associated with restricted rotation of the aromatic rings.

The n.m.r. behavior of both the *p*-NO_2 and *o*-NO_2 thiols and sulfanes indicates that these members of the series are significantly different from the other substituted arylsulfanes. The SH proton shift in the *p*-NO_2 case is markedly concentration dependant. The difference between the 1 *M* value and infinite dilution values is 8–10 Hz (0.15 τ). There seems little doubt that intermolecular hydrogen bonding is responsible for this concentration dependence. Confirmation of this conclusion is found in the lack of corresponding proton shift dependence in the *o*-NO_2 case where intramolecular hydrogen bonding would be expected. The added complication of hydrogen bonding, whether intra- or intermolecular, makes it unwise to speculate at this time regarding the relative position of the nitroarylsulfanes in Fig. 3. The anomalous upfield position of the disulfanes relative to the smooth curve prediction noted in the parent, chloro, and methyl substituted series is nonetheless more pronounced in the nitro substituted cases. More extensive examination of the relative roles of hydrogen bonding and conformation effects would be necessary to permit precise analysis of the observed nitro compound shifts but it is unlikely that the upfield shift observed on extending the sulfur chain from one to two atoms is simply an artifact of concentration.

Experimental

Thiols not commercially available were prepared by the standard literature methods indicated below. Each compound was recrystallized or distilled *in vacuo* using a spinning band column just prior to use. All melting points (m.p.) were determined on a Kofler hot stage and are corrected. Boiling points (b.p.) designated by * are converted to pressure used in this work. Some of the thiols were observed to undergo rapid oxidation in the presence of air, particularly in solution. Precautions were therefore taken to minimize contact of the reagent with air.

The work with sulfanes and chlorosulfanes requires special care and cleanliness. All glass apparatus with which these materials come in contact must be thoroughly cleaned with hot chromic acid, carefully dried, and stored in a dust-free atmosphere. All reactions must be protected from moisture and pure starting materials must be used since the intermediates and end products were not purified by distillation due to their very considerable tendency to disproportionate.

Sources of Materials and Reagents

Chlorine (Matheson of Canada Ltd.), was dried and used without further purification. Dichloromonosulfane (sulfenylchloride) (SCl_2) (Hooker Electro Chemical Co.), was stabilized with PCl_3 and redistilled at atmospheric pressure just prior to use. The middle fraction, b.p. 59–60 °C, was employed. Dichlorodisulfane (S_2Cl_2) (Hooker Electro Chemical Co.), was redistilled just prior to use, b.p. 29°C/12 mm. Hydrogen sulfide (Matheson of Canada Ltd.), from a steel cylinder was passed through columns containing $CaCl_2$ and a tube containing P_2O_5, and finally into a container placed in a Dry Ice – acetone bath, where it was condensed and liquefied. The liquefied H_2S was then re-evaporated from this trap into the reaction flask passing through P_2O_5 drying tubes. Carbon disulfide (Fisher Scientific Spectro Grade) was used without further purification. Benzenethiol (Matheson Coleman and Bell) was redistilled before use, b.p. 51–52 °C/12 mm (lit. b.p. 51 °C/12 mm (15)). *p*-Methylbenzenethiol (Aldrich), was recrystallized from ethanol, m.p. 44 °C (lit. m.p. 44 °C (16)). *p*-Chlorobenzenethiol (Matheson Coleman and Bell) was recrystallized from ethanol, m.p. 53–54 °C (lit. m.p. 53–54 °C (17)). *o*-Nitrobenzenethiol was prepared by reduction of the disulfane with glucose and sodium hydroxide following essentially the procedure of Claasz (18). Yield 60% m.p. 57–58° (lit. m.p. 57–58 °C (18)). *p*-Nitrobenzenethiol

was prepared in the same manner as the *o*-isomer. Yield 63%, m.p. 77–78 °C (lit. m.p. 77 °C (19)). 2,2′-Dinitrodiphenyldisulfane was prepared by a procedure based on that of R. Möhlau *et al.* (20) from *o*-chloronitrobenzene and sodium disulfide in refluxing ethanol. Yield 64%, m.p. 195 °C (from CH_3CO_2H) (lit. m.p. 195 °C (20)). 4,4′-Dinitro-diphenyldisulfane was prepared from *p*-chloronitrobenzene and sodium disulfide in refluxing ethanol as described by Zinke and Lenhardt (21). Yield 75%, m.p. 181 °C (lit. m.p. 181 °C (21)). Diphenyldisulfane. Benzenethiol in aqueous NH_3 was oxidized with air following the procedure of Steinkopf and Müller (22). Yield 76%, m.p. 61–61.5 °C (lit. m.p. 61.5 °C (22)). Diphenyltrisulfane: the compound was prepared by the method of Chakravarti (23) and recrystallized from ether. Yield 36%, m.p. 28–30 °C (lit. m.p. 30 °C (24)). Diphenyltetrasulfane: following essentially the procedure of Lecher and Holzschneider (25) benzenethiol in dry ether was treated with the calculated amount of S_2Cl_2 to yield the tetrasulfide in 87% yield as crude product. Recrystallization from ether gave pure product, m.p. 33–34 °C (lit. m.p. 34–35 °C (25)). 4,4′-Dimethyl-diphenyltrisulfane was prepared by the same procedure used for diphenyltrisulfane. Recrystallization from acetic acid gave pure product, m.p. 81 °C (lit. m.p. 81–82 °C (16)). 4,4-Dimethyl-diphenyltetrasulfane in the crude form was prepared in the above way (25) in 90% yield and was recrystallized from ethanol, m.p. 75 °C (lit. m.p. 75 °C (26)).

Arylchlorosulfanes

Arylchloromonosulfanes (ArSCl)

The aromatic chloromonosulfanes were synthesized by means of two essentially similar methods involving the interaction of elemental chlorine with the thiols or diaryldisulfanes. The halogenation was conducted at relatively low temperatures under anhydrous conditions in solvents such as CS_2 and CCl_4.

Phenylchloromonosulfane—This was prepared by a slight modification of the method of Lecher and Holzschneider (27). A solution of 5 g freshly distilled thiophenol in 50 ml dry CS_2 was added dropwise under stirring into 150 ml dry CS_2 kept at −5 °C through which a slow current of chlorine dried with sulfuric acid was passed. After evaporating the solvent the product was obtained by fractionating *in vacuo*. Yield 90%, b.p. 78–80 °C/12 mm (lit. b.p. 78–80 °C/12 mm (27)).*

p-Methylphenylchloromonosulfane—This was prepared from *p*-methyl-thiophenol and chlorine at −10 °C as described under the preparation of phenylchloromonosulfane. Yield 80%, b.p. 63–66 °C/1 mm (lit. b.p. 64–66 °C/1 mm (28)).

p-Chlorophenylchloromonosulfane—This compound was prepared from *p*-chlorothiophenol and chlorine as described under the preparation of phenylchloromonosulfane. Yield 82%, b.p. 50–51 °C/0.03 mm (lit. b.p. 50 °C/0.03 mm (29)).

p-Nitrophenylchloromonosulfane—This was prepared from the disulfide and chlorine in CCl_4 at 50–60 °C following the procedure of Zinke and Lenhardt (21). Yield 83%, m.p. 52 °C (lit. m.p. 52 °C (21)).

o-Nitrophenylchloromonosulfane—This was prepared in the same manner as the *p*-isomer above. Yield 70%, m.p. 75 °C (lit. m.p. 75 °C (30)).

Arylchlorodi- and Arylchlorotrisulfanes (ArS_2Cl, ArS_3Cl)

Except for slight variations, each compound was prepared in the same way by reacting an excess of the chloromono- or chlorodisulfane with the corresponding thiol, followed by evaporation of the solvent and of the excess reactant.

General Procedure—A 300 ml, three-necked round-bottomed flask was fitted with a low-temperature thermometer, magnetic stirrer, addition funnel, and condenser. Freshly distilled SCl_2 or S_2Cl_2 was placed in the flask and cooled to −70 °C. Under conditions of careful exclusion of moisture the thiol, dissolved in CS_2, was added dropwise to the chlorosulfane as slowly as was practicable. It was generally found that the more slowly the thiol was added to the chlorosulfane the better the yield. Stirring was continued for 30 min and the mixture then allowed to warm to room temperature. The excess of SCl_2 (or S_2Cl_2) and the solvent were removed by evaporation at reduced pressure and the last traces in high vacuum. The molar ratio of the thiol to chlorosulfane was between 1:20 and 1:30.

Arylchlorodi- and arylchlorotrisulfanes thus prepared were used immediately without further purification.

Arylsulfanes ($Ar—S_xH$)

General Procedure

The reaction was carried out in a 300 ml, two-necked round-bottomed flask, provided with a low-temperature thermometer, addition funnel, Dry Ice condenser, and a magnetic stirrer.

Hydrogen sulfide gas was purified and dried as described above and distilled into the reaction flask, passing through $CaCl_2$ and P_2O_5 tubes. The reaction flask was cooled with a Dry Ice – acetone bath and the gas thus liquefied. The arylchlorosulfane, dissolved in CS_2 was carefully added drop by drop over a period of time under vigorous stirring to the liquefied H_2S, the temperature being maintained at −70 °C. After stirring at −70 °C for 1 h, the excess H_2S was slowly evaporated. The last traces were removed under reduced pressure. The desired product was generally a clear yellow oily liquid. The products were analyzed by n.m.r. and by iodometric titration.

Phenyldisulfane—Following the above method 2.88 g (0.02 mol) of phenylchloromonosulfane and 140 g (4 mol) hydrogen sulfide yielded 2.78 g (95%) product. This was oxidized by iodine and gave diphenyltetrasulfane, m.p. 33–34 °C, mixed m.p. with an authentic sample 33–34 °C. The n.m.r. spectrum showed one sulfhydryl proton at 6.62 τ (—SH) and five aromatic protons at 2.68 τ (center of the multiplet). The product contained also 8% contamination of $C_6H_5S_3H$ as determined by n.m.r. Iodometric titration Calcd. for 0.2482 g substance: 17.45 ml 0.1 *N* I_2. Found: 16.96 ml.

p-Methylphenyldisulfane—In the above way there was obtained 3.10 g (98%) of disulfane from 3.17 g (0.02 mol) of *p*-methylchloromonosulfane and 140 g (4 mol) hydrogen sulfide. The product was oxidized by iodine and gave 4,4′-dimethyldiphenyltetrasulfane, m.p. 75 °C, mixed m.p. with an authentic sample 75 °C. The n.m.r. spectrum showed three methyl protons at 7.70 τ, one sulfhydryl proton at 6.61 τ (—SH), and four aromatic protons at 2.83 τ (center of the multiplet). N.m.r. indi-

cated that the product contained 12% p-$CH_3C_6H_4S_3H$. Iodometric titration Calcd. for 0.2362 g substance: 15.12 ml 0.1 N I_2. Found: 14.75 ml.

p-Chlorophenyldisulfane—From 3.58 g (0.02 mol) *p*-chlorophenylchlorosulfane and 140 g (4 mol) hydrogen sulfide, 3.46 g (98%) of product was obtained. The n.m.r. spectrum showed one sulfhydryl proton at 6.53 τ (—SH) and four aromatic protons at 2.84 τ (center of the multiplet). Iodometric titration Calcd. for 0.2031 g substance: 11.49 ml 0.1 N I_2. Found: 11.40 ml.

p-Nitrophenyldisulfane—From 3.80 g (0.02 mol) *p*-nitrophenylchlorosulfane and 140 g (4 mol) hydrogen sulfide, 3.50 g (94%) of product was obtained. The n.m.r. spectrum showed one sulfhydryl proton at 6.42 τ (—SH) and four aromatic protons at 2.04 τ (center of the multiplet). N.m.r. indicated that the product was greater than 99% disulfane. Iodometric titration Calcd. for 0.2851 g substance: 15.23 ml 0.1 N I_2. Found: 15.11 ml.

o-Nitrophenyldisulfane—From 2.0 g (0.01 mol) *p*-nitrophenylchlorosulfane was 70 g (2 mol) hydrogen sulfide, 1.56 g (79%) of product was obtained. The n.m.r. spectrum showed one sulfhydryl proton (—SH) at 6.81 τ and four aromatic protons at 2.25 τ (center of the multiplet). N.m.r. indicated that the product was greater than 99% disulfane. Iodometric titration Calcd. for 0.3064 g substance: 16.36 ml 0.1 N I_2. Found: 16.49 ml.

Phenyltrisulfane—From 1.8 g (0.01 mol) phenylchlorodisulfane and 105 g (3 mol) hydrogen sulfide, 1.60 g (90%) of product was obtained. This was allowed to react with phenylchloromonosulfane and gave diphenyltetrasulfane, m.p. 33–34 °C, mixed m.p. with an authentic sample 33–34 °C. The n.m.r. spectrum showed sulfhydryl proton resonance at 6.11 τ (—SH) and aromatic protons at 2.74 τ (center of the multiplet). N.m.r. indicated that the product was 82.2% phenyltrisulfane and 17.8% phenyldisulfane. Iodometric titration Calcd. for 0.2671 g: 15.34 ml 0.1 N I_2. Found: 15.98 ml.

p-Methylphenyltrisulfane—From 2.30 g (0.012 mol) *p*-methylchlorodisulfane and 110 g (3.4 mol) hydrogen sulfide, 2.18 g (96%) of product was obtained. This was allowed to react with *p*-methylchloromonosulfane and gave 4,4′dimethyl-diphenyltetrasulfane, m.p. 75 °C, mixed m.p. with an authentic sample 75 °C. The n.m.r. spectrum showed sulfhydryl proton resonance at 6.18 τ (—SH) and aromatic protons at 2.82 τ (center of the multiplet). N.m.r. indicated that the product was 84.1% *p*-methyltrisulfane and 15.9% *p*-methyldisulfane. Iodometric titration Calcd. for 0.2605 g substance: 13.84 ml 0.1 N I_2. Found: 14.32 ml.

Phenyltetrasulfane—Freshly prepared phenylchlorotrisulfane 2 g (0.01 mol) and 70 g (2 mol) hydrogen sulfide yielded 1.5 g (73%) of product. The n.m.r. spectrum showed sulfhydryl proton resonance at 6.02 τ ($—S_4H$), at 6.11 τ ($—S_3H$), and aromatic protons at 2.62 τ (center of the multiplet). The material contained 60% phenyltetrasulfane and 40% phenyltrisulfane as analyzed by n.m.r. Iodometric titration Calcd. for 0.2541 g substance: 12.31 ml 0.1 N I_2. Found: 9.41 ml.

p-Methylphenyltetrasulfane—From 4.2 g (0.02 mol) *p*-methylphenylchlorotrisulfane and 70 g (2 mol) hydrogen sulfide, 3.2 g (80%) of product was obtained. N.m.r. indicated that the material contined 59% *p*-methylphenyltetrasulfane, sulfhydryl proton resonance at 6.07 τ ($—S_4H$), and 41% *p*-methylphenyltrisulfane, sulfhydryl proton resonance at 6.18 τ (S_3H). The aromatic protons are observed at 2.89 τ (center of the multiplet). Iodometric titration Calcd. for 0.1963 g substance: 8.91 ml 0.1 N I_2. Found 9.41 ml.

Chemical Analysis

For the determination of the arylsulfanes the iodometric method of Böhme and Zinner (3) was employed.

Procedure

The sample 0.10–0.20 g was weighed in a small weighing pipette and dissolved in 20 ml carbon disulfide. An excess of a standard solution of iodine was added and the mixture immediately shaken. Since the titration of the iodine with thiosulfate requires a long time, a back-titration method was adopted, an excess of thiosulfate being first added and the excess then determined by means of a 0.1 N I_2 solution to the starch end point.

Nuclear Magnetic Resonance Analysis

A Varian A-60 high-resolution n.m.r. spectrometer was used to analyze the reaction products. The n.m.r. spectra were determined at 35 °C (probe temperature) using TMS as internal standard. Chemical shifts are given on the τ scale in p.p.m. relative to TMS (τ = 10.00). The chemical shifts for the sulfhydryl and the phenyl protons taken at the center of the multiplet structure are presented in Table 2. Relative areas determined by cutting out tracings of the spectra or counting squares yielded a quantitative measure of relative concentrations of aromatic and sulfhydryl protons of the various sulfanes.

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