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Advances in the Chemistry of Aliphatic Diazosulphones

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Methods for the synthesis of α-diazosulphones are examined and a systematic account is given of the literature data on the physicochemical properties and ultraviolet, infrared, and NMR spectroscopy of this interesting class of aliphatic diazo-compounds. Much attention is devoted to chemical reactions of α-diazosulphones via the intermediate formation of carbonium ions and sulphonyl carbenes as well as reactions involving the nitrogen of the diazo-group. In many cases a comparative description is given of the chemical properties of α-diazosulphones and α-diazoketones. The review constitutes the first compilation of the chemistry of α-diazosulphones available in the literature.
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I. INTRODUCTION

A number of interesting reviews have been published recently on the chemistry of aliphatic diazo-compounds[1-8], dealing mainly with methods of synthesis, properties, and structures of diazoalkanes or diazocarbonyl compounds, but the chemistry of α-diazosulphones has not been considered. Nevertheless this class of aliphatic diazo-compounds has been attracting attention because of the presence in the molecule of both the sulphonyl and diazo-groups. The combination of these groups makes it possible to synthesise new types of sulphones, whose preparation by other procedures is difficult. Furthermore, α-diazosulphones are of theoretical interest as regards the comparison of their reactivities with those of α-diazoketones, diazophosphines, and silyldiazoalkanes.

The first diazosulphonyl compound—potassium diazomethionate—was synthesised by Pechmann and Mank in 1895.[9] After that not a single new method of synthesis of α-diazosulphones and not a single new compound of this class were described until 1962.

A fruitful stage in the chemistry of α-diazosulphones began in 1962, when the Dutch chemists Strating and Lensen[10] described a method for the preparation of monosulphonyldiazomethanes and the German investigators Klages and Bott[11] published a report on bis-(phenylsulphonyl)diazomethane. Subsequent advances in the synthesis of diazosulphones (of which about 50 are now known) stimulated an increase of interest in the structure and properties of these compounds.

The aim of the present review is to give a systematic account of the literature data on the methods of synthesis, structures, and chemical properties of diazosulphones.

II. METHODS OF SYNTHESIS

The classical method of synthesis of α-diazoketones[12] by the interaction of carboxylic acid chlorides with an excess of diazomethane,

$$RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 + CH_2Cl + N_2 ,$$

leads to positive results only in the case of toluene-*p*-sulphonyl chloride[13], which give rise in this reaction to tolylsulphonyldiazomethane and α-chloro-α-tolylsulphonylmethane:

$$CH_3C_6H_4SO_2Cl \xrightarrow{CH_2N_2} CH_3C_6H_4SO_2CHN_2 + CH_3C_6H_4SO_2CH_2CH_2Cl.$$

The interaction with 2-phenylethanesulphonyl chloride takes place in the presence of base via the intermediate 2-phenylthioacetaldehyde *SS*-dioxide to give benzylethylene sulphone[14]:

$$C_6H_5CH_2CH_2SO_2Cl \xrightarrow{CH_2N_2} \begin{cases} \not\rightarrow\ C_6H_5CH_2CHSO_2CH_2N_2 \\ \rightarrow\ [C_6H_5CH_2CH{=}SO_2] + C_6H_5CH_2CH{-}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\quad SO_2 \end{cases}$$

α-Diazosulphone is not formed under these conditions[15]. Evidently diazomethane is incapable of attacking the sulphur atom in view of its inadequate electrophilic properties. This is why α-diazosulphones, with the exception of potassium diazomethionate, remained unknown for a long time.

It is noteworthy that the synthesis of α-phenyl-α-(*p*-toylsulphonyl)diazomethane from toluene-*p*-sulphonyl chloride and phenyldiazomethane is described in one of the latest communications[16]:

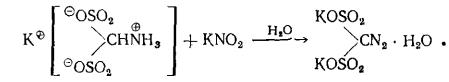
$$CH_3C_6H_4SO_2Cl + C_6H_5CHN_2 \xrightarrow{-HCl} CH_3C_6H_4SO_2\overset{C_6H_5}{\underset{|}{C}}N_2 .$$

We believe that this procedure for the preparation of α-diazosulphones requires a detailed study, since it has been described for only one example and the diazo-derivative was not isolated in a pure form.

The main methods for the synthesis of α-diazosulphones were developed in the 1960s. They include the oxidation of the hydrazones of disulphonylketones, the introduction of the diazo-group into an activated methylene group with the aid of tosyl azide, and the alkaline cleavage of *N*-nitrosourethanes and α-diazo-β-oxosulphones. The above methods are not equivalent as regards ease, universality, and simplicity. However, considered together, they make it possible to obtain α-diazosulphones with various substituents.

1. Diazotisation of Aminomethionic Acid Salts

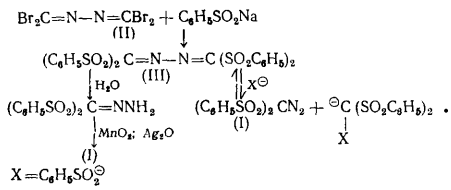
The method consists of the diazotisation of potassium aminomethionate[9] (or the sodium salt[17]) with nitrite ions at an elevated temperature:



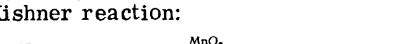
It has been described only for two compounds. However, one cannot rule out the possibility that it can be used to diazotise other derivatives of aminomethionic acids.

2. Oxidation of Bis(arenesulphonyl)formaldehyde Hydrazone

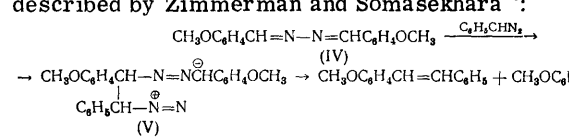
The method has been developed for the synthesis of bis(benzenesulphonyl)diazomethane (I).[18,19] It is obtained from carbonyl bromide azine (II) and sodium benzenesulphinate:



The bis(benzenesulphonyl)formaldehyde azine (III) formed in the first stage is hydrolysed to the corresponding hydrazone, which is oxidised with activated manganese dioxide or silver oxide to bis(benzenesulphonyl)diazomethane. Bis(benzenesulphonyl)methane is isolated as a side product, being formed according to the authors via the Wolff–Kishner reaction:



The interaction of the azine (II) with sodium benzenesulphinate in the absence of moisture and subsequent treatment of the reaction mixture with alumina also make it possible to obtain a high yield of the diazosulphone (I). The intermediate azine (III) probably reacts readily with the nucleophilic agent ($X^{\ominus}$) present in the reaction mixture. A similar base-catalysed decomposition of *p*-methoxybenzylideneazine (IV) by phenyldiazomethane has been described by Zimmerman and Somasekhara[20]:

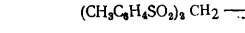


In this case phenyldiazomethane attacks the azine (IV). The resulting unstable intermediate adduct (V) decomposes into 1-(*p*-methoxyphenyl)-2-phenylethylene and *p*-methoxyphenyldiazomethane with evolution of nitrogen.

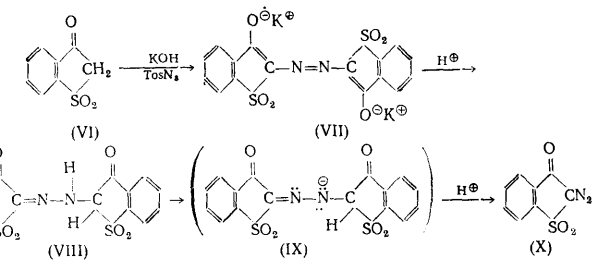
It is noteworthy that the above method of synthesis of α-diazo-β-disulphones can probably by used also to prepare substituted bis(arenesulphonyl)diazomethanes, but the initial bis(arenesulphonyl)formaldehyde hydrazones are difficult to obtain.

3. The Reactions of Tosyl Azide with Compounds Containing an Activated Methylene Group

The method was described in 1964 for the synthesis of bis(arenesulphonyl)- and bis(alkanesulphonyl)-diazomethanes[21]. Thus bis(toluene-*p*-sulphonyl)diazomethane is obtained by treating an aqueous alcoholic solution of bis(toluene-*p*-sulphonyl)methane and sodium hydroxide with an ethereal solution of tosyl azide:

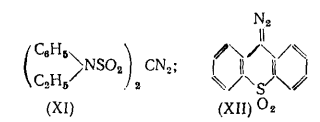


Subsequently in 1965–1970 the method was used to synthesise α-diazo-β-oxosulphones[22–25] and 4-benzenesulphonyl-1,3-dioxo-2,4-bisdiazoalkanes[26]. In particular, the interesting synthesis of 2-diazo-2,3-dihydrothionaphthen-3-one 1,1-dioxide (X) has been achieved by this reaction[22]:

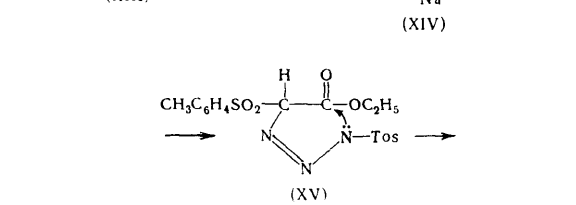


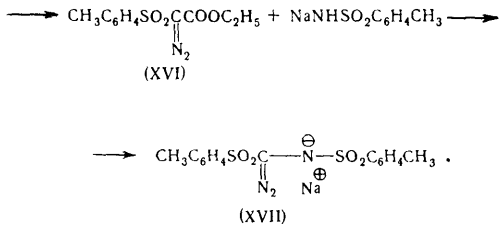
In the first stage 2,3-dihydrothianaphthen-3-one 1,1-dioxide (VI) is converted under the influence of tosyl azide in an alkaline medium into a dipotassium salt of the azo-compound (VII). On being acidified, compound (VII) is converted into the hydrazone (VIII), which is further converted on being refluxed in ethylene glycol into the diazosulphone (X) via the intermediate (IX). The diazosulphone can be converted into the dipotassium salt (VII) on treatment with alkali and the initial compound (VI). Triethylamine[24] or potassium ethoxide[27] can be used as bases and acetonitrile as the solvent[26].

The bis(ethylphenylanilide) of diazomethionic acid (XI)[21] and 9-diazothioxanthene *SS*-dioxide (XII)[27] have been synthesised by this method:



Depending on the solvent and the base, the reaction of tosyl azide with ethyl toluene-*p*-sulphonylacetate (XIII) proceeds in two ways. When equimolecular amounts of sodium ethoxide and tosyl azide are used in an absolute ethanol–ether mixture at 0°C, the sodium salt of *N*-(toluene-*p*-sulphonyl)toluene-*p*-sulphonyldiazoacetamide (XVII) is formed almost immediately. The authors believe that the carbanion (XIV), formed initially from the sulphone (XIII) under the influence of the base, reacts with tosyl azide to form the intermediate adduct (XV). Its decomposition leads to the formation of ethyl toluene-*p*-sulphonyldiazoacetate (XVI) and the sodium salt of toluene-*p*-sulphonamide. The interaction of these two compounds yields the final reaction product—the sodium salt of the diazosulphone (XVII):





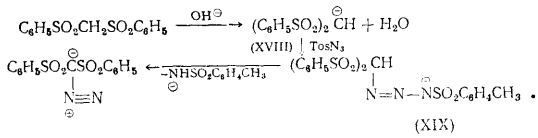
(XVI)

(XVII)

The intermediate diazosulphone (XVI) can be isolated when equimolecular amounts of tosyl azide and the sulphone (XIII) interact in methylene chloride in the presence of triethylamine[25]. The possibility of isolating the diazosulphone (XVI) can be accounted for in this case by the weak solvation of the reaction products by solvent molecules.

The method for the introduction of the diazo-group into bis(arenesulphonyl)methanes with the aid of tosyl azide has been modified recently[28]. The authors suggested that an alkaline aqueous alcoholic solution of the initial bis-(arenesulphonyl)methane be added to a threefold excess of tosyl azide in alcohol. This enables one to obtain stable yields of diazosulphones, while the initial procedure makes it possible to isolate the hydrazones of bis(arenesulphonyl)-formaldehyde in a low yield and only insignificant amounts of bis(arenesulphonyl)diazomethanes.

The reaction involves the formation of the carbanion (XVIII) and the product (XIX) resulting from its coupling with tosyl azide as well as the cleavage of the latter into bis(arenesulphonyl)diazomethane and the toluene-*p*-sulphonamide anion. In particular, bis(mesitylenesulphonyl)-diazomethane has been synthesised by this method:



(XVIII) (XIX)

In view of the critical comments by Heyes and Holt[28] concerning the method for the reduction of the diazo-group into bis(arenesulphonyl)methanes proposed by Klages and Bott[21], we analysed the above investigations and concluded that the method of Heyes and Holt is more effective, since it makes it possible to obtain α-diazo-β-disulphones in high yields and is less laborious.

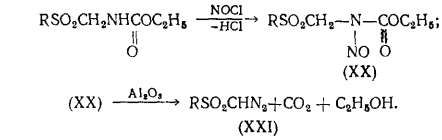
4. Cleavage of *N*-Nitrosourethanes

The alkaline cleavage of *N*-nitrosourethanes is widely used for the synthesis of diazoalkanes and α-diazoketones. This method of synthesis has been most thoroughly developed also in relation to diazosulphones. It is sufficient to point out that the vast majority of alkyl- and aryl-α-diazosulphones[29] and also certain α-alkyl-α-sulphonyldiazomethanes[16] and β-sulphonyldiazo-compounds[30] have been synthesised by this procedure.

The synthesis consists of two stages.

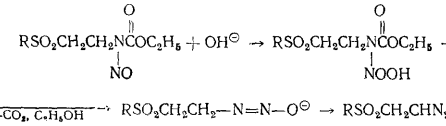
(1) Nitrosation of the initial urethane. Nitrosyl chloride is used as the nitrosating agent. The synthesis of the initial *N*-arenesulphonyl- and *N*-alkanesulphonyl-methylurethanes has been thoroughly worked out[31,32] and does not present much difficulty.

(2) The cleavage of *N*-nitrosourethane to diazosulphone by alumina. The reaction is carried out on a chromatographic column:



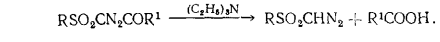
(XX) (XXI)

The cleavage of *N*-nitrosourethanes with alkali is preferable for the synthesis of certain β-diazosulphones[30]. The reaction can be described schematically as follows:

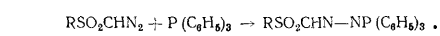


5. The Cleavage of α-Diazo-β-Oxosulphones

The method reduces to the cleavage of α-diazo-β-oxosulphones with triethylamine in dry methanol[24]:



The resulting diazosulphone is isolated in the form of triphenylphosphazine:



It is noteworthy that the cleavage reaction is undergone only by α-diazo-β-oxosulphones in which there is an electron-donating substituent (OCH_3, CH_3) in the *para*- and *ortho*-positions of the aryl residue relative to the sulphonyl group. The cleavage of α-acetyl- and α-benzoyl-(*p*-nitrobenzenesulphonyl)diazomethane by triethylamine in methanol leads to products of unknown structure. The cleavage of the above α-diazo-β-oxosulphones to *p*-nitrobenzenesulphonyldiazomethane proceeds without difficulty on alumina in a chloroform–ethanol mixture.

The synthesis of α-diazosulphones by the above method is of limited applicability owing to the low yields of the final products (30–45%) and the difficulties associated with their isolation from the reaction mixture.

III. GENERAL CHARACTERISTICS, STRUCTURE, AND SPECTRA

1. The Characteristics of Diazosulphones

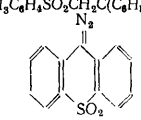
Diazosulphones are bright-yellow substances, the majority of which crystallise readily. Derivatives of monosulphonyldiazomethane[29] and also α-diazo-β-oxosulphones[22–24] can be stored for a long time in the dark at −20°C. Their stability varies widely and is approximately proportional to their melting points. Liquid benzenesulphonyldiazomethane decomposes in the course of several days. The introduction of alkyl substituents in the *p*-position of the benzene ring reduces the stability of α-diazosulphones and they decompose completely in the course of several hours at room temperature. The stability of these compounds increases in ethereal solutions. Crystalline aryl-substituted α-diazosulphones are more stable, although they too decompose slowly at room temperature and in the light. Certain α-diazosulphones (for example phenylmethanesulphonyldiazomethane) show no change in the melting point on storage in the dark in

the course of four months. Derivatives of bis(alkanesulphonyl)- or bis(arenesulphonyl)-diazomethanes are even more stable[21]. They can be stored for a long time in the light at room temperature.

On the other hand, β-diazosulphones are extremely unstable and can exist only in solution[30]. However, their stability increases after the introduction of a phenyl substituent at the α-carbon atom. Thus, as in the case of α-diazoketones, the accumulation of electron-accepting substituents in the diazosulphone molecule and their greater proximity to the diazo-group stabilise the diazo-derivative and increase its thermal and photolytic stabilities.

Derivatives of monosulphonyldiazomethane, α-diazo-β-oxosulphones, and bis(alkanesulphonyl)- and bis-(arenesulphonyl)-diazomethanes are soluble in ether, dichloromethane, and other organic solvents. Potassium diazomethionate is readily soluble in water and slightly in dimethyl sulphoxide. In contrast to diazoalkanes and many α-diazoketones, diazosulphones have no odour. The toxicity of diazosulphones has not been investigated. It has only been noted that these compounds possess no dangerous properties[29]. We believe that it is desirable to investigate the physiological activity of diazosulphones, particularly their carcinogenic and antitumour activities, since these have been shown by other aliphatic diazo-compounds.

Table 1. Parameters of the infrared and ^{1}H NMR spectra of certain diazosulphones.

Diazosulphone	i.r.spectrum $\nu(N_2)$, cm^{-1}	Chemical shift of α-proton τ, p.p.m.	References
$CH_3OC_6H_4SO_2CHN_2$	2101	4.76	29
$NO_2C_6H_4SO_2CHN_2$	2108	4.57	29
$C_6H_5SO_2CHN_2$	2104	4.61	29
$(CH_3)_3CSO_2CHN_2$	2106	4.90	29
$(C_6H_5SO_2)_2CN_2$	2130	—	21
$CH_3C_6H_4SO_2CN_2COCH_3$	2110	—	24
$CH_3C_6H_4SO_2CN_2COOC_2H_5$	2137	—	25
$CH_3C_6H_4SO_2CH_2C(C_6H_5)N_2$	2050	—	30
	2075	—	27
$NO_2C_6H_4SO_2CN_2COCH_3$	2115	—	24

2. Structure and Spectra

Infrared and NMR spectroscopic data[29] (Table 1) reveal a similarity between the structures of the diazo-groups of α-diazosulphones and α-diazoketones. The diazo-group of α-diazosulphones absorbs in the infrared in the region of 2115 ± 15 cm^{-1} and the absorption does not in fact differ from that of α-diazoketones, but is displaced towards higher wavenumbers compared with diazoalkanes. This indicates an increase of the multiplicity of the bond between the nitrogen atoms in the diazo-group of α-diazosulphones compared with diazoalkanes, i.e. the contribution of structure (XXII) to the resonance hybrid is greater than that of structure (XXIII).

$$\underset{\text{(XXII)}}{RSO_2\overset{\ominus}{C}H-\overset{\oplus}{N}\equiv N} \longleftrightarrow \underset{\text{(XXIII)}}{RSO_2CH=\overset{\oplus}{N}=\overset{\ominus}{N}}.$$

The sulphonyl group in α-diazosulphones is responsible for absorption in the region of 1330 and 1140 cm^{-1} in the infrared spectra. In the NMR spectra of α-diazosulphones[29] (Table 1) the CHN_2 proton gives rise to a signal between τ = 4.57 and 4.98. The α-proton in α-diazoacetone gives rise to τ = 4.82. In the series of aryl-substituted α-diazosulphones *para*-substituents have some influence on the position of the absorption band of the diazo-group in the infrared spectra and on the α-proton chemical shift. Electron-donating substituents, for example the methoxy-group, promote an increase of electron density at the α-carbon atom. This is indicated by infrared and NMR spectroscopic data. Thus the absorption of the diazo-group in the infrared spectra of *p*-methoxybenzenesulphonyldiazomethane and *p*-nitrobenzenesulphonyldiazomethane is at 2103.3 and 2108.2 cm^{-1} respectively and the α-proton signals in the NMR spectra have τ = 4.75 and 4.57 respectively. Naturally an increase of electron density of the α-carbon atom of the diazosulphone leads to enhanced shielding of the α-proton and hence to higher chemical shifts.

Owing to the magnetic anisotropy of the benzene ring, the chemical shifts of the α-protons of aryl-substituted α-diazosulphones are smaller than for the alkyl-substituted derivatives[29].

The introduction of a second arenesulphonyl group into the α-diazosulphone molecule tends to increase the contribution of structure (XXII) to the resonance hybrid of the α-diazosulphone, as shown, for example, by the shift of the absorption band of the diazo-group in the infrared spectrum towards higher wavenumbers by 20–30 cm^{-1}. Thus the diazo-group in bis(benzenesulphonyl)diazomethane[21] absorbs in the region of 2130 cm^{-1}, while that in benzenesulphonyldiazomethane absorbs in the region of 2104 cm^{-1}. The substitution of the α-hydrogen atom in diazosulphones by an acyl or alkoxycarbonyl residue also tends to shift the infrared absorption band of the diazo-group towards higher wavenumbers. This is illustrated by α-acetyl-α-(*p*-nitrobenzenesulphonyl)diazomethane[24], *p*-nitrobenzenesulphonyldiazomethane[29], and ethyl toluene-*p*-sulphonyldiazoacetate[25] (Table 1).

Table 2. Parameters of the ultraviolet spectra of certain α-diazosulphones* *m*-$XC_6H_4SO_2CHN_2$.

X	ν_{max}, nm	lgε	X	ν_{max}, nm	lgε
CH_3O	390	1.87	CF_3	383	1.84
CH_3	390	1.79	NO_2	385	1.97
Cl	385	1.84			

*The spectra were recorded in solution in 40% dioxan–water.

The introduction of the methylene group into α-diazosulphones leads to the breakdown of conjugation between the diazo- and sulphonyl groups, i.e. to a decrease of the contribution of structure (XXII) to the resonance hybrid. All these factors are clearly reflected in the infrared spectra of β-diazosulphones, where the absorption of the diazo-group is displaced towards lower wavenumbers by 30–50 cm^{-1} compared with α-diazosulphones. For example, 1-phenyl-2-(toluene-*p*-sulphonyl)diazomethane[30] and 9-diazothioxanthene SS-dioxide[21] absorb in the region of 2050 and 2075 cm^{-1} respectively.

The ultraviolet spectra of α-diazosulphones have not been investigated in detail[33–35]. Those of *m*-substituted aryldiazosulphones, whose parameters are presented in

Table 2, [34] show that diazosulphones absorb in the region of 390 nm, which corresponds to the $n \rightarrow \pi^*$ transition in the diazo-group.

Table 3. The influence of the solvent on the frequency of the $n \rightarrow \pi^*$ transition in the ultraviolet spectra of $RSO_2.CHN_2$.

R	Solvent	ν_{max}, cm^{-1}	$\lg \varepsilon_{max}$
m-$CH_3C_6H_4$	CCl_4	25000	1.88
	C_2H_5OH	25300	1.84
	40% dioxan-H_2O	25600	1.79
m-$CH_3OC_6H_4$	CCl_4	24700	1.88
	C_2H_5OH	25200	1.86
	40% dioxan-H_2O	25600	1.87
$(CH_3)_3C$	CCl_4	25600	1.21
	C_2H_5OH	25800	1.23
	40% dioxan-H_2O	26300	1.26

The polarity of the solvent influences the energy of the $n-\pi^*$ transition, which is reflected in the position of the absorption maximum of the diazo-group. Table 3 shows that more polar solvents shift the absorption maximum of α-diazosulphones towards shorter wavelengths.

Like α-diazoketones, α-diazosulphones form hydrogen bonds[35,36]. In both cases the methine hydrogen of the diazo-fragment serves as the proton donor and the acceptor is the sulphonyl or carbonyl group. α-Diazosulphones are more powerful proton donors and weaker proton acceptors than α-diazoketones.

IV. CHEMICAL PROPERTIES

Three types of reactions are characteristic of diazosulphones: (1) reactions with evolution of nitrogen; (2) reactions involving the nitrogen of the diazo-group; (3) substitution of the α-hydrogen atom.

Reactions of the first type have been most completely investigated and those of the second and particularly of the third type much less so. In discussing the chemical properties of diazosulphones, one must bear in mind that these compounds have been studied for only 10–15 years and therefore many interesting reactions of this class of compounds have still not been investigated.

The chemical reactions of diazosulphones known at present are summarised below in relation to different types of reaction mechanisms.

1. Reactions Involving the Formation of Carbonium Ions

Reactions of this series include those of diazosulphones with water, acids, t-butyl hypochloride, sulphuryl chloride, and nitrogen oxides.

The study of the hydrolysis of α-diazosulphones[34,37-40] in water and water–dioxan mixtures showed that the acid-catalysed decomposition proceeds via the bimolecular A-2 mechanism. The initial diazosulphone is reversibly protonated in the first stage, while in the second, rate-determining stage the resulting diazonium ion interacts with a molecule of the nucleophilic agent to form the final reaction product:

$$RSO_2CHN_2 \overset{H^\oplus}{\rightleftharpoons} RSO_2CH_2N_2^\oplus$$

$$RSO_2CH_2N_2^\oplus + \text{nucleophilic agent} \xrightarrow{\text{slow}} \text{product} + N_2 .$$

Studies in recent years established[41] that the hydrolysis of 4-methylbenzenesulphonyldiazomethane in a water–dioxan mixture in the presence of perchloric acid involves the protonation of the oxygen of the sulphonyl group and the A-1 mechanism, and the A-2 mechanism in the presence of hydrochloric acid in view of the more marked nucleophilic properties of chloride ions.

Electron-accepting substituents diminish and electron-donating substituents increase the rate of hydrolysis of aryl-substituted α-diazosulphones[34]. Similar observations had been made previously in the series of α-diazoketones[42] and aryldiazomethanes[43].

It is noteworthy that the hydrolysis of α-methyl-α-(toluene-p-sulphonyl)diazomethane[16] in a water–dioxan mixture under the influence of perchloric acid takes place differently and, depending on the reaction time, gives rise to different products. After 30 min, the reaction mixture contains toluene-p-sulphinic acid, acetaldehyde, and toluene-p-sulphonylethylene, and after 36 h acetaldehyde and 1,2-di(toluene-p-sulphonyl)ethane. The latter is formed as a result of the reaction of toluene-p-sulphonylethylene with the toluene-p-sulphinic acid present in the reaction mixture.

The decomposition of potassium diazomethionate[44] in aqueous solutions is catalysed by strong inorganic acids. However, the reaction begins only at a fairly high acid concentration. The hydrolysis is particularly rapid in the presence of sulphuric and perchloric acids. The addition of chloride ions reduces appreciably the reaction rate. The mechanism of the decomposition of potassium diazomethionate has not been described. Presumably in the first stage of the reaction the stronger acid displaces diazomethionic acid from its salt and the former is then cleaved.

In inert solvents α-diazosulphones form with inorganic and organic acids the esters of the corresponding α-hydroxymethyl sulphones. Certain differences between the reactivities of mono- and di-substituted α-diazosulphones and α-diazo-β-oxosulphones have been noted.

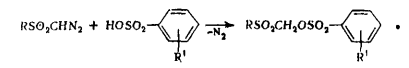
The reactions of monosubstituted α-diazosulphones with 70% perchloric acid[45,46] in methylene chloride give rise to the formation of the covalent perchlorates (XXIV) in 45% yield and α-hydroxymethyl sulphones (XXV) in 10% yield:

$$RSO_2CHN_2 + HClO_4 \begin{cases} \xrightarrow{CH_2Cl_2} RSO_2CH_2N_2^\oplus \cdot ClO_4^\ominus \rightarrow RSO_2CH_2OClO_3 \\ \qquad\qquad (XXVI) \qquad\qquad (XXIV) \\ \xrightarrow[CH_2Cl_2]{H_2O} RSO_2CH_2OH \\ \qquad\qquad (XXV) \end{cases}$$

In acetonitrile or propionitrile the yield of the perchlorate (XXIV) is lower and sulphonylmethylamides of acetic and propionic acids ($RSO_2CH_2NHCOAlk$; Alk = CH_3 or C_2H_5) are formed. The authors believe that the ion pair (XXVI), formed as a result of attack by perchloric acid, is readily converted into the perchlorate (XXIV) owing to the low polarity of the solvent. The hydroxy-derivative (XXV) is formed as a result of competition between water and perchloric ions in attacking the diazonium ion. When the ion pair (XXVI) is attacked by the alkyl cyanide, which is facilitated by the solvation of (XXVI) by the polar solvent molecules, and the resulting intermediate adduct (XXVII) is hydrolysed, sulphonylmethylamides are formed:

$$(XXVI) + R^1CN \rightarrow \underset{(XXVII)}{RSO_2CH_2^\oplus NCR^1ClO_4^\ominus} \rightarrow RSO_2CH_2NHCOR^1 + HClO_4 .$$

On interaction with α-diazosulphones, aromatic sulphonic acids give rise to sulphonates derived from α-hydroxymethyl sulphones[45,47]:



The trifluoromethanesulphonates derived from α-hydroxymethyl sulphones, which are readily formed when α-diazosulphones react with trifluoromethanesulphonic acid, are of considerable interest[48]:

$$CH_3C_6H_4SO_2CHN_2 + HSO_3CF_3 \rightarrow CH_3C_6H_4SO_2CH_2OSO_2CF_3 + N_2 .$$

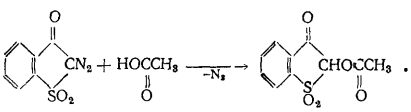
These compounds react readily with various nucleophilic agents via an S_N2 mechanism with formation of α-substituted sulphones. α-Diazosulphones react without difficulty with nitric and hydrochloric acids[29,49], forming derivatives of these acids:

$$RSO_2CHN_2 + HX \rightarrow RSO_2CH_2X + N_2 ;$$
$$X = Cl^{\ominus},\ ONO_2^{\ominus} .$$

The reaction of di(benzenesulphonyl)diazomethane with hydriodic acid[50] results in the formation of di(benzenesulphonyl)methane instead of the expected di(benzenesulphonyl)iodomethane. Evidently the intermediate di(benzenesulphonyl)iodomethane is reduced by a second molecule of hydriodic acid to di(benzenesulphonyl)methane:

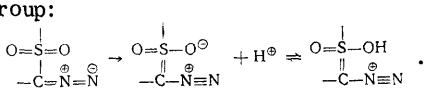
$$(C_6H_5SO_2)_2CN_2 \xrightarrow[-N_2]{HI} [(C_6H_5SO_2)_2CHI] \xrightarrow[-I_2]{HI} (C_6H_5SO_2)_2CH_2 .$$

α-Diazo-β-oxosulphones are less reactive with respect to acids than α-diazosulphones. Thus 2-diazo-2,3-dihydrothianaphthen-3-one 1,1-dioxide reacts with acetic acid only on heating and in the presence of copper as the catalyst[22]:



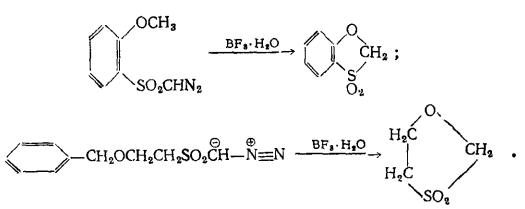
Bis(arenesulphonyl)diazomethanes are even more resistant to acids. For example, bis(benzenesulphonyl)-diazomethane[19] can be recrystallised from glacial acetic acid.

This behaviour of α-diazo-β-oxosulphones and bis-(arenesulphonyl)diazomethanes can be accounted for by the capture of the proton attacking the α-carbon atom by the sulphonyl group:

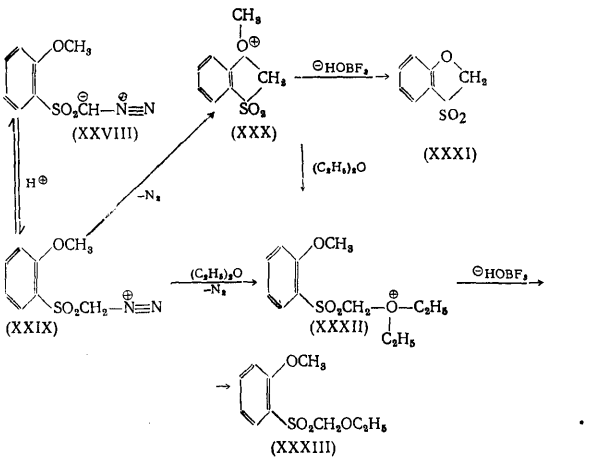


Similar observations were made also in the series of α-diazoketones. However, owing to the greater reactivity of the sulphonyl group, these phenomena are more pronounced in the case of α-diazosulphones.

Under the influence of acids, some α-diazosulphones cyclise. Thus *o*-methoxybenzenesulphonyldiazomethane and the benzyl ether of hydroxyethanesulphonyldiazomethane in ethereal solutions are converted under the influence of hydrated boron trifluoride into 1,3-benzoxathiolan 3,3-dioxide and 1,3-oxathiolan 3,3-dioxide respectively[51]:



In the first reaction stage the initial diazosulphone (XXVIII) is protonated and the resulting diazonium ion (XXIX) splits off nitrogen, being converted into the oxonium ion (XXX). The latter is converted into the final product—1,3-benzoxathiolan 3,3-dioxide. When (XXIX) or (XXX) reacts with the solvent, the intermediate oxonium ion (XXXII) is formed and then converted into α-ethoxy-α-(*o*-methoxybenzenesulphonyl)methane (XXXIII):



When ethyl ether is excluded from the reaction mixture and the reaction is carried out in methylene chloride, the yield of the oxathiolan (XXXI) increases to 72% compared with 65%.

Potassium diazomethionate reacts with hydrogen halides to form salts of halogenomethionic acids[9,52]:

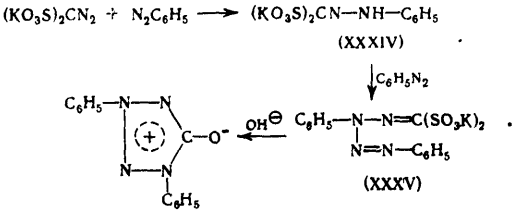
$$(KO_3S)_2CN_2 + HHal \xrightarrow{Hal=I,Br} (KO_3S)_2CHHal + N_2 .$$

When potassium diazomethionate was allowed to react with iodine[9], the potassium salt of diiodomethanedisulphonic acid was isolated:

$$(KO_3S)_2CN_2 + I_2 \rightarrow (KO_3S)_2CI_2 + N_2 .$$

It is noteworthy that the relatively little investigated methionic acid derivatives formed in these reactions are of significant interest as chemical reagents.

Potassium diazomethionate reacts with aromatic diazo-compounds. Thus the reaction with benzenediazonium acetate gives rise to the phenylhydrazone (XXIV)[53] which is converted in the presence of an excess of benzenediazohydroxide into potassium diazobenzenephenylhydrazonomethanedisulphonate (XXXV). The latter is converted under the influence of alkali into 1,3-diphenyltetrazolone[54]:



Sodium diazomethionate readily reacts with sodium bisulphite to form the salt of methanetrisulphonic acid[9,17]:

$$(NaO_3S)_2CN_2 + NaHSO_3 \rightarrow (NaO_3S)_2CHSO_3Na .$$

The interaction of α-diazosulphones with t-butyl hypochlorite proceeds via an ionic mechanism. Various products may be obtained, depending on the solvent[55]:

$$RSO_2CHN_2 + (CH_3)_3COCl \begin{cases} \xrightarrow[\text{or } CH_2Cl_2]{(CH_3)_3COH} RSO_2CH(Cl)OC(CH_3)_3 + N_2 \\ \text{(XXXVII)} \\ \xrightarrow{C_2H_5OH} RSO_2CH(Cl)OC_2H_5 + N_2 \\ \text{(XXXVIII)} \end{cases}$$

The first stage of this interesting reaction involves the addition of the electrophilic chlorine of t-butyl hypochlorite to the α-carbon atom of the diazosulphone with formation of the ion pair $RSO_2CH(Cl)N_2^+.BtO^-$ (XXXVI) solvated by t-butyl alcohol. The sulphone (XXXVII) is formed as a result of the displacement of nitrogen either by the t-butoxide anion or by t-butyl alcohol. In ethanol the sulphone (XXXVIII) is produced as a result of the solvolysis of the ion pair (XXXVI). It is noteworthy that the decomposition of (XXXVI) is accompanied by the formation of several side products, the composition of which has not so far been established.

In contrast to α-diazosulphones, α-diazoketones react with t-butyl hypochlorite to form acetals[55]:

$$RCOCHN_2 + (CH_3)_3COCl \xrightarrow{C_2H_5OH} RCOCH\langle^{OC_2H_5}_{OC_2H_5}$$

This can be accounted for by the different capacities of the chlorine atom in α-alkoxy-α-chloromethylsulphones (XXXVII) or (XXXVIII) and α-alkoxy-α-chloromethylketones (XXXIX) for nucleophilic substitution[56]:

$$RCOCH(Cl)OC_2H_5 + C_2H_5OH \xrightarrow[-HCl]{} RCOCH(OC_2H_5)_2,$$

$$RSO_2CH(Cl)OC_2H_5 + C_2H_5OH \not\rightarrow RSO_2CH(OC_2H_5)_2.$$

The driving force of the reaction of α-diazosulphones with sulphuryl chloride in ether[57] is attack on the diazo-derivative by the chloronium cation formed when sulphuryl chloride reacts with ether. The resulting diazonium ion (XL) is converted in ether into the oxonium ion (XLI). As a result of nucleophilic attack by the chloride ion, the latter is converted into α-alkoxy-α-chloro-sulphone:

$$SO_2Cl_2 + ROR \rightarrow SO_2 + Cl^{\oplus} + Cl^{\ominus} + ROR;$$

$$R^1SO_2CHN_2 + Cl^{\oplus} \rightarrow R^1SO_2CHCl\overset{\oplus}{N_2}; \quad \text{(XL)}$$

$$(XL) + ROR \xrightarrow[-N_2]{} R^1SO_2CHCl\overset{\oplus}{O}R_2;$$

$$(XLI) + Cl^{\ominus} \rightarrow R^1SO_2CHClOR + RCl.$$

It is noteworthy that there has recently been a growth of interest in reactions of diazo-derivatives with compounds which behave as donors of positive halogenonium ions. Many of these reactions make possible new methods for the synthesis of acetals and halogeno-derivatives of ethers, sulphones, heterochain compounds, and heterocyclic compounds. As an example, one may quote the reactions of diazomethane and diazoacetic ester with bromotrinitromethane[58], which lead respectively to 3-nitroisoxazoline *N*-oxide and ethyl α-bromo-ββ-trinitropropionate:

$$BrC(NO_2)_3 \begin{cases} \xrightarrow{CH_2N_2} H_2C\langle^{C(NO_2)_2}_{N^{\oplus}-O^{\ominus}}\rangle O \\ \xrightarrow{C_2H_5OOCCHN_2} C_2H_5OCCHBrC(NO_2)_3 \\ \quad \| \\ \quad O \end{cases}$$

Presumably further investigation of these reactions of α-diazosulphones will lead to the synthesis of new interesting sulphones.

The reaction of α-diazosulphones with sulphenyl chlorides leads to the formation of α-alkanesulphenyl-α-chlorosulphones[59]:

$$RSO_2CHN_2 + R^1SCl \rightarrow RSO_2CH(Cl)SR^1 + N_2.$$

These compounds have four different substituents at the same carbon atom and are thus asymmetric derivatives of orthoformic acid. According to the authors[59], there are three possible aspects of the investigation of this new class of compounds: the study of the reactivity of chlorine in nucleophilic substitution reactions; the removal of hydrogen attached to the central atom by basic reagents, which should lead to the formation of carbenoid compounds; the study of the Favorskii rearrangement in the case of $R = ArCH_2$.

The reaction of α-diazosulphones with nitrogen trioxide has been described recently[60]. It begins with attack on the diazo-derivative by the nitrosonium cation. The intermediate diazonium ion (XLII) splits off nitrogen, being converted into the nitrilic oxide (XLIII), or reacts with a nitrite ion to form the nitrolic acid (XLIV), which is also converted into the nitrilic oxide (XLIII) after splitting off nitrous acid. Compound (XLIII) dimerises to the furoxan (XLV):

$$RSO_2CHN_2 \xrightarrow{N_2O_3} \left[RSO_2\underset{|}{\overset{N_2}{C}}H-NO \right]_{(XLII)} \xrightarrow[-H^+]{-N_2} RSO_2C\equiv N^{\oplus}-O^{\ominus} \quad (XLIII)$$

(XLII) $\xrightarrow{-N_2,\ NO_2^{\ominus}}$ $RSO_2-C(NOH)-NO_2$ (XLIV)

(XLII) $\xrightarrow{-HNO_2}$ (XLIII)

(XLIII) $\rightarrow$ $RO_2S-C(=N-O)-C(=N^{\oplus}-O^{\ominus})-SO_2R$ (XLV)

The synthesis of furoxans is of significant interest, since these compounds exhibit antileukaemic activity[61] and accelerate the growth of plants[62].

2. Reactions with Formation of Sulphonylcarbenes

Diazosulphones constitute a convenient source of sulphonylcarbenes. The formation of the latter was observed in the synthesis of the corresponding cyclopropane derivatives by the photolysis of α-diazosulphones in the presence of olefins[63,64]:

$$CH_3OC_6H_4SO_2CHN_2 \xrightarrow[-N_2]{h\nu} CH_3OC_6H_4SO_2\ddot{C}H;$$

$$CH_3OC_6H_4SO_2\ddot{C}H + R_2C=CH_2 \rightarrow \begin{matrix} R_2C \\ | \\ H_2C \end{matrix}\rangle CHSO_2C_6H_4OCH_3.$$

The reaction is carried out in a 10:1 alkene–benzene mixture in an atmosphere of nitrogen. Benzene is added to increase the solubility of the diazosulphone. The high yields of cyclopropanes (75–85%) justify this operation, although benzene itself is also used to bind carbenes. However, in this case sulphonylcarbenes react with alkenes much faster than with benzene.

The addition of sulphonylcarbene to *cis*- and *trans*-but-2-enes is *cis*-stereospecific[64], which indicates the singlet state of the free electrons in the carbene.

The formation of *p*-methoxybenzenesulphonylcarbene was postulated in the decomposition of *p*-methoxybenzenesulphonyldiazomethane in methanol[62]. The reaction proceeds on irradiation with ultraviolet light in the presence

of silver oxide and leads to the formation of *p*-methoxyphenyl methoxymethyl sulphone:

$$CH_3OC_6H_4SO_2CHN_2 \xrightarrow[-N_2]{h\nu,\ CH_3OH,\ Ag_2O} CH_3OC_6H_4SO_2CH_2OCH_3 .$$

The formation of a sulphonylcarbene is also observed in the thermal decomposition of benzenesulphonyldiazomethane in benzene[65]. Together with a carbene dimerisation product—1,2-di(benzenesulphonyl)ethylene, a small amount of the product resulting from the insertion of the carbene in the C–H bond of benzene—benzenesulphonylphenylmethane—is formed[65]. Apart from these products, the ester of benzenesulphonic acid and benzenesulphonylmethanol (XLIX) is produced. The authors believe that its formation can be accounted for by the decomposition of the initial diazosulphone into the benzenesulphonyl radical $RSO_2^{\cdot}$, which captures oxygen. The resulting sulphonyl oxide radical $RSO_2^{\cdot}$ reacts with the benzenesulphonylmethyl radical formed by the reaction

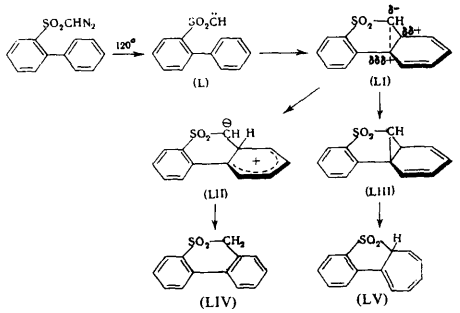
$$C_6H_5SO_2CH: + RH \rightarrow C_6H_5SO_2CH_2\cdot + R\cdot$$

The dimerisation of the above radicals gives rise to the final ester (XLIX). Compound (XLVII) is not in fact formed in the photolysis of (XLVI) in benzene, the yield of (XLVIII) remains the same, and the yield of (XLIX) increases appreciably:

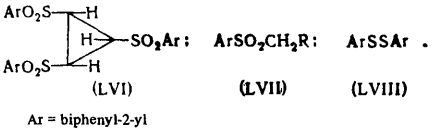
$$C_6H_5SO_2CHN_2\ (XLVI) \xrightarrow{C_6H_5SO_2CHN_2} C_6H_5SO_2CH{=}CHSO_2C_6H_5\ (XLVII)$$
$$C_6H_5SO_2CHN_2\ (XLVI) \xrightarrow{C_6H_6} C_6H_5SO_2CH_2C_6H_5\ (XLVIII)$$
$$C_6H_5SO_2CHN_2\ (XLVI) \rightarrow C_6H_5SO_2CH_2OSO_2C_6H_5\ (XLIX)$$

The photolysis and thermolysis of compound (XLVI) in cyclohexene[65] lead to an *exo*- and *endo*-7-benzenesulphonylnorcaranes in proportions of 68 : 32; compounds (XLVII) and (XLIX) were not detected. The thermal decomposition of benzenesulphonyldiazomethane in cyclohexane leads to the formation of the insertion product $C_6H_{11}CH_2SO_2C_6H_5$ in 43% yield and of compound (XLIX) in 6.9% yield. The photolysis of the diazosulphone (XLVI) in the same solvent gives rise to the same insertion product in 12% yield and to compound (XLIX) in 39% yield.

The thermal decomposition of biphenyl-2-sulphonyldiazomethane at 120°C leads to intramolecular products resulting from the insertion of a carbene (L) in a C–H or C–C bond[66]. According to the authors, this reaction proceeds via an intermediate intramolecular complex (LI), which is converted into the σ-complex (LII) or into the intermediate norcaradiene (LIII). The latter is converted into the product resulting from insertion in a C–H bond [compound (LIV)] or a C–C bond [compound (LV)]:



Apart from the two cyclic sulphones (LIV) and (LV), the authors detected the cyclopropane derivative (LVI), the sulphone (LVII), and the disulphide (LVIII):



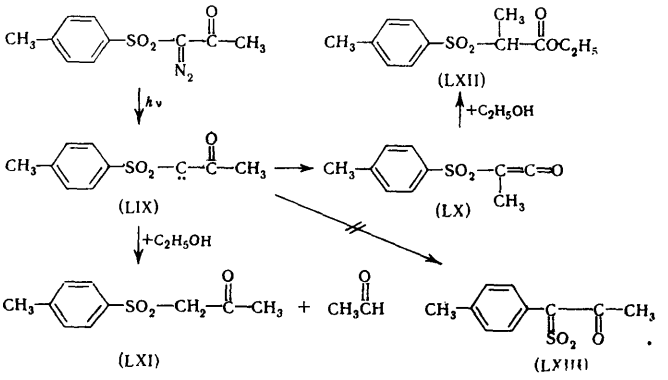
Ar = biphenyl-2-yl

The formation of compound (LVIII) can be explained by the decomposition of the initial diazosulphone into aryl-substituted sulphonyl groups with subsequent reduction and dimerisation. The sulphone (LVII) is produced as a result of the insertion of the sulphonylcarbene in a C–H bond of the solvent and the cyclopropane (LVI) is normally formed as a result of the trimerisation of an arenesulphonylcarbene.

The formation of sulphonylcarbenes on ultraviolet irradiation of di(benzenesulphonyl)diazomethane in polar solvents made it possible to develop an interesting method for the synthesis of ylids[19]:

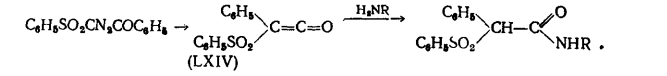
$$(C_6H_5SO_2)_2CN_2 \xrightarrow[-N_2]{} (C_6H_5SO_2)_2C: \xrightarrow{(CH_3)_2SO} (CH_3)_2\overset{\oplus}{S}-\overset{\ominus}{C}(SO_2C_6H_5)_2 .$$

Attempts to carry out the Wolff rearrangement for compounds in the series of α-diazo-β-oxosulphones during their photolytic or thermal decomposition have been described. However, the study of the photolysis of α-acetyl(toluene-*p*-sulphonyl)diazomethane[67] in ethanol showed that the carbene (LIX) formed after the elimination of nitrogen rearranges either into the keten (LX) (an α-ketocarbene-like behaviour) or reacts with ethanol, being converted into acetyl(toluene-*p*-sulphonyl)methane (LXI) and acetaldehyde. On interaction with ethanol, methyl(toluene-*p*-sulphonyl)keten (LX) gives rise to ethyl α-(toluene-*p*-sulphonyl)propionate (LXII):

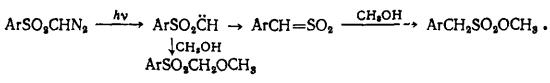


The product of the addition of ethanol to acetyl tolyl sulphene (LXIII) was not isolated. This is evidence that the rearrangement of the carbene (LIX) into the sulphene (LXIII), resembling the Wolff rearrangement, does not occur in this case.

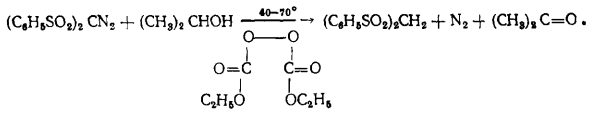
The thermolysis of α-benzoylbenzenesulphonyldiazomethane at 100–110°C in mesitylene[25] leads to formation of phenylbenzenesulphonylketen (LXIV), which is converted in the presence of amines into *N*-substituted phenylbenzenesulphonylacetamides:



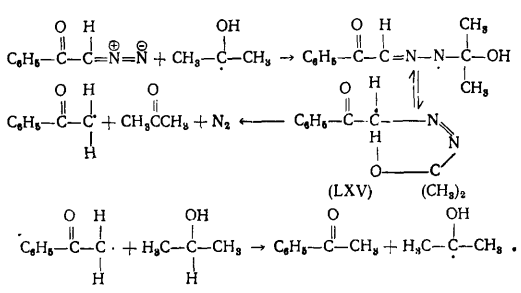
When aryl-substituted α-diazosulphones were irradiated in methanol at −10°C in an atmosphere of nitrogen[67], the methyl ether of arenesulphonylmethanol and (in a low yield) the methyl ester of α-arylmethanesulphonic acid were isolated. The last compound is probably formed as a result of the Wolff rearrangement of the arenesulphonylcarbene into an aryl sulphene, which then interacts with methanol:



When di(benzenesulphonyl)diazomethane is heated with isopropyl alcohol in the presence of diethyl peroxydicarbonate, the products are radicals which react with the above diazosulphone to form the product of the reductive elimination of nitrogen[69]:

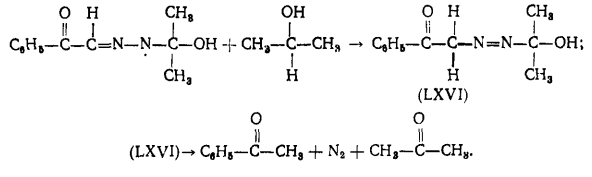


The reaction with α-diazoketones proceeds similarly. The following mechanism has been proposed:



The decomposition of diethyl peroxydicarbonate results in the elimination of a proton from isopropyl alcohol with formation of the isopropyl radical, which reacts with the diazoketone to form a hydrazonyl radical with an unpaired electron at the nitrogen atom. The latter is in equilibrium with the C-radical form (LXV). The radical (LXV) decomposes into acetone, nitrogen, and a benzoylmethyl radical. The interaction of the last species with the solvent leads to the product of the reductive elimination of nitrogen and the initial isopropyl alcohol.

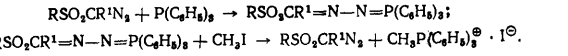
According to an alternative mechanism, the hydrazonyl radical formed in the first stage reacts with the solvent to produce the azo-compound (LXVI), which decomposes with evolution of nitrogen into the final reaction product and acetone:



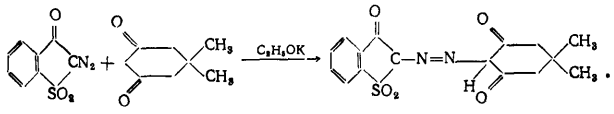
3. Reactions Involving the Nitrogen of the Diazo-Group

An important section of the chemistry of diazosulphones comprises reactions involving the nitrogen of the diazo-group; some of these were studied previously for other diazo-derivatives.

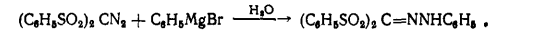
Triphenylphosphine reacts with diazosulphones to form triphenylphosphazines[19,24,27,29,30], which can be used to identify diazosulphones and to obtain them in a pure form:



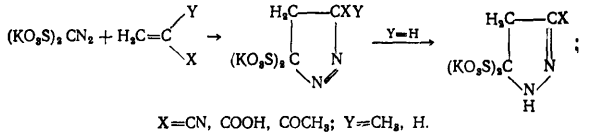
α-Diazo-β-oxosulphones react with compounds containing an activated methylene group to form azo-derivatives[22]:



Diekmann[19] observed the formation of the phenylhydrazone of di(benzenesulphonyl)formaldehyde in the reaction of di(benzenesulphonyl)diazomethane with phenylmagnesium bromide:

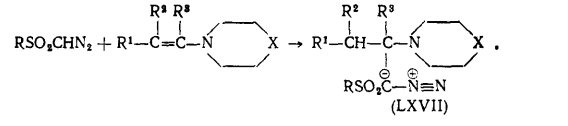


The reaction involving the formation of pyrazolines, which is well known in the series of diazoalkanes[70], has also been described for diazosulphones in relation to the interaction of potassium diazomethionate with a number of unsaturated compounds[71]:

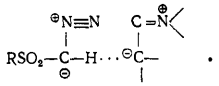


X=CN, COOH, $COCH_3$; Y=CH_3, H.

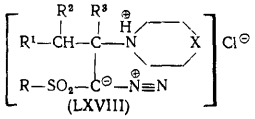
It has recently been observed that α-diazosulphones readily add to the double bonds of substituted enamines[72] with formation of products of the *C*-alkylation of the α-carbon atom of the diazosulphone [compound (LXVII)], but not pyrazolines (as happens with α-diazoketones):



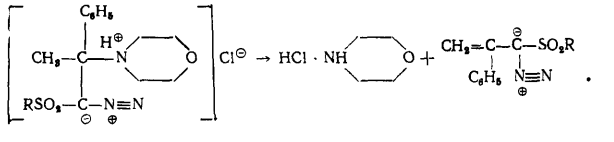
This difference in the behaviour of α-diazosulphones and α-diazoketones was explained by the greater capacity of the methylidyne protons of α-diazosulphones for the formation of hydrogen bonds with enamines in the transition complex:



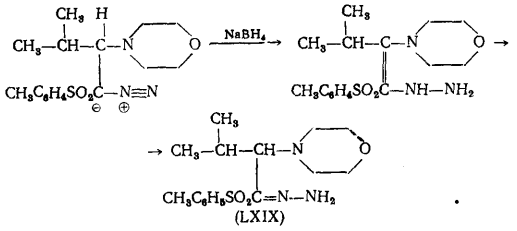
The adduct (LXVII) is stable, forming with hydrochloric acid in ether the hydrochloride (LXVIII), which can undergo further reactions:



Thus, for $R^1 = R^2 = H$, $R^3 = C_6H_5$, and X = O, morpholine hydrochloride is split off in chloroform at room temperature and an unsaturated diazosulphone—3-diazo-2-phenyl-3-(toluene-*p*-sulphonyl)prop-1-ene—is formed:

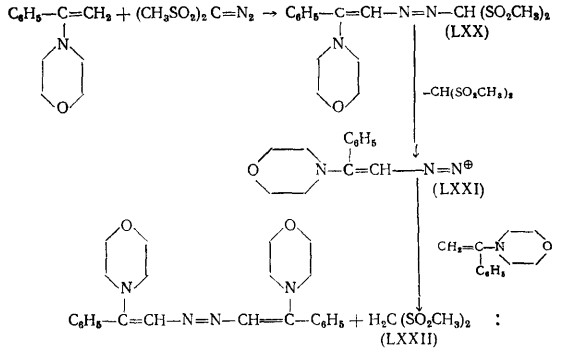


The diazosulphone (LXVII) (R = $CH_3C_6H_4$, $R^1 = R^2 = CH_3$, R^3 = H, and X = O) is reduced with sodium tetrahydroborate in methanol to 1-hydrazino-3-methyl-2-morpholino-1-(toluene-*p*-sulphonyl)but-1-ene, which isomerises to the hydrazone (LXIX) under the influence of hydrochloric acid:



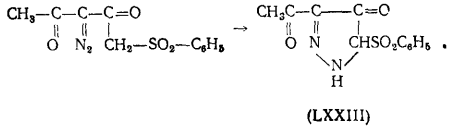
(LXIX)

The reaction of di(alkanesulphonyl)diazomethanes with enamines proceeds via a different mechanism. In the reaction of di(methanesulphonyl)diazomethanes[73] with α-morpholinostyrene the initial product is the azo-compound (LXX), which splits off the anion of di(methanesulphonyl)methane, forming the diazonium ion (LXXI). The latter reacts with a second enamine molecule to form 1,6-dimorpholino-1,6-diphenyl-3,4-diaza-1,3,5-hexatriene and di(methanesulphonyl)methane (LXXII):



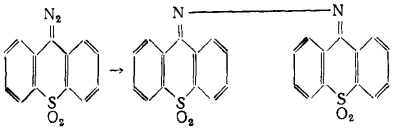
(LXX) (LXXI) (LXXII)

The interesting intramolecular cyclisation of 3-diazo-5-benzenesulphonylpentane-2,4-dione to the corresponding pyrazolone (LXXIII) under the influence of potassium ethoxide[74] belongs to the class of reactions proceeding without the evolution of nitrogen:

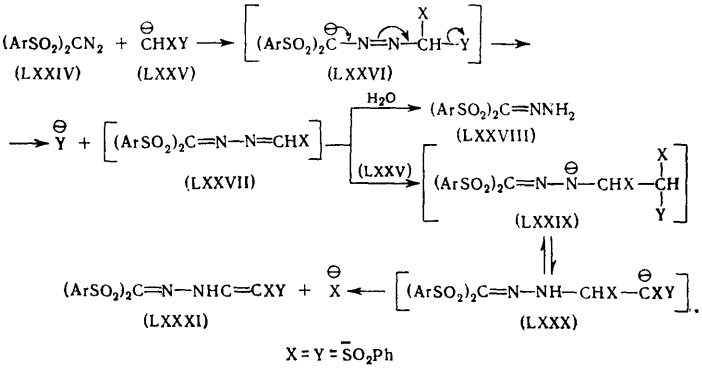


(LXXIII)

Under the same conditions, 9-diazothioxanthene *SS*-dioxide forms the azene derived from 9-oxothioxanthene *SS*-dioxide[27]:



Heyes and Holt[28] described recently an interesting reaction between di(arenesulphonyl)diazomethanes and the sodium salt of di(benzenesulphonyl)methane. It proceeds in tetrahydrofuran at 0°C and leads to the formation of sodium benzenesulphinate and a vinylhydrazone (LXXXI):

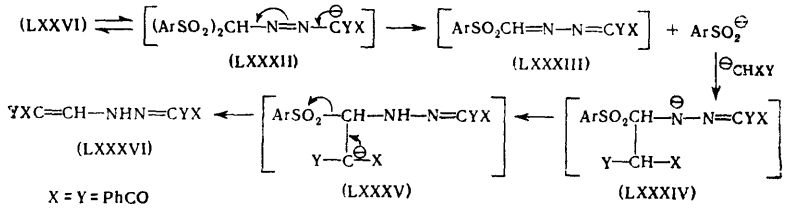


(LXXIV) (LXXV) (LXXVI) (LXXVII) (LXXVIII) (LXXIX) (LXXX) (LXXXI)

X = Y = SO_2Ph

The authors explain the formation of vinylhydrazones by the coupling of the aryldiazosulphone (LXXIV) to the carbanion (LXXV). The coupling of diazosulphones to triphenylphosphine and phenylmagnesium bromide has already been mentioned. According to the authors, this reaction is a first example of reactions where the nucleophilic agent substitutes a hydrogen atom at a carbanionic centre. The elimination of the arenesulphinate ion from the adduct (LXXVI) probably leads to the azine (LXXVII), which hydrolyses to the hydrazone (LXXVIII) in aqueous solvents. In a non-aqueous medium the nucleophilic attack on the azine (LXXVII) by a second carbanionic species leads to the formation of the adduct (LXXIX), whose tautomer (LXXX) can split off a sulphinate ion to form the vinylhydrazone (LXXXI).

If the carbanion contains carbonyl groups, then the adduct (LXXVI) is probably converted into the tautomer (LXXXII). Otherwise it is impossible to explain the splitting off of the sulphinate ion [(LXXXII) → (LXXXIII)]. This view is supported by the finding that the remaining sulphonyl group is split off from the azine (LXXXIII) with subsequent attack by a second carbanionic species, probably in accordance with the scheme (LXXXIII) → (LXXXIV) → (LXXXV) → (LXXXVI). The tetracarbonylvinylhydrazone (LXXXVI) is formed via a mechanism involving the formation of a tetrasulphonylvinylhydrazone:



(LXXXII) (LXXXIII) (LXXXIV) (LXXXV) (LXXXVI)

X = Y = PhCO

---o0o---

From the time when α-diazosulphones began to be studied on a wide scale, 12 years have elapsed. However, during this brief period the fundamentals of their chemistry have been worked out, their characteristics have been discovered, and practical applications of this interesting class of compounds have been outlined.

The interest in α-diazosulphones is due to various causes. In the first place one should mention that these compounds are valuable preparative reagents, which permit the introduction of the sulphonyl group into various organic compounds. α-Diazosulphones lead to interesting heterocyclic system, such as sulphonylfuroxans[60], oxathiolans[51], etc.[54,71]. They serve as the starting materials for the synthesis of sulphonylcyclopropanes[63,64].

The study of the biological activity of α-diazosulphones is of considerable interest. The stable and relatively non-toxic potassium diazomethionate, which exhibits antitumour activity, is striking in this respect. By analogy with α-diazoketones, α-diazosulphones can evidently exhibit mutagenic and anticonvulsant activity[75].

The presence of the nitrogen atom, which can be split off on heating or under the influence of chemical agents, permits the use of α-diazosulphones, particularly potassium diazomethionate, as agents for the formation of sponge rubber[76].

A number of characteristics of the chemical behaviour of α-diazosulphones have been discovered. Thus, in contrast to α-diazoketones, α-diazosulphones do not as a rule undergo the Wolff rearrangement, add readily to the double bond of enamines with retention of the diazo-group, react in a characteristic manner with t-butyl hypochlorite, etc.

Further elucidation of the differences between the structures and chemical properties of the diazo-group in α-diazosulphones and other aliphatic diazo-compounds will help deepen our knowledge of this field of chemistry.

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