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Geminal Sulphones

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The literature data on the method of synthesis, structures, and chemical properties of compounds containing geminal sulphonyl groups are surveyed and described systematically. The available information about the thermodynamic and kinetic acidities of the compounds and the stability and reactivity of the carbanions stabilised by two (and more) sulphonyl groups is discussed. The bibliography includes 222 references.

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I. INTRODUCTION

Compounds containing geminal sulphonyl groups were first synthesised at the end of the last century but for a long time their number was small, they were difficult to obtain, and they were inadequately investigated. The first representatives of geminal sulphones (GS) were β-disulphones (DS). Subsequently numerous publications were devoted to the chemistry of DS and at the present time these are the most thoroughly investigated representatives of GS. Studies have developed mainly in two directions during the last three decades on the basis of these compounds: (1) investigation of the thermodynamic and kinetic acidity of GS and the problems of the formation, stabilisation, and reactivity of the corresponding carbanions associated with it; (2) the search for methods of synthesis of various types of GS.

The first direction is represented by studies in which, together with the investigation of the acid properties of GS and of the factors influencing the stabilisation of carbanions and their reactivity (hybridisation of the carbon atom, configuration, conformation, and $2p,3d$-orbital interaction), problems concerning the proton-donating activity of certain representatives of GS in the formation of hydrogen bonds with electron donors were solved.

The second direction developed rapidly in recent years when appreciable advances were achieved in the synthesis of unsaturated GS, in the use of GS for the introduction of sulphonyl groups into heterocyclic compounds, and also in the synthesis of new organophosphorus and organofluorine compounds. It was found that unsaturated GS have specific properties characteristic only of these compounds.

The amount of available information in the literature and the synthesis of properties of GS is sufficient for its survey and systematic treatment. Nevertheless there has so far been no review on the chemistry of GS. Even in the familiar monograph of Oae[1] and the review by Magnus[2] little attention has been devoted to GS.

In the present review the first attempt is made to fill this gap. The data dealt with in the review are described in the following order: we start with the chemistry of β-disulphones and then proceed to unsaturated compounds and more complex structures containing geminal sulphonyl groups.

Information which appeared in the literature during the last forty years, up to July, 1984, has been used in the review. Earlier studies are quoted only when necessary. In considering the theoretical problems concerning the thermodynamic acidity of GS and the stabilisation of the corresponding carbanions, certain aspects of the chemistry of monosulphones are discussed to achieve a fuller description of the problem. Compounds containing geminal sulphonamide groups are not considered in this review.

II. METHODS OF SYNTHESIS

The methods of preparation of aliphatic GS containing an unsubstituted methylene or methylidyne group reduce to the following fundamental schemes with rare exceptions: (1) synthesis and subsequent oxidation of the geminal bis-sulphides (thioacetals) or tris-sulphides (trithio-orthoesters); (2) the introduction of SO_2R groups (or SR groups with subsequent oxidation) in the α-position in compounds containing two geminal electron-accepting groups, one of which is the sulphonyl group. Both methods lead to the formation of methane derivatives. Higher homologues of aliphatic GS are obtained from DS or geminal trisulphones (TS) by alkylation with alkyl halides or via the Michael reaction.

The higher reactivity of the methylene group in DS makes it possible to employ a wide variety of DS for the synthesis of certain unsaturated GS.

1. Linear and Cyclic Disulphones

Linear symmetrical GS with a free methylene group (1) were obtained for the first time by condensing formaldehyde[3,4] or its trimer[5,6] with thiophenols or merceptans in the presence of acids with subsequent oxidation of the bis-sulphide formed. These reactions proceed as a rule with satisfactory yields and the availability of the DS is therefore determined by the availability of the corresponding thiol. Methylene chloride[7] or bromide[8] in the presence of alkali metal alkoxides is used much more rarely in the synthesis of bis-sulphides instead of formaldehyde:

$$RSH \xrightarrow[CH_2X_2,\ EtONa]{CH_2O,\ H^+} \xrightarrow{[O]} \underset{(I)}{(RSO_2)_2CH_2}\ ;$$

$$R = Alk, Ar;\ X = Cl, Br\ .$$

A wide variety of oxidants are used in the oxidation stage, among which nitric acid,[9] hydrogen peroxide,[6,10] chromium trioxide,[11,12] peracids,[13] hydroperoxides,[14] and potassium permanganate[15] are most common.

Various aromatic and aliphatic DS have been synthesised by the method which is based on the oxidation-reduction cleavage of arene- or alkane-sulphinylacetic acids obtained from S-substituted mercaptoacetic acid:[16]

$$RSCH_2COOH \xrightarrow[HAc]{H_2O_2} [RSOCH_2COOH] \xrightarrow{H^+} (RS)_2CHCOOH \xrightarrow{H_2O_2} (I)\ ;$$
$$R = Alk, Ar\ .$$

Disulphones with an unsubstituted methylene group (I) have also been synthesised by nucleophilic substitution of halogen atoms in α-halogenosulphones by treating them with alkali metal thiolates and oxidising the resulting sulphone sulphides,[17,18] by chlorinating aryl methyl sulphides with subsequent disproportionation of aryl chloromethyl sulphides on alumina and oxidation of the resulting bis-sulphide,[19] and by oxidising the bis-sulphides formed in the radical reaction of a monochloromethyl ether in the presence of thiols.[20]

Symmetrical DS (II), in which the hydrogen atoms of the methylene group have been substituted by various aliphatic groups, are usually obtained by alkylating unsubstituted DS (see below), although the synthesis by the oxidation of substituted thioacetals and thioketals is also known:[21]

$$RR^1C(SR^2)_2 \rightarrow RR^1C(SO_2R^2)_2\ ;$$
$$\text{(II)}$$
$$R, R^1 = Alk;\ R^2 = Alk, Ar\ .$$

A universal method of synthesis of both symmetrical and asymmetric DS has been proposed by Gibson,[22,23] who obtained various DS in high yields by making use of the availability of various alkane- and arene-sulphonyl acetones, the high reactivity of the methylene group in these compounds in thioalkylation and thioarylation reactions, and also the ready heterolytic abstraction of the acetyl group (sometimes even in the oxidation process):

$$RSO_2CH_2COMe \xrightarrow[EtONa]{R^1SX} RSO_2CH(SR^1)COMe \xrightarrow[HAc]{H_2O_2} RSO_2CH_2SO_2R^1\ ;$$
$$R, R^1 = Alk, Ar;\ X = Hal, SO_2Alk, SO_2Ar\ .$$

Substituted DS containing a third electron-accepting substituent at the carbon atom are synthesised by introducing a second sulphonyl group (or SR group with subsequent oxidation) at the methylene carbon atom in compounds of the type RSO_2CH_2S. As a rule, the reaction proceeds only with the most reactive sulphonyl chlorides:[24]

$$\left.\begin{array}{l} MeSO_2CH_2CN + PhSO_2Cl \xrightarrow{(>3\%)} \\ PhSO_2CH_2CN + MeSO_2Cl \xrightarrow{(70\%)} \end{array}\right| \rightarrow PhSO_2CH(CN)SO_2Me\ .$$
$$\text{(III)}$$

Owing to the low reactivity of aromatic sulphonyl chlorides, DS substituted by two aromatic groups are synthesised using the corresponding aryl thioesters of sulphinic acid or arenesulphenyl chlorides:[24]

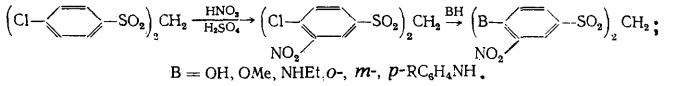
$$PhSO_2CH_2CN \xrightarrow{PSO_2SPh} PhSO_2CH(SPh)CN \xrightarrow{[O]} (PhSO_2)_2CHCN\ .$$
$$\text{(IV)}$$

Substituted DS of type (III) substituted by aliphatic and aromatic groups are obtained by employing methanesulphonyl chlorides, which makes it possible to shorten the synthesis by one stage. Asymmetric DS with electron-accepting substituents (CN, COOMe, COOEt, COMe, and COPh) at the methylidyne carbon atom have been synthesised in this way.[25]

Bis(benzenesulphonyl)ethoxycarbonylmethane (V) has been obtained from ethyl dichloroacetate and thiophenol with subsequent oxidation of the reaction product:[26]

$$PhSH + Cl_2CHCOOEt \xrightarrow{EtONa} (PhS)_2CHCOOEt \xrightarrow{[O]} (PhSO_2)_2CHCOOEt\ .$$
$$\text{(V)}$$

Nitrodisulphones cannot be obtained by the direct nitration of the methylene group. Nitration of bis(benzenesulphonyl)-methane leads to bis(3-nitrobenzenesulphonyl)methane.[27] Bis(4-chlorobenzenesulphonyl)methane is converted into bis(4-chloro-3-nitrobenzenesulphonyl)methane on nitration.[28] A series of DS containing various substituents in the aromatic ring have been obtained by the nucleophilic substitution of chlorine atoms of the last compound:[28]



$$B = OH, OMe, NHEt, o\text{-}, m\text{-}, p\text{-}RC_6H_4NH\ .$$

A disulphone with the nitro-group at the methylene carbon atom has been obtained by the alkaline cleavage of tris-(methanesulphonyl)nitromethane:[29]

$$(MeSO_2)_3CNO_2 \xrightarrow{NaOH} (MeSO_2)_2CHNO_2 + MeSO_3Na\ .$$
$$\text{(VI)}$$

The synthesis of DS with the CF_3SO_2 group has been described.[30] The authors used the usual method for the preparation of the bis-sulphide and oxidised the latter to DS with chromium trioxide in acetic acid:

$$p\text{-}XC_6H_4SNa \xrightarrow{ClCH_2SCF_3} p\text{-}XC_6H_4SCH_2SCF_3 \xrightarrow[HAc]{CrO_3} p\text{-}XC_6H_4SO_2CH_2SO_2CF_3\ ;$$
$$X = H, Cl, NO_2\ .$$

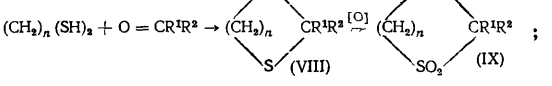
Disulphones with two perfluoroalkyl groups have been obtained from perfluorinated sulphonyl fluoride and Grignard reagents.[31,32] The reaction takes place in several stages and makes it possible to obtain a DS with an unsubstituted or substituted methylene group:

$$R_FSO_2F + RCH_2MgX \xrightarrow[25°C]{THF} (R_FSO_2)_2CHR\ ;$$
$$R = H, Me;\ R_F = CF_3, C_4F_9, C_8F_{17}\ .$$

Methanedisulphonyl fluoride has been synthesised by the reaction of methionic acid chloride (methanedisulphonyl chloride) with anhydrous zinc fluoride:[33,34]

$$CH_2(SO_2Cl) + ZnF_2 \rightarrow CH_2(SO_2F)_2\ .$$
$$\text{(VII)}$$

Cyclic DS are usually obtained by oxidising 1,3-dithiacycloalkanes, which are in their turn synthesised from the corresponding αω-dithiol and a carbonyl compound (an aldehyde or ketone). The use of formaldehyde or its trimer with subsequent oxidation lead to cyclic 1,3-disulphones with a free methylene group:[35]

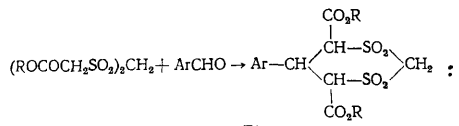


$$R^1, R^2 = H, Alk;\ n = 2-4\ .$$

The reaction of αω-dihalogenoalkanes with sodium thiosulphate is a convenient method of synthesis of 1,3-dithiacycloalkanes.[36] The polymethylenebisthiosulphonate formed as an intermediate reacts with carbonyl compounds to form 1,3-dithiacycloalkanes, which are then oxidised by hydrogen peroxide to cyclic 1,3-disulphones:[37]

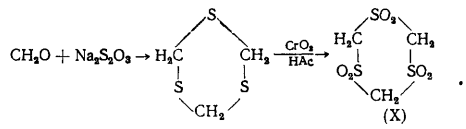
$$X-(CH_2)_n-X + Na_2S_2O_3 \rightarrow (CH_2)_n(SSO_2ONa)_2 \xrightarrow{R^1COR^2} (VIII) \xrightarrow{[O]} (IX)\ ;$$
$$R^1, R^2 = Alk;\ X = Cl, Br;\ n = 2-4\ .$$

Cyclic 1,3-disulphones containing oxygen atoms in the ring have been synthesised by an analogous procedure.[38] A method of synthesis of ring-substituted 1,3-dithiane 1,1,3,3-tetroxides with a free methylene group by the condensation of bis(alkoxycarbonylmethanesulphonyl)methane with various aldehydes in the presence of ammonium acetate has been published recently:[39]



R = Me, Et .

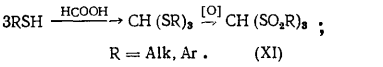
sym-Trithianes, which are products of the interaction of aldehydes or ketones with hydrogen sulphide,[40,41] are readily oxidised to cyclic trisulphones containing three free or substituted methylene groups. 2,4,6-Trimethylene-1,3,5-trisulphone (TTS) (X) has been most thoroughly investigated. It is usually synthesised by the reaction of formaldehyde with sodium thiosulphate[42,43] and the oxidation of the tris-sulphide formed by chromium trioxide in acetic acid:



2,4,6-Tri(methylmethylene)-1,3,5-trisulphone (TMTS) has been synthesised by the same method.[45]

2. Geminal Trisulphones

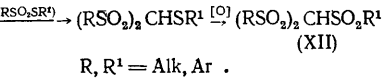
Two methods of synthesis of geminal trisulphones have been described in the literature. Symmetrical aliphatic and aromatic TS are obtained by oxidising orthothioesters:[46]



R = Alk, Ar . (XI)

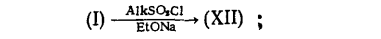
The orthothioesters are synthesised by the Houben method.[47] Owing to their high tendency to hydrolyse, the oxidation is carried out very cautiously using peracetic[48] and perphthalic[22] acids or an alkaline solution of potassium permanganate[48] as oxidants.

Owing to the low yields of the TS, this method of their synthesis has not been widely employed. A more convenient procedure for the synthesis of TS, both symmetrical and mixed, involves the introduction of an alkylthio- or arylthio-group into the molecule of bis(alkanesulphonyl)- or bis-(arenesulphonyl)-methane and its subsequent oxidation:[22,49,50]



R, R¹ = Alk, Ar .

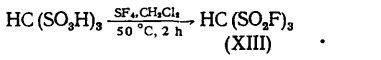
The reaction of alkanesulphonyl chlorides with TS in the presence of alkali metal alkoxides is a convenient method of synthesis of TS:[8,22,25,51]



Alk = Me, Et, $PhCH_2$.

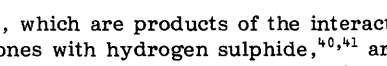
Many of the TS described in the literature, including those with a chiral carbon atom in the methylidyne group, have been synthesised by this method in satisfactory yields.[22,51] A limitation of this method consists in the impossibility of synthesising TS with three aromatic substituents, since arenesulphonyl chlorides do not enter into this reaction being weak electrophiles.

Methanetrisulphonyl fluoride has been obtained by treating methanetrisulphonic acid with sulphur tetrafluoride:[34]



3. Other Alkanes with Geminal Sulphonyl Groups

Alkanes (ethane, propane, etc.) containing geminal sulphonyl groups (GSG) at one end of the chain are obtained by alkylating DS having the necessary set of alkane- or arene-sulphonyl groups:[23,52]

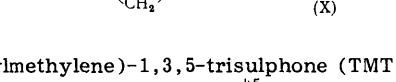


R = Me, Ph; R¹ = Me, Et; X = Hal, *p*-$MeC_6H_4SO_3$.

The ease of the alkylation of the DS makes it possible to synthesise alkanes containing GSG in the middle of the aliphatic chain by this procedure:[52]

X = Hal, *n* = 0, 1, 2 .

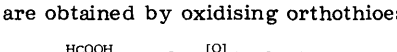
Certain ethane derivatives containing GSG are obtained analogously to disulphonylethane (I) by employing acetaldehyde instead of formaldehyde:[22]

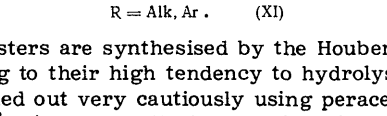


R = Me, Ph .

1,1,2,2-Tetrakis(methanesulphonyl)-1,2-bis(methanesulphonylthio)ethane has been obtained by the reaction of thiophosgene with sodium methanesulphinate.[53]

The Michael reactions of DS and TS with methyl vinyl sulphone[54] or 1,1-bis(arenesulphonyl)ethylenes lead to polysulphonylpropanes (XV)–(XVII). Compounds (XVII) have also been obtained by the reaction of DS with paraformaldehyde in the presence of bases:[55–59]

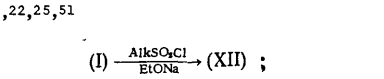




A pentane containing four benzenesulphonyl groups at the C(1) and C(5) atoms has been described.[57]

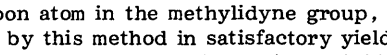
4. Unsaturated Compounds

Ethylenes with GSG have been described comparatively recently.[56,58,60,61] They were obtained by the thermal decomposition of Mannich bases obtained by condensing DS, formaldehyde, and a secondary amine (usually piperidine or pyrrolidine):



R = Alk, Ar.

The condensation of aromatic DS with aromatic aldehydes usually leads to 1,1,2-trisubstituted ethylenes:[60]



Aliphatic aldehydes condensed in this way give rise to isomerisation products together with normal products.[60] The reaction of bis(ethanesulphonyl)methane with benzaldehyde is accompanied by a rearrangement with degradation of the geminal functional group.[62]

The fluorine-containing 1,1-bis(ethanesulphonyl)-2,2-bis(trifluoromethyl)ethylene has been obtained by oxidising a fluorine-containing thioketal with trifluoroperacetic acid:[63]

The majority of ethylenes with 2,2-GSG containing reactive functional groups at C(1) were discovered after the successful development of the reaction of DS with ethyl orthoformate, which made available 2,2-disulphonyl-substituted ethyl vinyl ethers (XX):[62,64,65]

$$(I) + CH(OEt)_3 \xrightarrow[Ac_2O]{ZnCl_2} \underset{(XX)}{(RSO_2)_2C{=}CHOEt} ;$$
$$R = Alk, Ar .$$

The nucleophilic exchange of the ethoxy-groups, which takes place readily in these compounds, makes it possible to synthesise a wide variety of functional derivatives of ethylenes with 2,2-GSG.[64,65]

Polysulphonylethylenes were unknown until recently despite repeated attempts at their synthesis.[66-68] The report[69] of the synthesis of tetrakis(2-chloroethylsulphonyl)-ethylene [69] proved to be erroneous. Even the synthesis of the intermediate tetrakis(alkylthio)- and tetrakis(arylthio)-ethylenes presented considerable difficulties.[70,71] It was not until the end of the 1970's that a convenient and highly effective method was proposed for the synthesis of unsaturated tetrakis-sulphides from tetrachloroethane and thiolates in aprotic solvents (DMF, DMSO, HMP, etc.), significantly accelerating nucleophilic exchange, which made compounds of this class available:[72,73]

$$Cl_2C{=}CCl_2 \xrightarrow[DMF,\ DMSO,\ HMP]{RS^-} (RS)_2C{=}C(SR)_2 ;$$
$$R = Alk, Ar .$$

This reaction as a rule involves the formation of 10–15% of tris-derivatives. Tris- and tetrakis-sulphonylethylenes (TSE) were obtained by the same investigators[74] by oxidising the corresponding tetrakis-sulphides with trifluoroperacetic acid in methylene chloride:

$$(RS)_2C{=}C(SR)_2 \xrightarrow[CH_2Cl_2]{CF_3CO_3H} \underset{(XXI)}{(RSO_2)_2C{=}C(SO_2R)_2} .$$

Propenes with GSG have been synthesised[64,75,76] by condensing ethyl vinyl ethers containing geminal electron-accepting groups (one of which is the sulphonyl group) with DS in the presence of sodium alkoxide:

$$(I) + \begin{matrix} ArSO_2 \\ X \end{matrix}\!\!>\!C{=}CHCOEt \xrightarrow[EtOH]{EtONa} \begin{matrix} ArSO_2 \\ X \end{matrix}\!\!>\!C{=}CHCH(SO_2R)_2 ;$$
$$(XXII)$$
$$X = COPh, CN, R = Alk, Ar .$$

It is striking that the synthesis of 1,1,3,3-tetrasulphonylpropenes (XXII, X = RSO_2) by this procedure using 2,2-disulphonyl-substituted ethyl vinyl ethers is unsuccessful because of the high rate of the competing reaction involving the dissociation of the electron-deficient double bond in these ethers.

III. STRUCTURE AND PHYSICAL PROPERTIES

Geminal sulphones are high-melting colourless crystalline substances. They are insoluble in water; DS and TS with an unsubstituted methylidyne group dissolve in aqueous solutions of alkali or sodium carbonate.

The structure of tris(methanesulphonyl)methane has been determined by X-ray diffraction. The S–C–S angles (110.8 ± 0.4°) proved to be close to the tetrahedral value. The central C–S bonds are formally single with a length of 1.83 + 0.01 Å. The lengths of the other bonds are 1.43 ± 0.01 Å for S=O and 1.73 ± 0.02 Å for S–CH_3.[77,78] The structures of bis(*p*-bromobenzenesulphonyl)methane [79] and 2-(3-piperidinopropyl)-1,3-dithiane 1,1,3,3-tetraoxide [80] have been determined by X-ray diffraction.

The nature of the S=O bonds and the character of the interaction of the sulphonyl group with the rest of the molecule remain the most controversial questions in the chemistry of sulphones. The hypothesis that, apart from the σ-bond, there is additional d_π,p_π bonding between the S and O atoms so that S=O should be regarded as a (σ + π)-bond and not a semipolar bond has nowadays received increasing confirmation.[81-84] The dipole moments of a series of aromatic DS [85] suggest that the transoid conformation of these compounds is most stable, but their values (4.7–5.8 Å) preclude an unambiguous conclusion about the character of the sulphur–oxygen bond. The dipole moments of a series of aromatic unsubstituted aliphatic DS have been investigated.[86,87]

The question of the character of the interaction of the SO_2 group with aromatic and unsaturated groups in sulphones is insufficiently clear. Analysis of the IR spectra of a large number of different diaryl sulphones led to the conclusion that there is a weak interaction between the π electrons of the rings and the S=O bonds.[88] Raman spectroscopic data for aryl cyclopropyl sulphones revealed the presence of a barrier to electronic conduction generated by SO_2 groups as a result, according to the authors, of the absence of free electrons in such groups.[89] A marked weakening of the electronic influence of the substituent on the absorption frequency of the CF_3 group has also been observed in a series of *p*-substituted trifluoromethylthiobenzenes [90] and in *m*-trifluoromethylthiostyrene on oxidation of the sulphide sulphur atom to the SO_2 group.[90,91] The study of the photoelectron spectra of dimethyl, methyl vinyl, and divinyl sulphones showed that in the last two compounds there is conjugation between the π MO of the vinyl group and the MO of the SO_2 group. The conjugation effect is insignificant (0.2–0.3 eV) and the SO_2 group exhibits a strong inductive effect (~1 eV).[92] The inductive constants of alkane- or arenesulphonyl substituents (σ* = 0.57–0.60), determined by Charton[93] from the pK_a of aliphatic acids, also indicate a strong inductive effect of these groups. The constants σ*(SO_2CF_3) = 0.64 and σ*(SO_2F) = 0.86 are close to σ*[$N^+(Me)_3$] = 0.92.[94]

By virtue of the presence of characteristic intense absorption bands,[88] GS can be reliably identified with the aid of IR spectroscopy. The spectra of these compounds contain absorption bands characteristic of the S=O bond in the region of symmetrical (1120–1180 cm^{-1}) and asymmetric (1300–1380 cm^{-1}) stretching vibrations. Substituents of different nature in the rings of aromatic DS cause hardly any shift of the absorption bands of the SO_2 group.[28] The absorption bands of such groups in a series of unsaturated GS are in the same region.[58,63,65] The stretching vibration frequencies of the SO_2 groups are sensitive to the state of aggregation; they are higher by 10–20 cm^{-1} for the substances in solution than in the crystalline state. The solvent as a rule removes the band splitting which is frequently observed. The study of the IR spectra of 2,2-bis(arenesulphonyl)vinyl ethyl ethers[62,65] and 1,1-bis(arenesulphonyl)ethylenes [57] yielded direct evidence for the absence of conjugation of the SO_2 groups with the C=C double bond. The ^1H NMR spectra of a series of aromatic DS have been investigated.[95] The signals of the methylene protons are manifested by a narrow unresolved peak in the range 4–4.5 p.p.m. ($CDCl_3$) or 6–6.5 p.p.m. (DMSO). The downfield shift of the signals in DMSO can be accounted for by the formation of intermolecular hydrogen bonds between the substrate and the solvent (for a more detailed discussion of this problem, see Section IV). The effective correlation of the chemical shifts of the methylene protons with the Hammett σ constants led the authors to the conclusion, without ruling out the

possibility of the transmission of the substituent effect through space, that the electronic influence is transmitted via the SO_2 group with the possible participation of the 3*d* orbitals of sulphur in the formation of the S=O bond and that d_π, p_π conjugation is present. The ^{1}H NMR spectra of polysulphonylpropanes,[55] 1,1-bis(benzenesulphonyl)-ethylene,[58] and propenes containing GSG [75] have been published. The ^{13}C NMR spectrum of tetrakis(benzene-sulphonyl)ethylene has been published by Petukhova et al.[74]

α-Alkylated aromatic [96] and cyclic [97] DS have been used as convenient subjects for the study by ^{1}H NMR of the possibility of the formation of an intramolecular hydrogen bond between the hydrogen atom of the methylidyne group and the electron-donating group in the ω-position in the aliphatic chain. The OMe, $N(Me)_2$, $N(Et)_2$, piperidino-, and morpholino-groups were used as electron donors. The presence of an intermolecular hydrogen bond in compounds with two and three carbon atoms in the aliphatic chain has been demonstrated from the shift of the methylidyne proton signal.

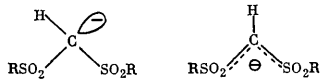
The mass-spectra of $PhCH_2SO_2CH_2SO_2Me$ have been investigated in order to confirm the mechanism of the rearrangement, analogous to the Ramberg–Bäcklund reaction of α-halogenosulphones, which takes place in compounds of this series.[98] The rearrangements of monosulphones induced by electron impact have been discussed in a review.[99]

IV. CH ACID PROPERTIES

The acid properties of DS and some of their derivatives were noted already in the first publications. Subsequently the acid properties of compounds activated by two (and more) sulphonyl groups as well as the study of factors influencing the stabilisation of the corresponding carbanions and their reactivity attracted much attention among investigators. The thermodynamic acidities of numerous DS and TS were determined experimentally, methods were developed for the generation of carbanions, and a study was made of the dependence of the reactivity of carbanions with GSG on the configuration of the carbon atom of the methylene or methylidyne group, on the molecular conformation, and on the 2*p*, 3*d* orbital interaction. The proton-donating activities of certain GS and the formation of hydrogen bonds with electron donors and their kinetic acidity were investigated.

1. Thermodynamic Acidity and Stabilisation of Carbanions

The reactivities of DS or TS as CH acids are determined by the ease of deprotonation (thermodynamic factor) and the rate of reaction of the carbanions formed (kinetic factor). Two extreme structures can be put forward for carbanions generated from DS–(A), where the charge is localised at the carbon atom, and (B), where the charge is fully delocalised over the sulphonyl groups:



(A) (B)

The nature of the RSO_2 substituents in the molecule of the initial CH acid and its geometry determine the degree of delocalisation of the charge in the carbanion. According to the molecular orbital perturbation theory, an increase in the degree of charge delocalisation entails a decrease of the energy of the highest occupied molecular orbital, an increase of the stability of the carbanion, a decrease of its nucleophilicity, and an increase of the acidity of the CH acid.

Titrimetric determination of the dissociation constants of DS have become part of the practical research routine after the introduction of electrochemical titration methods in non-aqueous media (potentiometry and conductimetry). Owing to the inadequate solubility in water of the majority of GS, the dissociation constants of many of them have been determined by potentiometric titration in organic solvents. The available literature data and the experimental acidity constants of DS in aqueous solutions are limited (Table 1).

Table 1. The acidity constants of DS (H_2O, 25 °C).

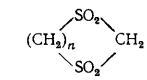
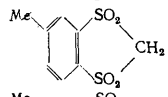
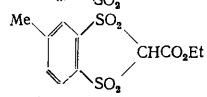
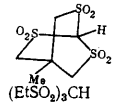
Compound	pK_a	Refs.
$(MeSO_2)_2CH_2$	12.50	[100]
$(PhSO_2)_2CH_2$	11.21;11.50	[100,101]
$(PhOSO_2)_2CH_2$	7.60	[102]
	13.9 (*n*=2)	[100]
	12.61 (*n*=3)	[100]
	11.75 (*n*=4)	[100]
	10.99 (*n*=5)	[100]
	13.00	[101]
	3.35	[101]
$(PhSO_2)_2CHCO_2Et$	4.60	[101]
	3.30	[103]
$(EtSO_2)_3CH$	≪3.30	[103]
$(CF_3SO_2)_2CH_2$	0.23	[32]

Table 2. The acidity constants of DS (DMF, 25 °C).[106,107]

No.	Compound	pK_a
1	$(PhSO_2)_2CH_2$	13.80
2	$(p\text{-}MeC_6H_4SO_2)_2CH_2$	14.16
3	$(p\text{-}ClC_6H_4SO_2)_2CH_2$	12.85
4	$(p\text{-}O_2NC_6H_4SO_2)_2CH_2$	10.43
5	$(4\text{-}EtNH\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$	13.84
6	$(4\text{-}PhNH\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$	13.25
7	$(4\text{-}Me\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$	12.30
8	$(4\text{-}Cl\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$	11.08
9	$(4\text{-}HO\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$	11.53
10	$(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4Me\text{-}p$	9.15
11	$(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4OEt\text{-}p$	9.32
12	$(p\text{-}MeC_6H_4SO_2)_2CHCSNHPh$	8.80
13	$(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4Cl\text{-}p$	8.25
14	$(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4Br\text{-}p$	8.20
15	$(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4I\text{-}p$	8.05
16	$(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4NO_2\text{-}p$	7.36

The principal relations between the conformation, configuration, and stability of the α-sulphonyl carbanion have been formulated in Cram's well known monograph[105] on the basis of the conformations of the α-sulphonyl-carbanion calculated by the molecular orbital method[104] and also the analysis of the thermodynamic stabilities of

sulphones (Table 1) and certain phenols with the SO_2R group.[100]

The acidity constants of GS have been determined by potentiometric titration in DMF [106,107] (Table 2). The pK_a values (compounds 1–4 and 5–9, Table 2) are satisfactorily correlated with the σ constants of the substituent ($\rho = 2.094$ and 2.557, $r = 0.995$ and 0.996, and $s = 0.192$ and 0.100 respectively).

Table 3. The acidity constants of substituted DS and TS (96% alcohol, 25 °C).[25]

Compound	pK_a	Compound	pK_a
$PhSO_2CH(SO_2Me)CN$	2.84	p-$MeC_6H_4SO_2CH(SO_2Me)COPh$	5.81
p-$MeC_6H_4SO_2CH(SO_2Me)CN$	2.78	p-$ClC_6H_4SO_2CH(SO_2Me)COPh$	4.77
p-$ClC_6H_4SO_2CH(SO_2Me)CN$	2.83	$PhSO_2CH(SO_2Me)COOEt$	6.06
$(EtSO_2)_2CHSO_2Me$	2.99	p-$MeC_6H_4SO_2CH(SO_2Me)COOEt$	6.36
$(PhSO_2)_2CHSO_2Me$	3.00	p-$ClC_6H_4SO_2CH(SO_2Me)COOEt$	5.24
$(p$-$MeC_6H_4SO_2)_2CHSO_2Me$	3.06	$PhSO_2CH(SO_2Me)CONH_2$	7.51
$(p$-$ClC_6H_4SO_2)_2CHSO_2Me$	2.95	p-$MeC_6H_4SO_2CH(SO_2Me)CONH_2$	7.65
$PhSO_2CH(SO_2Me)COPh$	5.32	p-$ClC_6H_4SO_2CH(SO_2Me)CONH_2$	7.00

Table 4. The acidity constants of substituted propenes p-$RC_6H_4SO_2C(CN)=CHCH(SO_2R^1)_2$ (25 °C).[75,76]

R	R^1	pK_a	
		acetone	96% alcohol
H	Et	−0.94	2.76
Me	Et	−1.10	2.76
Cl	Et	−1.57	2.70
H	Ph	−0.94	2.81
H	p-MeC_6H_4	−0.54	—
H	p-ClC_6H_4	−1.90	—
Me	Ph	−0.74	2.81
Me	p-MeC_6H_4	−0.49	—
Cl	p-ClC_6H_4	−1.29	2.79
Cl	p-MeC_6H_4	−1.00	—

The character of the change in the acid properties of asymmetric DS when the hydrogen atom of the methylene group is substituted by a third electron-accepting group has been investigated[25] (Table 3) and the authors established that the electronic nature of the substituents in the p-position in the aromatic ring of the SO_2Ar group has little influence on the acidity of the compound, while the introduction of a third electron-accepting substituent at the methylidyne carbon atom greatly increases it. In terms of their effect on the acidity of $MeSO_2CH(R)SO_2Ph$, the substituents at the α-carbon atom can be arranged in the sequence $CN \geq SO_2Ph \gg COPh > COOEt > CONH_2$. The acid properties of propenes with GSG (Table 4) have been studied in order to compare them with the acidity of DS containing electron-accepting substituents in the α-position (Table 3) and in order to elucidate the nature of the activating effect of the vinyl group with two electron-accepting substituents at the β-carbon atom.[75,76] The propenes (Table 4) are strong CH acids. The delocalisation of the charge and the stabilisation of the corresponding carbanions are achieved by virtue of the $-I$ effects of the arene- or alkane-sulphonyl groups and the $-M$ effect of other electron-accepting substituents.

The first quantitative study of the selective solvation of aliphatic DS by ^1H NMR in mixed aqueous binary systems (1,4-dioxan–H_2O, 1,3-dioxan–H_2O, and dimethoxyethane–H_2O) was carried out by Remerie and Engberts.[108]

2. The Proton-Donating Capacity and Kinetic Acidity

Studies carried out during the last decades have shown that the C–H groups polarised by strong electron-accepting substituents form hydrogen bonds (HB) as proton donors.

Table 5. Thermodynamic characteristics of the hydrogen bonds with DMSO, acetone, and pyridine.[109,110]

No.	Compound	DMSO		Acetone		
		$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1}K^{-1}	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1}K^{-1}	pK_a
1	$(PhSO_2)_2CH_2$	9.2	20.9	12.6*	31.0*	11.2
2	p-$ClC_6H_4SO_2CH(COPh)SO_2Me$	13.8	23.0	10.5	20.9	4.77
3	$PhSO_2CH(COPh)SO_2Me$	14.2	25.5	9.6	18.0	5.32
4	p-$MeC_6H_4SO_2CH(COPh)SO_2Me$	12.6	21.3	10.0	21.3	5.81
5	p-$ClC_6H_4SO_2CH(COOEt)SO_2Me$	10.9	16.7	11.3	21.3	5.24
6	$PhSO_2CH(COOEt)SO_2Me$	10.9	18.8	9.6	23.4	6.06
7	p-$CH_3C_6H_4SO_2CH(COOEt)SO_2Me$	10.9	19.2	10.5	22.2	6.36

*In pyridine.

The strength of the $R_nCH_{4-n}\ldots B$ bonds depends both on the nature and number of substituents R and on the electron-donating capacity of the base B. The proton donating capacity of bis(benzenesulphonyl)methane in the formation of HB with DMSO and pyridine and also of the trisubstituted methanes ($MeSO_2$) (p-$XC_6H_2SO_2$)CHR in similar reactions with acetone and DMSO has been studied by ^1H NMR in the series of GS.[110] It follows from the results presented in Table 5 that the enthalpy of the HB formed by the compounds investigated with DMSO is in the range 9.2–14.2 kJ mol^{-1}. The strength of the HB between trisubstituted methanes and DMSO is higher, in conformity with their more acid character, than for bis(benzenesulphonyl)methane. However, in the series of trisubstituted methanes there is no general relation between the quantities K_a and ΔH embracing all the compounds investigated. The kinetics and thermodynamics of proton transfer from trisubstituted methane to γ-collidine have been investigated by ^1H NMR in CD_2Cl_2 by Pogorelyi et al.[111,112], while the kinetics of the proton exchange in the trisubstituted methane–triethylamine systems have been investigated by the same workers in Ref. 113. According to their data,[111] the proton transfer to γ-collidine is preceded by the formation of hydrogen-bonded complexes:

$$\geq CH + N \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \geq CH \ldots N \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \geq C^- \ldots HN^+ \diagup .$$

The proton transfer is completed by the formation of an ion pair which does not dissociate in CD_2Cl_2 (having a low dielectric constant ε) and is a kinetically independent species. The results of calculations of the kinetic and thermodynamic characteristics are presented in Table 6.

According to Table 6, the activation energies for deprotonation E_+ are significantly smaller for all the compounds investigated than the values of E_- characterising

the reverse process; this shows that the proton abstraction reaction is exothermic ($\Delta Q < 0$). The characteristics of the equilibrium ($\lg K$ and ΔQ) vary in parallel with the equilibrium acidity (pK_a). The authors[111] believe that, since the degree of delocalisation of the free electron pair in the carbanion is high in the DS investigated, the transition state of the reaction is reactant-like according to Hammond's postulate, i.e. the degree of proton transfer in the transition state is low. The conjugation effect is therefore manifested mainly in the anion and not in the transition state of the deprotonation reaction of the CH acid, which induces an increase of E_-. The small change in E_+ in the series of compounds investigated is evidence for an insignificant difference in the effect of the substituents PhCO and COOEt on the polarity and strength of the C–H bond. On the other hand, in conformity with their mesomeric effects, these substituents affect significantly the protonation energy of the carbanion E_-. In the series of compounds with identical R, the substituents X also have a greater effect on E_- than on E_+. Consequently substituents influence mainly the kinetic characteristics of the protonation of the carbanion and have a very weak effect on the rate of deprotonation of the acid. Analysis of the relations between pK_a, E_+, E_-, and k_+ (the kinetic acidity of R_3CH) or k_- (the kinetic basicity of R_3C^-), carried out in the above study,[111] permits the conclusion that the equilibrium acidity of R_3CH^- is determined mainly by the stability of the carbanion and depends to a much lesser extent on the strength and polarity of the C–H bonds.

Table 6. Thermodynamic and kinetic characteristics of the proton transfer from the DS p-$XC_6H_4SO_2CH(R)SO_2Me$ to γ-collidine.[111]

No.	X	pK_a (alcohol)	$\lg K^{293}$	$-\Delta Q$, kJ mol^{-1}	$-\Delta S$, J mol^{-1}K^{-1}	$\lg k_+^{293}$	E_+, kJ mol^{-1}	$\lg A_+$	$\lg k_-^{293}$	E_-, kJ mol^{-1}	$\lg A_-$
1	PhCOCl	4.77	2.8	52	120	3.8	22	8	1.0	74	14
2	PhCOMe	5.81	1.7	37	92	3.3	27	8	1.6	63	13
3	COOEtCl	5.24	1.9	32	76	5.7	18	9	3.8	51	13
4	COOEtMe	6.36	0.9	24	62	5.1	17	8	4.2	41	12

The observed relations were interpreted by the same workers[112] in terms of the Bell–Evans–Polanyi potential curves, which confirmed that there is no general relation between the thermodynamic or kinetic acidity and the strength of the HB with DMSO (ΔH) in the series of trisubstituted methanes with GSG.

The experimental data obtained in the study of the kinetics of proton exchange in the $(MeSO_2)(p\text{-}XC_6H_4SO_2)CHR$–triethylamine (R = COPh or COOEt) systems by ^1H NMR in CD_2Cl_2 made it possible to establish the mechanism of the process.[113]

V. REACTIVITY

The reactivities of the majority of GS are determined by the activating influence of the sulphonyl groups. DS and TS as well as certain higher alkanes activated by GSG as CH acids are involved in the chemical reactions as a rule in the form of the conjugated bases (carbanions), so that electrophilic substitution reactions are characteristic of the compounds enumerated above. The activation of the double bond in unsaturated GS is responsible for the ease of the nucleophilic substitution and addition reactions in the series of these compounds.

1. Electrophilic Substitution Reactions

(*a*) *Salts and complex formation.* Alkali metal salts are formed when DS are treated with the corresponding hydroxides or alkoxides:[12,52,114]

$$\underset{\text{(I)}}{} + MOH \rightarrow \underset{\text{(XXIII)}}{(RSO_2)_2\bar{C}HM^+} + H_2O\ ;$$

$$R = Alk, Ar;\ M = Li, Na, K, NH_4\ .$$

In the series of DS the second hydrogen atom of the methylene group is not substituted by a metal even when strong bases (BuLi) are used.[115] The silver salt of methanedisulphonyl fluoride was isolated after prolonged refluxing of the latter with silver oxide in anhydrous ether in the presence of a zeolite.[34] Bis(benzenesulphonyl)-methylmagnesium bromide has been obtained by the reaction of the corresponding DS with butenylmagnesium bromide in ether.[115] The salt-forming reaction between bis(benzenesulphonyl)methane and monoethanolamine has been investigated.[117]

Being stronger CH acids, trisulphones form salts with alkali metal or alkaline earth metal hydroxides, alkoxides, and carbonates[118] and also with organic bases.[119] The salts of tris(methanesulphonyl)methane with the NH_4^+, Li^+, K^+, Rb^+, Cs^+, and Tl^+ anions have been obtained for crystallographic analysis.[120] The salts $M[C(SO_2Et)_3]_2.6H_2O$ (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, or Cd^{2+}) have been prepared by heating aqueous suspensions of the metal carbonate and the TS. The manganese and cobalt salts react with pyridine (Py) and phenanthroline (L) to form the complexes $M(Py)_2.[C(SO_2Et)_3]_2$ and $[ML]_3.[C(SO_2Et)_3]_2$.[121]

In order to investigate the reactivities of the metal cation–carbanion ion pairs, the complexes of the sodium salts of TS with 15-crown-5-ether and of the potassium salt of bis-(benzenesulphonyl)methane with 18-crown-6-ether were synthesised.[122] These complexes proved to be relatively unreactive; this can be explained by the formation of a close ion pair comprising the anion and a complex cation, which creates steric hindrance to attack by the electrophile. TS give rise to high yields of tetra-alkylammonium salts on interaction with tetra-alkylammonium halides in the CH_2Cl_2–H_2O two phase system in the presence of alkali.[123]

(*b*) *Alkylation and sulphenylation.* The ion pair comprising aromatic and aliphatic DS $(RSO_2)_2CH^-M^+$ (XXIII) (M = alkali metal) is readily alkylated by alkyl halides to form mono- and di-alkyl derivatives:

$$\text{(XXIII)} \xrightarrow{R^1X} \underset{\text{(XIV)}}{(RSO_2)_2CHR^1}\ ;$$

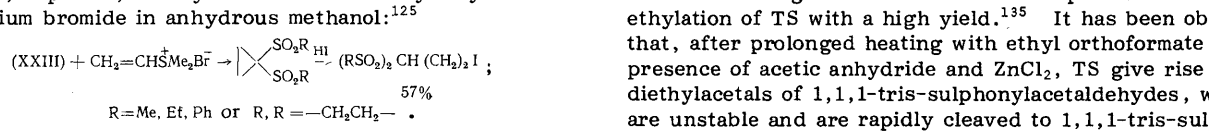
$$\text{(XXIII)} \xrightarrow{2R^1X} (RSO_2)_2CR^1_2\ ;$$

$$R^1 = Alk;\ X = Cl, Br, I\ .$$

2,2-Bis(benzenesulphonyl)propane has been isolated after the alkylation of bis(benzenesulphonyl)methane with methyl iodide in absolute alcohol in the presence of sodium ethoxide:[52] the analogous reaction with benzyl chloride (THF–hexane, BuLi) yields the monoalkylation product.[115] The silver salts of methanedisulphonyl fluoride[34] and bis-(trifluoromethanesulphonyl)methane[32] react with one molecule of the alkylating agent, while cyclic trimethylene

trisulphone (X) reacts with alkyl iodides in an aqueous-alcoholic alkaline solution to form hexa-alkyl-substituted derivatives.[45,124]

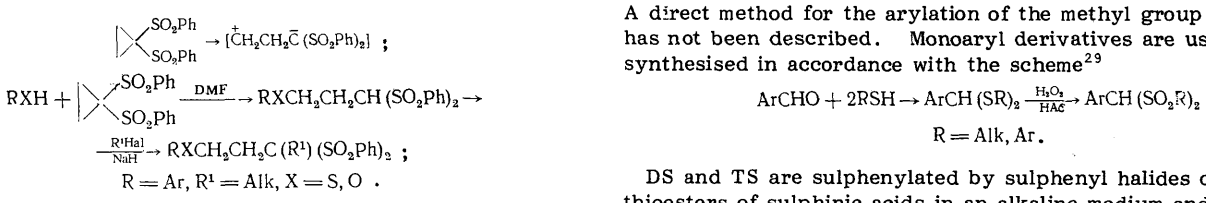
Cyclic alkylation products, derivatives of cyclopentane, have been obtained by the reaction of the sodium salts of aromatic, aliphatic, and cyclic DS with dimethylvinylsulphonium bromide in anhydrous methanol:[125]



(XXIII) + $CH_2{=}CH\overset{+}{S}Me_2Br^-$ → (XXIII) — $(CH_2)_2$ — (XXIII) ; 57%

R = Me, Et, Ph or R, R = $-CH_2CH_2-$.

When cyclopropanes are refluxed with hydriodic acid, 1,1-disubstituted 3-iodopropanes are formed. 1,1-Bis(benzenesulphonyl)cyclopropane reacts as the 1,3-dipolar ion:[126]



$$\text{RXH} + \text{(XXIII)} \xrightarrow{\text{DMF}} \text{RXCH}_2\text{CH}_2\text{CH}(\text{SO}_2\text{Ph})_2 \rightarrow \text{RXCH}_2\text{CH}_2\text{C}(\text{R}^1)(\text{SO}_2\text{Ph})_2 \ ;$$

$$\xrightarrow[\text{NaH}]{\text{R}^1\text{Hal}}$$

R = Ar, R^1 = Alk, X = S, O .

In the presence of sodium alkoxide, methylthiobis(methanesulphonyl)methane is alkylated by allyl bromide:[120]

$$(\text{MeSO}_2)_2\text{CHSMe} \xrightarrow[\text{EtONa}]{\text{CH}_2{=}\text{CHCH}_2\text{Br}} (\text{MeSO}_2)_2\text{C}(\text{SMe})\text{CH}_2\text{CH}{=}\text{CH}_2 \ .$$

The alkylation of bis(benzenesulphonyl)methane by dienes in the presence of catalysts has been investigated.[127]

In the study of the reaction of phenylmethanesulphonyl fluoride with phenyl-lithium, Shirota et al.[128] isolated α-benzenesulphonyl-α-phenylmethanesulphonyltoluene, whose formation can be explained by the competition of two processes occurring in this reaction: nucleophilic substitution at the sulphur atom and metallation of the methylene group:

$$\text{PhCH}_2\text{SO}_2\text{F} \xrightarrow{\text{PhLi}} \text{PhCH}_2\text{SO}_2\text{Ph} + \text{PhCHLiSO}_2\text{F} \ ;$$

$$\text{PhCH}_2\text{SO}_2\text{Ph} \xrightarrow{\text{PhLi}} \text{PhCHLiSO}_2\text{Ch} \xrightarrow{\text{PhCH}_2\text{SO}_2\text{F}} \text{PhCH}_2\text{SO}_2\text{CH}(\text{Ph})\,\text{SO}_2\text{Ph}.$$

Disulphones are readily alkylated by αβ-unsaturated compounds under the conditions of the Michael reaction. Aliphatic DS combine with two molecules of an αβ-unsaturated compound and aromatic DS combine with one such molecule.[54,129,130] γγ-Bis(arenesulphonyl)butyric and 4,4-bis(ethanesulphonyl)pimelic acid and many of their derivatives have been synthesised[129,130,131] by the reaction involving the addition of acrylonitrile to aromatic DS [129] and bis(ethanesulphonyl)methane.[130] The reactions of trimethylenetrisulphone (X) [132] and its derivatives[133] with acrylonitrile, ethyl acrylate, and 2-vinylbenzothiazole have been investigated. The alkylation of bis(benzenesulphonyl)-methane by the salt of a Mannich base, namely the hydrochloride of 1-dimethylamino-2-(2-thenoyl)ethane, which takes place with elimination of the amine, has been described.[134]

In contrast to DS, trisulphones are alkylated with difficulty, which can apparently be accounted for by the much lower nucleophilicity of their carbanions. The yield of 1,1,1-tris(methanesulphonyl)ethane in the reaction of the sodium salt of tris(methanesulphonyl)methane with methyl iodide is extremely low (3.6%).[120] The interaction of the silver salt of tris(benzenesulphonyl)methane with methyl iodide[118] and bromotris(methanesulphonyl)methane with methylmagnesium bromide[120] does not lead to methylation products. The products of the alkylation of TS are therefore obtained by alkylating alkyl- or aryl-thio-derivatives of DS or by sulphenylating alkylated DS with subsequent oxidation of the reaction products:[120]

$$\left.\begin{matrix}(\text{MeSO}_2)_2\text{CHSMe} \xrightarrow{\text{MeI}} \\ (\text{MeSO}_2)_2\text{CHMe} \xrightarrow{\text{MeSSO}_2\text{Me}}\end{matrix}\right\} \rightarrow (\text{MeSO}_2)_2\text{C}(\text{Me})\,\text{SMe} \rightarrow$$

$$\xrightarrow{\text{H}_2\text{O}_2} (\text{MeSO}_2)_3\text{CMe}.$$

An interesting method has been developed for the ethylation of TS with a high yield.[135] It has been observed that, after prolonged heating with ethyl orthoformate in the presence of acetic anhydride and $ZnCl_2$, TS give rise to the diethylacetals of 1,1,1-tris-sulphonylacetaldehydes, which are unstable and are rapidly cleaved to 1,1,1-tris-sulphonylpropanes and ethyl formate:

$$(\text{RSO}_2)_3\text{CH} \rightarrow [(\text{RSO}_2)_3\text{CCH}(\text{OEt})_2] \rightarrow (\text{RSO}_2)_3\text{CEt} + \text{HCOOEt} \ ;$$

R = Alk, Ar .

A direct method for the arylation of the methyl group in DS has not been described. Monoaryl derivatives are usually synthesised in accordance with the scheme[29]

$$\text{ArCHO} + 2\text{RSH} \rightarrow \text{ArCH}(\text{SR})_2 \xrightarrow[\text{HAc}]{\text{H}_2\text{O}_2} \text{ArCH}(\text{SO}_2\text{R})_2 \ ;$$

R = Alk, Ar.

DS and TS are sulphenylated by sulphenyl halides or the thioesters of sulphinic acids in an alkaline medium and the reaction proceeds as a rule more readily (particularly in the series of TS) than alkylation, since sulphenylating agents are stronger electrophiles. The reactions of DS with the thioesters of sulphinic acid[120,136,137] and sulphenyl chlorides[118,120,136] and of the silver salt of methanedisulphonyl fluoride with pentafluorobenzenesulphenyl chloride[34] have been described:

$$\text{(I)} \xrightarrow[\text{EtONa}]{\text{R}^1\text{SCl(R}^1\text{SSO}_2\text{R}^2)} \underset{\text{(XXIV)}}{(\text{RSO}_2)_2\text{CHSR}^1} \ ;$$

R = Me, Ph; R^1 = Me, $PhCH_2$, Ph; R^2 = Me, Ph, $(Ph)_2CH$.

DS can be alkane- and arene-sulphenylated in steps with formation of mono- and di-thio-derivatives.[120,137] TS are sulphenylated under the same conditions.[120]

The thioarylation[138] and selenoarylation[139] of bis(benzenesulphonyl)methane has been achieved in alkaline media by treatment with diaryl sulphide selenides (ArSSeAr) and diaryl diselenides (ArSeSeAr):

$$(\text{PhSO}_2)_2\text{CH}_2 + \text{RC}_6\text{H}_4\text{XSeC}_6\text{H}_4\text{R} \xrightarrow{\text{EtONa}} (\text{PhSO}_2)_2\text{CHXC}_6\text{H}_4\text{R} \ ;$$

R = H, *m*- or *p*-Me, *o*- or *p*-Cl, *m*- or *p*-NO_2, *p*-Br, *p*-MeO; X = S, Se.

The alkyl- and aryl-thiomethylation of aliphatic and aromatic DS by condensation with mercaptans and formaldehyde in alkaline media has been described:[140]

$$\text{(I)} + \text{CH}_2\text{O} + \text{R}^1\text{SH} \xrightarrow{\text{NaOH}} (\text{RSO}_2)_2\text{CHCH}_2\text{SR}^1 \ ;$$

R = n-Bu, Ph, cyclohexyl; R^1 = alkyl, aryl.

Bis(benzenesulphonyl)methane is more reactive in this reaction than its aliphatic analogue. When the merceptan is replaced by potassium hydrogen sulphide, 1,1,5,5-tetrasulphonyl-3-thiapentanes are formed:[141]

$$\text{(I)} \xrightarrow[\text{dioxan,MeOH,H}_2\text{O}]{\text{CH}_2\text{O,KSH}} [(\text{RSO}_2)_2\text{CHCH}_2]\text{S}_2 \ ;$$

20°, 12 h, R = alkyl, aryl.

The reaction of bis(methanesulphonyl)methane with carbon disulphide in DMSO in the presence of t-BuOK (20 °C, N_2) and subsequent methylation of the reaction product with methyl iodide lead to 1,1-bis(methanesulphonyl)-2,2-bis(methylthio)ethylene:[68]

$$(\text{MeSO}_2)_2\text{CH}_2 \xrightarrow[\text{t-BuOK, DMSO}]{\substack{1)\text{CS}_2 \\ 2)\text{MeI}}} (\text{MeSO}_2)_2\text{C}{=}\text{C}(\text{SMe})_2 \ .$$

The hydrolysis of mono- and di-mercapto-substituted DS in the presence of bases (NaOH, piperidine) and acids (HCl, H_2SO_4) proceeds with successive elimination of alkyl- or aryl-thio-groups. Sulphinic acids, diaryl and dimethyl thiocarbonates, thioesters of sulphinic acids, and dialkyl disulphides have been found among the reaction products:[142]

Tris(methanesulphonyl)methanes with a substituent at the carbon atom of the methylidyne group split off one $MeSO_2$ group on heating in an alkaline medium:[120]

$$(MeSO_2)_3CX \xrightarrow{H_2O,NaOH} (MeSO_2)_2CHX + MeSO_3Na\ ;$$
$$X = Me, Ph, MeS, NO_2\ .$$

The hydrolysis of substituted tris(methanesulphonyl)-methanes in the presence of organic bases has been investigated.[143]

(c) *Halogenation. Properties of halogeno-derivatives.* In aqueous alkaline media DS and TS are halogenated by freshly prepared hypohalites,[32,46,114,118,130,144,145] while in organic solvents (CCl_4–$CHCl_3$ mixture,[144] acetic acid[146]) they are halogenated by elemental halogens (Cl_2, Br_2). In a series of DS the ease of the halogenation reaction creates appreciable difficulties in the synthesis of the monohalides. They are obtained by treating the substrate in dilute aqueous alkaline solutions with an equimolar amount of a hypohalite[114,130] and by halogenating a DS salt with elemental halogen in an organic solvent.[32] The monohalides of DS have also been synthesised by halogenating the esters of bis(sulphonyl)acetic acids:[26]

$$\underset{(V)}{(RSO_2)_2CHCOOR^1} \xrightarrow{Hal_2} (RSO_2)_2CHalCOOR^1 \xrightarrow[-R^1OH]{H_2O} \rightarrow (RSO_2)_2CHalCOOH \xrightarrow[-CO_2]{} \underset{(XXV)}{(RSO_2)_2CHHal}\ ;$$
$$R = Alk, Ar;\ Hal = Cl, Br\ .$$

The halogenation of trimethylenetrisulphone (X) in aqueous alkaline media leads to the formation of hexahalogeno-derivatives.[124,147] Disulphones containing a third electron-accepting substituent (NO_2, COMe) at the α-carbon atom are readily hydrogenated by hypohalites,[29,148] but the acetyl group is not then eliminated.[148]

The silver salt of methanetrisulphonyl fluoride (XIII) is brominated and iodinated in Khladon 113 with formation of tris(fluorosulphonyl)halogenomethanes.[134] tris(Fluoro-sulphonyl)iodomethane is the first iodo-derivative of DS and TS described in the literature. Halogenation with hypo-halites in an aqueous alkaline medium is a very rapid process mainly owing to the high concentration of the electrophilic Br^+ species and the "carbanionic state" of the substrate. Halogenation in organic solvents with elemental halogens proceed much more slowly. Tris(ethanesulphonyl)methane is brominated in acetic acid much more slowly than its potassium salt;[146] the addition of water accelerates the process.

Certain monobromo-derivatives of DS can be synthesised by disproportionation into the dibromo-derivative of the DS and an unsubstituted compound.[145] Tribromotrimethylene-trisulphone has been obtained by the reaction of TTS hexa-bromide and the unsubstituted TTS.

The equilibrium in the disproportionation reaction of a mixture of $(RSO_2)_2CH_2$ and $(RSO_2)_2CHal_2$ with formation of $(RSO_2)_2CHHal$ (R = alkyl or aryl) has been investigated.[26] It is noted that the disproportionation is reversible and proceeds more readily for the bromo-derivatives than for the chloro-derivatives.

Bromination of bis(ethanesulphonyl)methane by hypo-bromite in an aqueous alkaline medium is a reversible process; the equilibrium at 20 °C is displaced towards the formation of the dibromo-derivative:[130]

$$\underset{10\%}{(EtSO_2)_2CH_2} \underset{OH^-}{\overset{KBrO}{\rightleftarrows}} \underset{30\%}{(EtSO_2)_2CHBr} \underset{OH^-}{\overset{KBrO}{\rightleftarrows}} \underset{60\%}{(EtSO_2)_2CBr_2}\ .$$

The properties of the DS and TS halides are determined by the character of the C–Hal bond in these compounds. By virtue of the strong electron-accepting effect of the sulphonyl groups on the polarisation of the C–Hal bond, the halogen atom becomes the positive end of a dipole, assumes a cationoid character, and is capable of breaking off in the form of a cation. The mono- and di-bromo-derivatives of DS are reduced by iodide ions and can be determined quantitatively by iodometric titration.[114,130,144] The chloro-derivatives of TS also have this property:[144]

$$\rangle C{-}Hal + 2NaI \xrightarrow[25°C]{MeCN} \rangle CNa + I_2 + NaHal\ ;$$
$$Hal = Br, Cl\ .$$

DS and TS bromides are brominating agents which brominate *NN*-dimethylaniline [144] and toluene (in the presence of $AlCl_3$).[32] Hexabromotrimethylenetrisulphone has analogous properties.[149] DS mono- and di-bromides and TS chlorides and bromides react with alkalis to form DS or TS salts and hypohalites.[29,114] The hexachloro- and hexabromo-deriva-tives of trimethylenetrisulphone and the trichloro- and tribromo-derivatives of tris(methylmethylene)trisulphone react with organic bases (pyridine, αα-bipyridyl, quinoline, piperidine, and morpholine) to form complexes having the composition $(CHal_2SO_2)_3.(Nu)_n$ and $(MeCHalSO_2)_3(Nu)_n$ (Nu = organic base, n = 2, 3, 5),[150,151] which have the structure of quaternary ammonium salts according to the authors. The reaction of dibromobis(methanesulphonyl)-methane with copper powder is a radical process among the products of which tris(methanesulphonyl)methane was found.[152] The monohalogeno-derivatives of DS are stronger CH acids than the unsubstituted compounds, although the acidifying effect of chlorine and bromine is small.[26] They are alkylated by diazomethane [26] and in the presence of bases they react with alkyl halides and benzenesulphenyl chloride.[26] The monochloro-derivatives of aromatic DS react in an aqueous alkaline medium with arenediazonium salts to form bis(arenesulphonyl)arylazochloromethanes [114] and they combine with acrylonitrile.[152]

$$\underset{(XXVI)}{(ArSO_2)_2CHCl} \begin{cases} \xrightarrow{ArN_2^+} (ArSO_2)_2CClN{=}NAr\ ; \\ \xrightarrow{CH_2=CHCN} (ArSO_2)_2CClCH_2CH_2CN\ . \end{cases}$$

The bromine atom in bromobis(trifluoromethanesulphonyl)-methane (XXVI) is more mobile than the hydrogen atom of the methylidyne group and is involved in the Michael reaction with αβ-unsaturated compounds instead of the latter:[32]

$$\underset{(XXVI)}{(CF_3SO_2)_2CHBr} + CH_2{=}CHR \rightarrow (CF_3SO_2)_2CHCH_2CHBrR\ ;$$
$$R = CH_2CH_2Cl\ (70\%),\ CH_2COOH\ (50\%),\ C_6H_{13}\ (32\%)\ .$$

The interaction of the bromo-derivative (XXVI) with Na_2CO_3 at 150 °C leads to the formation of only the sodium salt of the initial CH acid instead of the expected 1,1,2,2-tetrakis-(trifluoromethanesulphonyl)ethylene (by analogy with the reaction of bromomalonic ester).[32]

(d) *Nitration.* As shown above (Section II), DS are not nitrated at the methylene group in sulphuric acid, since a reactive carbanion is absent from such a solution. In the

series of TS, which are stronger CH acids, the carbanionic character of the carbon atom of the methylidyne group is more pronounced and they can be nitrated by the usual nitrating mixture. The low nucleophilicity of TS is compensated by the strength of the electrophile (nitronium cation). Tris-(methanesulphonyl)nitromethane has been obtained in high yields by the nitration of tris(methanesulphonyl)methane (XI) (100 °C, 15 min):[120]

$$(XI) \xrightarrow{HNO_3,H_2SO_4} (MeSO_2)_3CNO_2 \ .$$

It has been shown that, in the nitration of mixed TS, the aromatic ring of the arenesulphonyl groups are first nitrated, while at elevated temperatures the methylidyne group is also nitrated:[154]

$$(4\text{-}RC_6H_4SO_2)_2CHSO_2Me \xrightarrow[20°C]{HNO_3,H_2SO_4} \underset{(XXVII)}{(4\text{-}R\text{-}3\text{-}O_2NC_6H_4SO_2)_2C(NO_2)SO_2Me} \ ;$$

R=H, Me, Cl .

Disulphones with a strong electron-accepting substituent at the carbon atom of the methylidyne group have acidities similar to those of TS and are nitrated under analogous conditions:[154]

$$4\text{-}MeC_6H_4SO_2CH(CN)SO_2Me \xrightarrow{HNO_3,H_2SO_4} \rightarrow \underset{(XXVIII)}{4\text{-}Me\text{-}3\text{-}O_2NC_6H_4SO_2C(NO_2)(CN)SO_2Me} \ .$$

The nitromethanes (XXVII) and (XXVIII) undergo hydrolytic cleavage fairly readily. As a consequence of the steric hindrance arising as a result of the repulsion of the non-bonded oxygen atoms of the sulphonyl and nitro-groups, the loss of one of these groups reduces the free energy of the system. Furthermore, the presence of four strong electron-accepting substituents increases the electro-negativity of the carbon atom in the molecules of compounds (XXVII) and (XXVIII), since in each of them the substituent is somewhat less electronegative than in compounds not containing additional electron-accepting groups. The least electronegative of the four substituents (in the given case the methanesulphonyl group) can therefore be subjected to nucleophilic attack and, after the elimination of this substituent, a carbanion, stabilised by the three strong electron-accepting substituents, is formed. Even on heating in 8% aqueous $NaHCO_3$ solution, compounds (XXVII) split off the methanesulphonyl group and their treatment with freshly prepared potassium hypobromite in addition to the bromination of the intermediate carbanion.[154] On reaction with KBrO, the nitromethanes (XXVIII) also split off the $MeSO_2$ group with subsequent bromination of arene-sulphonylcyanonitromethane.[154]

Hydrolysis of tris(methanesulphonyl)nitromethane in the presence of alkali affords bis(methanesulphonyl)nitro-methane,[29] which reacts with chlorine and bromine in an alkaline medium[29] and reacts with Ag_2CO_3 as a strong CH acid to form a silver salt, which reacts with methyl iodide to produce 1,1-bis(methanesulphonyl)-1-nitroethane.[153,155]

(*e*) *Reactions with arenediazonium salts* Disulphones with a free methylene group interact with arenediazonium salts in alkaline media (pH 8–13). Depending on the structure of the DS and the diazonium salt, the reaction conditions and the reactant ratio, the interaction can proceed with formation of one or several reaction products. In the first studies devoted to this reaction,[156,157] it was already shown that aromatic TS react with diazonium salts to form the azo-coupling product

$$(I) \xrightarrow{ArN_2} \underset{(XXIX)}{(RSO_2)_2CHN{=}NAr} \rightleftarrows \underset{(XXX)}{(RSO_2)_2C{=}NNHAr} \ ;$$

R=Ph .

An unambiguous choice between the two possible structures (XXIX) and (XXX) was not made and it was shown only later that[158] the products of the coupling of DS and other methylene compounds to diazonium salts have the hydrazone structure (XXX). In his study of the reaction of bis-(benzenesulphonyl)methane with *p*-nitrobenzenediazonium tetrafluoroborate in a weakly alkaline medium (pH 8.2), Hunig[159] isolated three reaction products: *p*-nitrophenyl-hydrazone of bis(benzenesulphonyl)carbonyl (XXXI), *N*-benzenesulphonyl-*N'*-(*p*-nitrophenyl)diimide (XXXII), and 5-hydroxy-1,3-di(*p*-nitrophenyl)tetrazolium betaine (XXXII):

$$(I) \xrightarrow{p\text{-}O_2NC_6H_4N_2^+BF_4^-} \underset{(XXXI)}{(PhSO_2)_2C{=}NNHC_6H_4NO_2\text{-}p} +$$

$$+ \underset{(XXXII)}{p\text{-}O_2NC_6H_4N{=}NSO_2Ph} + \underset{(XXXIII)}{p\text{-}O_2NC_6H_4{-}\overset{+}{N}{=}N\text{-}C(=N\text{-}C_6H_4NO_2\text{-}p)\text{-}O^-} \ .$$

A mechanism of the formation of the betaines (XXXIII) has been proposed[159] on the hypothesis of a higher reactivity of the NH group of the hydrazone (XXXI) which is formed in the first stage and reacts with a second molecule of the diazonium salt to form the "*N*-azo-derivative" (XXXIV). The rapid hydrolysis of the arenesulphonyl groups in the product (XXXIV) and subsequent ring closure lead to the betaine (XXXIII):

$$(XXXI) \xrightarrow{p\text{-}NO_2C_6H_4N_2^+BF_4^-} \left[(PhSO_2)_2C{=}NNC_6H_4NO_2\text{-}p \ \big| \ N{=}NC_6H_4NO_2\text{-}p\right] \rightarrow (XXXIII) + 2PhSO_2^- \ \textbf{(XXXIV)};$$

$$PhSO_2^- + p\text{-}NO_2C_6H_4N_2^+BF_4^- \rightarrow (XXXII) \ .$$

Subsequently it was shown that aromatic DS form hydrazones in an alkaline medium (pH 8–13) in the presence of an equimolar reactant ratio, while the betaines (XXXIII) are formed under the same conditions when the reaction is carried out with a twofold excess of the diazonium salt containing electron-accepting substituents in the *p*- or *m*-position in the aromatic ring.[12,28,148,160,161] Aliphatic DS are more reactive in this reaction. The interaction of bis(ethanesulphonyl)methane with diazonium salts terminates at the hydrazone stage only when *o*-substituted salts are employed, while *m*- and *p*-substituted salts in both strongly alkaline (pH 11) and weakly alkaline (pH 8.2) media react with formation of betaines (XXXIII).[162] The reactions of arenesulphonyltrifluoromethanesulphonylmethanes with diazonium salts in a weakly alkaline medium (pH 8.3) lead to the formation of hydrazones.[30]

Trimethylenetrisulphone (TTS) reacts with diazonium salts in an alkaline medium (pH 9) to form the TTS trisaryl-hydrazone,[163] while in a neutral medium (pH 7) TTS bisaryl-hydrazones were obtained[164] whose structure was demonstrated by spectroscopic methods.[165]

Tris(methylmethylene)trisulphone (TMTS) gives rise to its bisarylazo-derivatives in an alkaline medium (pH 9–10).[166]

In a strongly alkaline medium (pH 12–13) TTS reacts with a threeefold excess of diazonium salts with the opening of the ring, the elimination of one SO_2 group, and the formation of formazans (XXXV):[167]

$$\underset{\text{TTS}}{\text{cyclo-}(CH_2SO_2CH_2SO_2CH_2SO_2)} \xrightarrow[\text{pH 12–13}]{3ArN_2^+} \underset{(XXXV)}{ArN{=}N\text{-}C(=NNHAr)\text{-}CSO_2CSO_2Me} \ .$$

Disulphones with the methanesulphonyl group and electron-accepting substituents at the carbon atom of the methylidyne group (CN, COMe, COOEt) react in anhydrous

DMF,[168] in a weakly alkaline (pH 8.2) aqueous alcoholic medium,[169] or in the form of sodium salts in aqueous solution[170] with diazonium salts containing electron-accepting substituents to form arylazo-derivatives. The elimination of $MeSO_2$ and MeCO groups is not observed under these conditions:

$$ArSO_2CH(R)SO_2Me \xrightarrow{R^1C_6H_4N_2^+} ArSO_2C(R)(SO_2Me)(N{=}NC_6H_4R^1);$$
$$R = CN, COMe, COOEt;\ R^1 = o\text{-}, m\text{-}, p\text{-}Cl, Br, NO_2.$$

Trisulphones with the methanesulphonyl group interact in an aqueous alkaline medium (pH 8–9) or in anhydrous DMF with diazonium salts containing electron-accepting substituents in the *o*- and *p*-position, forming arenediazonium trisulphonylmethanides $ArN_2^+\,\bar{C}(SO_2R)_3$. On decomposition, the latter give rise to sulphonylazo-compounds of type (XXXII) together with arylhydrazones of type (XXXI) (in DMF) or betaines of type (XXXIII) (in an aqueous alkaline medium).[170]

In their reaction with tris(fluorosulphonyl)methane in water, arenediazonium chloride exchange the anion with formation of water-insoluble arenediazonium tris(fluorosulphonyl)methanides. The decomposition of the latter on heating leads to the *aci*-forms of the aryl esters of tris(fluorosulphonyl)methane:

$$RC_6H_4N_2^+Cl^- + HC(SO_2F)_3 \xrightarrow{H_2O} RC_6H_4N_2^+C^-(SO_2F)_3 \xrightarrow[-N_2]{80-120^\circ C} RC_6H_4OS(F){=}O{=}C(SO_2F)_2;$$
(XIII)
$$R = H, p\text{-}, m\text{-}F, p\text{-}NO_2.$$

The structure of the latter has been confirmed by chemical reactions, spectroscopic methods (IR, ^1H NMR, and ^{19}F NMR), and X-ray diffraction analysis.[171] This is the first example of the arylation of the SO_2 group by diazonium salts described in the literature.

(*f*) *Arylcarbamoylation and arylthiocarbamoylation.* The interaction of aromatic DS with aryl isocyanates and allyl isothiocyanates was first described in 1966.[172] The potassium salts of DS in anhydrous acetonitrile form salt-like adducts, which are converted, after acidification, into the arylamides of bis-sulphonyl-substituted acetic and thioacetic acids:[172,173]

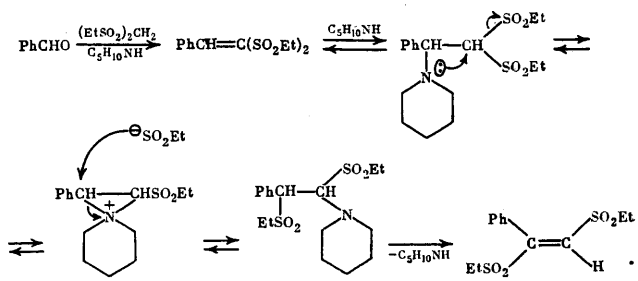
$$(ArSO_2)_2CHK \xrightarrow[MeCN,\,70-80^\circ C]{Ar^1NCX} (ArSO_2)_2C(K){-}C(X){-}NHAr^1 \xrightarrow{HCl} (ArSO_2)_2CH{-}C(X){-}NHAr^1;$$
(XXIII)
$$X = O, S.$$

The reactions of aromatic DS with aryl isothiocyanates were later achieved in absolute alcohol in the presence of sodium ethoxide.[148,174] A novel method for the introduction of arylthio-, heteroarylthio-, and arylalkylthio-carbamoyl groups into the molecule of an aromatic DS has been developed on the basis of the reaction of active methylene groups with the methyl esters of substituted dithiocarbamic acids:[175–178]

$$RNHCSSMe + (ArSO_2)_2CH_2 \xrightarrow{EtONa} (ArSO_2)_2CHCSNHR;$$
$$R = Ar, 2\text{-pyridyl}, PhCH_2.$$

This method and also the oxidative cyclisation of the arylamides of bis(arenesulphonyl)thioacetic acid by potassium hexacyanoferrate(II) in an aqueous alkaline medium[179] or by bromine in acetic acid[179] made it possible to obtain substituted heterocyclic compounds of the pyridine and benzothiazole series containing GSG in the side chain.

(*g*) *Interaction with aldehydes.* The pyridine-catalysed condensation of bis(ethanesulphonyl)methane with benzaldehyde is accompanied by a stereospecific intermolecular rearrangement with formation of *E*-αβ-bis(ethanesulphonyl)styrene [62] instead of the expected ββ-bis(ethanesulphonyl)styrene, the formation of which in this reaction had been erroneously reported earlier:[180,181]



As mentioned above (Section II), aromatic DS react with aldehydes to form 1,1,2-trisubstituted ethylenes; the interaction with aliphatic aldehydes is then frequently accompanied by the isomerisation of the final product owing to the prototropic allylic rearrangement.[60] In the condensation of bis(benzenesulphonyl)methane with isobutyraldehyde, the yields of the normal and isomerised reaction products were the same.[182] The condensation with other aliphatic aldehydes affords only isomerisation products:[182]

$$(PhSO_2)_2CH_2 \xrightarrow{\text{iso-PrCHO}} (PhSO_2)_2C{=}CHPr\text{-iso} + (PhSO_2)_2CHCH{=}CMe_2$$
$$50\% \qquad\qquad 50\%$$
$$\xrightarrow{RCH_2CHO} (PhSO_2)_2CHCH{=}CHR;$$
$$R = Et, Pr.$$

The reaction of DS with furfural yields the expected products—furfurylidenebis(sulphonyl)methanes, but under these conditions bis(benzenesulphonyl)methane and butyraldehyde react to form only the isomerisation product—1,1-bis(benzenesulphonyl)pent-2-ene.[183] Methanedisulphonyl fluoride reacts with *p*-dimethylaminobenzaldehyde in acetic anhydride to form ββ-difluorosulphonyl)-*p*-dimethylaminostyrene.[33] The condensation of DS with formaldehyde in the presence of bases leads to asymmetrically substituted propane with GSG at the terminal carbon atom.[55,57–59] Only the use of a large excess of piperidine and pyrrolidine makes it possible to carry out the Mannich reaction involving DS and to isolate the corresponding bases:[60,61]

$$(I) + CH_2O + HN\langle\rangle \rightarrow (RSO_2)_2CHCH_2N\langle\rangle$$

(*h*) *Reactions with mercury salts.* Organomercury compounds and mercury salts react with DS as electrophiles. Bis(benzenesulphonyl)methane and 1,1-bis(benzenesulphonyl)ethane reacts with *p*-dimethylaminophenylmercury hydroxide to form mercury derivatives of DS which are resistant to spontaneous disproportionation:[184]

$$p\text{-}Me_2NC_6H_4HgOH + (PhSO_2)_2CH_2 \rightarrow (PhSO_2)_2CHHgC_6H_4NMe_2\text{-}p.$$

The interaction with bis(arenesulphonyl)methanes with mercury diacetate affords mono- and di-mercurated products depending on the conditions:[185]

$$(p\text{-}RC_6H_4SO_2)_2CH_2 \xrightarrow{Hg(Ac)_2} \begin{cases} \rightarrow (p\text{-}RC_6H_4SO_2)_2CHHgAc; \\ \quad (XXXVI) \\ \rightarrow (p\text{-}RC_6H_4SO_2)_2C(HgAc)_2; \end{cases}$$
$$R = H, Me, Cl, NO_2.$$

Bis(arenesulphonyl)methylmercury halides are formed when the potassium salts of bis(arenesulphonyl)methanes or mercuriacetates (XXXVI) interact with mercury or potassium halides respectively:

$$(p\text{-}RC_6H_4SO_2)_2CHK \xrightarrow{HgX_2} (p\text{-}RC_6H_4SO_2)_2CHHgX\ ;$$
$$(XXXVI) \xrightarrow{KX} (XXXVII)$$
$$R=H, Me;\ X=Cl, Br, I\ .$$

The C–H bond in the series of DS is readily cleared by nucleophiles (Na_2S) but is comparatively resistant to attack by electrophiles: only prolonged reaction with bromine or hydrogen chloride leads to its cleavage.[185]

The study of the chemical properties and IR spectra of mercurated derivatives[185] established that the C–Hg bond is covalent, is appreciably polarised, and its character is close to that of the C–Br bond in the mono- and di-bromo-derivatives of DS.

(*i*) *Reactions with formation of ylides.* Disulphones are capable of acid-base interactions with phosphines. Tertiary phosphines react with fluorinated DS to form tertiary phosphonium salts. As a result of protonation at the nitrogen atom, aminophosphines form salts which are then converted into the dialkylammonium salts of α-phosphino-substituted DS (XXXVIII):[186]

$$RSO_2CH_2SO_2CF_3 \xrightarrow{R^1_3P} R^1_3P^{+}\text{---}{}^{-}CH(SO_2R)(SO_2CF_3) \rightleftarrows R^1_3\overset{+}{P}H\ \bar{C}H(SO_2R)(SO_2CF_3)\ ;$$
$$RSO_2CH_2SO_2CF_3 \xrightarrow{R^2_2PNEt_2} R^2_2\overset{+}{P}NHEt_2\ \bar{C}H(SO_2R)(SO_2CF_3) \longrightarrow$$
$$\longrightarrow R^2_2PCH(SO_2R)SO_2CF_3 + HNEt_2 \longrightarrow R^2_2P\bar{C}(SO_2R)SO_2CF_3\ H_2\overset{+}{N}Et_2\ ;$$
$$(XXXVIII)$$
$$R=Ph, CF_3;\ R^1=Et;\ R^2=Ph\ .$$

The salts (XXXVIII) are alkylated (with transfer of the reaction centre) at the phosphorus atom with formation of phosphorus ylides.[186]

Halogenophosphoranes react with aromatic DS in the presence of triethylamine to form phosphonium ylides with the halogen atom at the phosphorus atom—*P*-halogenoylides (XXXIX):[187]

$$Ph_nPHal_{5-n} + CH_2(SO_2Ph)_2 \xrightarrow{2NEt_3} Ph_nPHal_{3-n}{=}C(SO_2Ph)_2\ ;$$
$$(XXXIX)$$
$$n=2, 4;\ Hal=Cl, Br\ .$$

P-Halogenoylides (XXXIX) have also been obtained by treating with carbon tetrahalides the products of the reaction of tervalent phosphorus halides with bis(benzenesulphonyl)methane:[188,189]

$$R_2PCl + CH_2(SO_2Ph)_2 \xrightarrow{NEt_3} R_2P{-}CH(SO_2Ph)_2 \xrightarrow{CHal_4}$$
$$\rightarrow R_2\overset{\delta+}{P}{-}CH(SO_2Ph)_2\ \cdots\ Hal\ \cdots\ \overset{\delta-}{C}Hal_3 \rightarrow R_2P(Hal){=}C(SO_2Ph)_2 + CHHal_3\ .$$
$$(XXXIX)$$

Another method of synthesis of the ylides (XXXIX) involves the interaction of chloro- or bromo-bis(benzenesulphonyl)-methanes with chlorodiphenylphosphine in the presence of triethylamine.[190] *P*-Halogenoylides with GSG virtually lack basicity. They do not interact with hydrogen chloride and do not enter into the Wittig reaction with carbonyl compounds. The halogen atom in the ylides (XXXIX) readily undergoes nucleophilic substitution:

$$(XXXIX) \xrightarrow{R^1ONa} R_2P(OR^1){=}C(SO_2Ph)_2\ ;\ R^1=Me, Ph$$
$$\xrightarrow[Et_3N]{H_2O} R_2P(O)CH(SO_2Ph)_2\ ;\ (XL)$$
$$\xrightarrow{2RR^1NH} R_2P(NR^1_2){=}C(SO_2Ph)_2\ ;\ R{=}R^1{=}H, Alk;\ R{=}H, R^1{=}Alk\ ;$$
$$\xrightarrow[Et_3N]{EtSH} R_2P(SEt){=}C(SO_2Ph)_2\ .$$

The strong electron-accepting effect of the two benzenesulphonyl groups in the phosphine oxide (XL) determines the high acidity of the compound (pK_a = 3.27 in 95% alcohol), as a result of which reactions involving the oxygen of the phosphoryl group are typical of this compound.[191] The same effect is responsible for the occurrence of the phosphine oxide–hydroxy-ylide tautomerism of these compounds and for the possibility of the existence of phosphonium ylides with the OH group at the phosphorus atom:[192]

$$(XL) \xrightarrow{CH_2N_2(MeI)} Ph_2P(OMe){=}C(SO_2Ph)_2\ ;$$
$$Ph_2P{-}CH(SO_2C_6H_4P\text{-}p)_2 \rightleftarrows Ph_2P{=}C(SO_2C_6H_4R\text{-}p)_2\ ;$$
$$\|\ O \qquad\qquad |\ OH$$
$$R=Cl, H, Me, MeO\ .$$

The stable dimethylsulphonium di(fluorosulphonyl)-methylide has been obtained from methanedisulphonyl fluoride in DMSO in the presence of acetic anhydride.[33] When compound (VII) is acted upon by diacetoxyiodobenzene or the corresponding *m*-nitro-derivative, iodine ylides are formed:[33]

$$CH_2(SO_2F)_2 \xrightarrow[Ac_2O,\ 12\ h,\ 20\ ^\circ C]{Me_2S=O} Me_2S{=}C(SO_2F)_2\ ;$$
$$(VII) \xrightarrow{RC_6H_4I(OAc)_2} RC_6H_4I{=}C(SO_2F)_2\ ;$$
$$R=H, m\text{-}NO_2$$

(*j*) *Other reactions.* α-Diazo-β-disulphones (XLI) have been obtained by the interaction of tosyl azide with DS in an aqueous alcoholic medium in the presence of a base:[193]

$$(I) \xrightarrow[NaOH]{TsN_3} (RSO_2)_2CN_2\ ;$$
$$(XLI)$$
$$R=Ph, 2, 4\text{-}Me_2C_6H_3, 2, 4, 6\text{-}Me_3C_6H_2\ .$$

The coupling reaction between compounds (XLI) and the carbanions of CH acids proceeds with elimination of one arenesulphonyl group.[193] Thermal decomposition of compounds (XLI) and its mechanism have been investigated.[193,194]

Bis(methanesulphonyl)nitromethane reacts with diazomethane to form the *N*-oxide (XLII) and the reaction proceeds via oxathiazole oxide as an intermediate:[119]

$$(MeSO_2)CHNO_2 \xrightarrow{CH_2N_2} (MeSO_2)_2CH{-}\overset{O}{\overset{\uparrow}{N}}{-}CH_2{-}N{=}O \xrightarrow{-N_2} (MeSO_2)_2CH{-}N\begin{matrix}CH_2\\|\\O\end{matrix}$$
$$(XLII)$$

The final product (XLII) is readily converted to isonitrosobis(methanesulphonyl)methane (XLIII):

$$(XLII) \xrightarrow[-CH_2O]{H_2O} (MeSO_2)_2CHNO \rightleftarrows (MeSO_2)_2C{=}NOH\ .$$
$$(XLIII)$$

The isonitroso-compounds (XLIII) form salts with piperidine and hydrazine and are readily alkylated by dimethyl sulphate and acylated by acetic anhydride with formation of bis-(methanesulphonyl)-methoxyiminomethane or -acetoxyiminomethane.[119] Compound (XLIII) is unstable and it has been suggested that it decomposes via a radical mechanism.[195] On reaction of the isonitrosomethane (XLIII) with diazomethane under anhydrous conditions, 1-hydroxy-2,2-bis-(methanesulphonyl)aziridine was isolated:[196]

$$(XLIII) \xrightarrow[-N_2]{CH_2N_2} (MeSO_2)_2C{-}NOH$$
$$\qquad\qquad\qquad

The possibility of using the thiosulphonates $(RSO_2)_2.CHSSO_2R$ for the sulphenylation of aliphatic ketones and other compounds with an active methylene group in an alkaline medium has been reported.[198]

2. Chemical Properties of Unsaturated GS

(*a*) *1,1-Bis(arenesulphonyl)ethylenes.* The strong polarisation of the double bonds in 1,1-bis(arenesulphonyl)-ethylenes, caused by the overall electron-accepting effect of the two sulphonyl groups, lowers appreciably the π-electron density at the β-carbon atom, which facilitates the attack by the nucleophile and makes nucleophilic addition reaction characteristic of the given series of compounds. Highly basic nucleophiles promote (particularly in protic media) the competing double bond dissociation reaction. These factors are responsible for the wide variety of the chemical properties of 1,1-bis(arenesulphonyl)ethylenes.

The acid- and base-catalysed addition of water to 1,1-bis-(arenesulphonyl)ethylenes [57] does in fact lead to the formation of 1,1,3,3-tetrakis(arenesulphonyl)propanes (XVII).[57–60,199] A mechanism has been proposed for this reaction:[57]

$$\underset{\text{(XVIII)}}{(RSO_2)_2C{=}CH_2} \underset{}{\overset{H_2O}{\rightleftarrows}} \underset{\text{(C)}}{(RSO_2)_2CHCH_2OH} \rightleftarrows \underset{\text{(D)}}{(RSO_2)_2\bar{C}H} + CH_2O + H^+ ;$$

$$(C) \overset{H^+}{\rightleftarrows} (RSO_2)_2\overset{+}{C}HCH_2OH_2 \xrightarrow[-H_2O]{(D)} \underset{\text{(XVII)}}{[(RSO_2)_2CH]_2CH_2} ;$$

R = Ar .

The C–C bond in compounds (C) is appreciably polarised under the influence of the two arenesulphonyl groups and is capable of hydrolytic cleavage by bases or acids. The formation of the carbanion (D) is apparently the rate-limiting stage in the overall reaction. The final products can be formed both via the pathway indicated in the scheme and via the interaction of the initial olefin with the anion (D). In ahydrous CCl_4 the olefin (XVIII) combines with aromatic and heterocyclic thiols, while in the presence of acetic acid it can combine with sulphinates.[57] They are active acceptors in the Michael reaction and in the presence of F^- they readily combine with DS, TS, nitromethane, and arenesulphonylacetonitrile.[57] It has been shown that the reactions of the olefin (XVIII) with TS are also catalysed by a Lewis acid (BF_3 etherate),[56] while the interaction with β-diketones (acetylacetone and dibenzoylmethane) proceeds in dioxan in the presence of Triton B (200). ββ-Bis(benzenesulphonyl)styrene combines with malonic ester.[64] The use of 1,1-bis(benzenesulphonyl)ethylene as the dienophile in cycloaddition reactions with cyclopentadiene, cyclohexa-1,3-diene, cycloheptatriene, and other dienes has been described recently.[61] The study of the reactions of 1,1-bis(benzenesulphonyl)ethylene with various amines showed that, depending on the basicity of the amine, the reaction proceeds via two pathways: with formation of adducts (XLIV) or substituted propanes (XVII):[199]

$$(PhSO_2)_2C{=}CH_2 \begin{cases} \xrightarrow{\text{amines } (pK_a\ 1.0\text{–}6.9)} \underset{\text{(XLIV)}}{(PhSO_2)_2CHCH_2NHR} ; \\ \xrightarrow{\text{amines } pK_a\ 9.3\text{–}11.2)} \text{(XVII)} . \end{cases}$$

A mechanism has been proposed[199] for the reaction of 1,1-bis(benzenesulphonyl)ethylene with highly basic amines:

$$\underset{\text{(XVIII)}}{(PhSO_2)_2C{=}CH_2} \xrightarrow{RNH_2} \text{(XLIV)} \rightleftarrows$$

$$\rightleftarrows (PhSO_2)_2\bar{C}H + [CH_2 \cdots NHR]^+ \xrightarrow{RNH_2} CH_2(NHR)_2$$

$$\downarrow (PhSO_2)_2C{=}CH_2 \qquad (PhSO_2)_2\bar{C}H \downarrow$$

$$(PhSO_2)_2\bar{C}CH_2CH(SO_2Ph)_2 \xrightarrow{H^+} \text{(XVII)} .$$

The rate of heterolysis of the C–C bond in the amine (XLIV) exceed the rate of its formation, as a result of which the DS carbanion can react with both the initial olefin and with the second heterolysis product—the aminal (the nitrogen-containing derivative of formaldehyde), to form the propanes (XVII). The olefins (XVIII) interact with electrophiles only with difficulty. They combine with bromine in acetic acid on heating. Mercury acetate undergoes the Hofmann–Sand reaction with two ethylene molecules and the addition takes place contrary to the Markovnikov rule:[57]

$$(PhSO_2)_2C{=}CH_2 \xrightarrow{Hg(OAc)_2MeOH} [MeOCH_2C(SO_2Ph)_2]_2Hg .$$

ββ-Bis(benzenesulphonyl)styrene reacts with diazomethane to give a substituted pyrazoline, which is converted into 1,1-bis(benzenesulphonyl)-3-phenylprop-3-ene on heating:[64]

$$(PhSO_2)_2C{=}CHPh \xrightarrow{CH_2N_2} (PhSO_2)_2C(\text{—}N{=}N\text{—}CH_2\text{—})CHPh \rightarrow (PhSO_2)_2CHCH{=}CHPh .$$

A thermal stereospecific rearrangement catalysed by ammonium salts has been discovered for the olefins (XVIII). On heating (138–139 °C) in *p*- or *m*-xylene in the presence of catalytic amounts of ammonium salts, the *gem*-substituted olefins (XVIII) rearrange to *E*-1,2-bis(arenesulphonyl)-ethylenes:[201]

$$\text{(XVIII)} \xrightarrow[\text{ammonium salts}]{\Delta} p\text{-}RC_6H_4SO_2\text{—}C(H){=}C(H)\text{—}SO_2C_6H_4R\text{-}p ;$$

R = H, Me, Cl .

A rearrangement in the opposite direction has been observed in the nucleophilic vinyl substitution reaction when 1,2-bis-[alkane(or arene)sulphonyl]-1,2-dichloroethylenes are treated with amines:[202]

$$RSO_2C(Cl){=}C(Cl)SO_2R \xrightarrow{R^1NH_2} (RSO_2)_2C{=}C(NR^1)_2 ;$$

$R = Et, C_8H_{17}, Ph; R^1 = Ph, p\text{-}HOC_6H_4, p\text{-}NO_2C_6H_4$.

(*b*) *Polysulphonylethylenes.* The presence of four electron-accepting groups in the molecules of tetrasulphonylethylenes (TSE) (XLV) entails a high reactivity of these compounds. In aqueous solutions the TSE are hydrolysed with dissociation of the C=C bond[203] and the formation of disulphonylmethanes. This process proceeds readily in neutral, acid, and basic media. The mechanism of the hydrolysis of TSE [203] is based on a detailed study of the kinetics of the hydrolytic reactions of asymmetric olefins activated by several electron-accepting groups:[204,205]

$$(RSO_2)_2C{=}C(SO_2R)_2 \overset{H_2O}{\rightleftarrows} (RSO_2)_2C(OH)\text{—}\bar{C}(SO_2R)_2 \overset{H^+}{\rightleftarrows}$$

$$\rightleftarrows (RSO_2)_2C(OH)CH(SO_2R_2) \rightarrow \text{(I)} + [(RSO_2)_2C{=}O] \xrightarrow{H_2O_2} RSO_3H + CO_2 ;$$

R = Et, *n*-Bu .

The extremely ready fragmentation of TSE is the reason why their synthesis is possible only under anhydrous conditions.[74] Alcohols which react readily with TSE do not form fragmentation products. In the presence of urea, the reactions of TSE with alcohols lead to the esters of bis(alkanesulphonyl)acetic acids:[203]

$$\text{(XLV)} \xrightarrow{R^1OH} [(RSO_2)_2C{=}C(OR^1)SO_2R] \xrightarrow{R^1OH} (RSO_2)_2C{=}C(OR^1)_2 + 2RSO_3H ;$$

$$\downarrow H_2O \qquad\qquad (RSO_2)_2CHCOOR^1 \xleftarrow{H_2O} \downarrow$$

$R = Et, R^1 = Me, Et$.

The ideas concerning the course of the interaction of TSE with alcohols have been confirmed by a study of the reactions of TSE with thiols, where the intermediate thioacetals and their dioxides proved to be stable:[203]

$$(XLV) \xrightarrow{R^1SH} (RSO_2)_2C{=}C(SO_2R)(SR^1) + (RSO_2)_2C{=}C(SR^1)_2 ;$$
(XLVI)
R = Et, *n*-Bu, R^1 = Et, Ph .

Thioacetal *SS*-dioxides readily hydrolyse with the elimination of the SO_2R group:

$$(XLVI) \xrightarrow{H_2O} (RSO_2)_2CHCOSR^1 \rightleftarrows (RSO_2)_2C{=}C(OH)SR^1$$
(XLVII) (XLVIII) .

According to IR spectroscopic data, the hydrolysis products exist both in the form of the esters (XLVII, R = n-Bu, R^1 = Et) and in the enolic form (XLIII, R = Et, R^1 = Ph).

The reactions of TSE with secondary or bulky primary amines take place with formation of bis(sulphonyl)acetamides—the products of the hydrolysis of the unstable 1,1,2-tris-(sulphonyl)-2-(R-amino)methylenes.[206] A mechanism has been proposed for the reactions with amines on the basis of the Ad_N-E nucleophilic substitution mechanism for other electrophilic olefins.[207,208]

Together with the formation of disulphonylacetamides, primary amines give rise to the formation in this reaction of 1,1-bis[alkane(or arene)sulphonyl]-2,2-bis[alkyl(or aryl)amino]ethylenes—the products of the substitution of two sulphonyl groups.[206] Fragmentation has been observed only when highly basic amines were employed, bis-sulphonyl)methanes being apparently formed as a result of the competitive cleavage of the TSE by the amines.

(c) *2,2-Bis(alkanesulphonyl)- and 2,2-bis(arenesulphonyl)-vinyl ethyl ethers.* The different electronic natures of the substituents at C(1) and C(2) in these compounds are responsible for their unusual chemical behaviour. In contrast to unsubstituted ethyl vinyl ethers, 2,2-bis-(sulphonyl)vinyl ethers (VE) do not react with alcohols and do not form acylals on reaction with acetic acid. Addition reactions are not characteristic of these compounds. 2,2-Bis(benzenesulphonyl)vinyl ethyl ether forms a complex mixture of products on heating with bromine in CCl_4, from which bis(benzenesulphonyl)bromomethane was isolated (10%).[65] Like TSE, the VE hydrolyse in acid and alkaline media with rupture of the double bond and the formation of bis(arenesulphonyl)methanes.[65] VE react with ammonia to form 2,2-bis[alkane(or arene)sulphonyl]-vinylamines.[62,64,65] The latter are acylated by benzoyl chloride, react with ethyl and phenyl isocyanates to form substituted ureas, react with tosyl chloride (in the presence of BuLi),[62,65] and are reduced by sodium tetrahydroborate to 1,1-bis(alkanesulphonyl)- or 1,1-bis(arenesulphonyl)-ethanes.[58]

2,2-Bis(arenesulphonyl)vinylamines have also been synthesised from the sodium salts of bis(arenesulphonyl)-methanes, DMF, and dimethyl sulphate[58] or by the reaction of bis(arenesulphonyl)methanes with bis(trimethylsilyl)-formamide:[209]

$$(p\text{-}RC_6H_4SO_2)_2CH_2 \xrightarrow[\text{HCON(SiMe}_3)_2,\ 120°-140°C]{Me_2SO_4DMF} (p\text{-}RC_6H_4SO_2)_2C{=}CHNH_2 ;$$
R=H, CH_3, Cl .

2,2-Bis(toluene-*p*-sulphonyl)vinylamine reacts with phenyl isothiocyanate in the presence of triethylamine to form *N*-[2,2-bis(toluene-*p*-sulphonyl)vinyl]aniline and not a substituted thiourea as was expected:[210]

$$(p\text{-}MeC_6H_4SO_2)_2C{=}CHNH_2 \xrightarrow[Et_3N,120-140°C]{PhNCS} [(p\text{-}MeC_6H_4SO_2)_2C{=}CHNHCSNHPh] \xrightarrow{Et_3N} \rightarrow (p\text{-}MeC_6H_4SO_2)_2C{=}CHNHPh + (Et_3NH)^+SCN^- .$$

Ethyl vinyl ethers containing alkanesulphonyl groups (XLIX) react with aromatic[130] and aliphatic (primary and secondary) amines[62] in the presence of TsOH to form substituted vinylamines:

$$(RSO_2)_2C{=}CHOEt \xrightarrow[TsOH]{R^1R^2NH} (RSO_2)_2C{=}CHNR^1R^2 ;$$
(XLIX)
R = Me, Et; R^1 = Ph, R^2 = H or R^1, R^2 = Alk .

The same reaction of VE containing arenesulphonyl groups is accompanied by a competing process—the dissociation of the double bond, which greatly reduces the yield of the required products.[65] Ethyl vinyl ethers (L) react with dihydroresorcinol,[64] 2,4-dinitrophenylhydrazine,[65] and hydroxylamine[62] to form substitution products. Alkaline hydrolysis of the VE (L) at the interface between two phases leads to acetaldehyde with GSG:[64]

$$(ArSO_2)_2C{=}CHOEt \xrightarrow[CHCl_3]{KOH} (ArSO_2)_2CHCHO ;$$
(L)
Ar = Ph .

Nucleophilic substitution of the OEt group in the VE (L) by the carbanions of CH acids results in the formation of 1,1,3,3-tetrasubstituted propenes:[64,75]

$$(ArSO_2)_2C{=}CHOEt \xrightarrow[EtONa/EtOH]{R^1CH_2COOEt} (ArSO_2)_2C{=}CHCH(R^1)COOEt ;$$
R^1 = COMe, CN.

(d) *Polysulphonylpropenes.* Propenes with GSG at C(1) or C(3), containing simultaneously two other electron-accepting substituents at the terminal carbon atoms [C(3) and C(1) respectively] have been described.[64,75,76] In solution these compounds are involved in a tautomeric equilibrium:[75,76]

$$R^1R^2C{=}CHCHR^3R^4 \rightleftarrows R^1R^2CHCH{=}CR^3R^4 ,$$
(LI) : R^1=R^2=$PhSO_2$; R^3 = COMe; R^4 = COOEt ;
(LII) : R^1=$ArSO_2$; R^2=CN; R^3=R^4=SO_2Et, SO_2Ar .

The chemical reactions of propenes with GSG are determined mainly by their CH-acid properties (Table 4). The propenes (LII) form salts with alkali metals, react with diazonium salts and bromine, and form products resulting from the substitution of the hydrogen atom at C(1).[76] The propenes (LII, R^3 = R^4 = SO_2Ar) are nitrated with dissociation of the double bond and the formation of bis(4-R-3-nitrobenzene-sulphonyl)methanes.[27] The propene (LI) reacts with diazonium salts to form the product of substitution at C(3),[211] the nitration of compound (LI) is accompanied by the rupture of the double bond and leads to bis(3-nitro-benzenesulphonyl)methane, and nitrosation affords ethyl γγ-bis(benzenesulphonyl)-α-hydroxyiminovinylacetate:[27]

$$(LI) \xrightarrow[pH\ 8,3]{R^1C_6H_4N_2^+} (PhSO_2)_2C{=}CHC(N{=}NC_6H_4R^1)(COMe)COOEt ;$$
$$(LI) \xrightarrow{HNO_3,H_2SO_4} (3\text{-}O_2NC_6H_4SO_2)_2CH_2 ;$$
$$(LI) \xrightarrow{NaNO_2,HAc} (PhSO_2)_2C{=}CHC(COOEt){=}NOH ;$$
R^1 = *p*-Cl, *p*-Br, *m*-NO_2.

1,1-Bis(benzenesulphonyl)-2-cyano-2-ethoxycarbonylprop-1-ene, which has a similar structure but is much more acid (pE_a = 1.04 in acetone), reacts with diazonium salts in the tautomeric prop-3-ene form with substitution of the hydrogen atom at C(1), the elimination of the EtOCOC(CN) =CH group, and the formation of 1,3-diaryl-5-hydroxytetrazolium betaines (XXXIII).[211]

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Thus GS exhibit a varied reactivity. Further investigation of the chemistry of compounds of this class will lead to the discovery of their new practical applications as physiologically active preparations,[212] pesticides,[213] and in the manufacture of polymeric materials.[214-222]

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