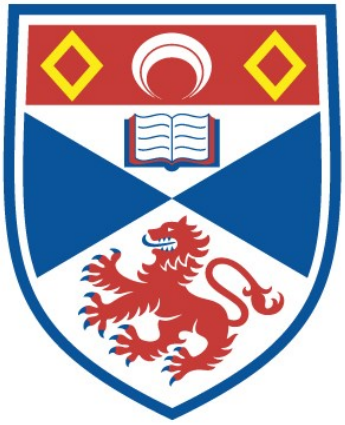
SOME REACTIONS OF SULPHONYLHYDROXYLAMINES LEADING TO AN INVESTIGATION OF SULPHONYLAMINYLOXIDES

John D. Birchall

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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SOME REACTIONS OF SULPHONYLHYDROXYLAMINES LEADING TO AN INVESTIGATION OF SULPHONYLAMINYLOXIDES

being a thesis

presented by

JOHN D. BIRCHALL, B.Sc.

to the

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in application for

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DECLARATION

I declare that this thesis is a record of the results of my own experiments, that it is my own composition, and that it has not previously been presented in application for a higher degree.

The work was carried out in the Department of Chemistry of the University of St. Andrews under the direction of Dr. C. Glidewell.

30/9/77.

CERTIFICATE

I hereby certify that Mr. John D. Birchall, B.Sc., has spent eleven terms at research work under my supervision, has fulfilled the conditions of the resolution of the University Court 1967, No. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Research Supervisor

30th September 1977.

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ABSTRACT

Mercury (II) and lead (II) ions, but not mercury (I) and thallium (I), react with both the nitrosyldisulphonate, $ON(SO_3)_2^{2-}$, and the hydroxylaminedisulphonate dianions, $HON(SO_3)_2^{2-}$, to yield the corresponding metal sulphate and a mixture of sulphate and sulphite ions. Silver (I) ions are reduced to the metal by both anions, but reacts with potassium imidodisulphonate, $HN(SO_3K)_2$, and tripotassium imidodisulphonate, $KN(SO_3K)_2$, to yield trisilver imidodisulphonate, $Ag_3NS_2O_6$, and disilver potassium imidodisulphonate, $Ag_2KNS_2O_6$. The reaction of some related salts are also reported. Mechanisms for some of the decompositions, and stoichiometric equations are proposed. No metal salts of hydroxylaminedisulphonates, $HON(SO_3M)_2$ were isolated. The silver imidodisulphonate salts failed to react with both alkyl and aryl halides.

A series of N,N-bis-(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOH$ were synthesised (X = H, Me, MeO, Cl and F). The species $(p\text{-}XC_6H_4SO_2)_2NO^{\cdot}$, $p\text{-}XC_6H_4SO_2NO$ and $p\text{-}XC_6H_4SO_2^{\cdot}$ are proposed as intermediates during the oxidation of the bis-species with PbO_2, silver (I,III) oxide, AgO, MnO_2, $Pb(O_2CMe)_4$ or nitric acid to N,N,O-tris-(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$ and nitrate ion. A mechanism involving hydroxylamine is ruled out. I.r. and n.m.r. spectra show that the tris-species are hydroxylamines, R_2NOR, rather than

amine oxides, R_3NO, and the structure is considered by a comparison with $(CF_3)_2NOH$ and $(CF_3)_2NO$. The e.s.r. spectra of the tris-species in benzene indicates the presence of a nitroxide radical. The bis-species are found to decompose to the tris-hydroxylamine and the corresponding arenesulphonic acid, while the tris-species decompose to the sulphonic acid. Oligomerisation of cyclohexene is observed during the oxidation of bis-hydroxylamines, while with bases, such as pyridine, the hydroxylamine is converted to a mixture of $(RSO_2)_2NH$, pyridine-N-oxide and a pyridinium arylsulphonate. N,N,O-tris-(Alkylsulphonyl)hydroxylamines could not be isolated. Nitrosylarenesulphinates, $p\text{-}XC_6H_4SO_2NO$ are proposed as intermediates but could not be isolated from the reactions of nitrosyl chloride and nitrogen (II) oxide with arylsulphonylhydroxylamines. $p\text{-}XC_6H_4SO_2NHOH$, $(p\text{-}XC_6H_4SO_2)_2NOH$ and $p\text{-}XC_6H_4SO_2NH_2$ (X=H, CH_3) are all are converted by NOCl to $p\text{-}XC_6H_4SO_2Cl$, but $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$ and $(p\text{-}XC_6H_4SO_2)_2NH$ are unaffected. Oxidation of $C_6H_5SO_2NHOH$ by a range of oxidants yielded, $C_6H_5SO_2Cl$, $C_6H_5SO_3H$, or $(C_6H_5SO_2)_2NOSO_2C_6H_5$, but not $C_6H_5SO_2NO$. Diene cycloaddition products of $p\text{-}XC_6H_4SO_2NO$ could not be isolated. $p\text{-}CH_3C_6H_4SO_2Na$ is converted by nitrosyl chloride to $p\text{-}CH_3C_6H_4SO_2Cl$ rather than to $p\text{-}CH_3C_6H_4SO_2NO$. $(p\text{-}CH_3C_6H_4SO_2)_2NH$ is inert to a wide range of oxidants. Both $(p\text{-}XC_6H_4SO_2)_2NOH$ and $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$ initiate free-radical halogenation by dichlorine and dibromine, but not by

diiodine, of benzene and cyclohexane. Simple carboxyamides also initiate free-radical chlorination of the same substrates. (N-aryl-N-arylsulphonyl)hydroxylamines were oxidised by PbO_2 and $Pb(O_2CMe)_4$, but not MnO_2, to a mixture of the corresponding [N-aryl-N,O-bis(arylsulphonyl)]hydroxylamine, nitrobenzene and azoxybenzene. The tris-species appears to contain the nitroxide radical, $ArSO_2N(O^{\cdot})Ar^1$. A similar mechanism to that for the oxidation of $(p\text{-}XC_6H_4SO_2)_2NOH$ is proposed.

CONTENTS

General Introduction

The development of aminyloxide† chemistry has rapidly increased during the last few decades and has been predominantly concerned with the synthesis and reactions of aryl, alkyl and heterocyclic radicals. Although the inorganic nitroxide†, potassium nitrosodisulphonate, $ON(SO_3K)_2$ has been known since 1845 and its reactions widely studied, no reports have been made concerning stable neutral analogues of Fremy's dianion.

The main aim of the research in this thesis is to investigate possible routes to the synthesis of such neutral analogues. A brief outline of the synthesis, structure and physical properties of the nitroxide function is considered first, followed by a discussion on Fremy's salt. This is considered to give any other workers in this field a look at the early development of the chemistry of Fremy's salt. The introduction finally outlines some synthetic methods that could be employed to form these radicals via various analogues. These analogues could be either alkyl or aryl hydroxylaminedisulphonates, $HON(SO_3R)_2$; N,N-bis-(arylsulphonyl)-hydroxylamines; N,N-bis-(arylsulphonyl)imides or (N-aryl-N-aryl-sulphonyl)hydroxylamines. The reactions of heavy-metal cations with nitrosodisulphonate, hydroxylaminedisulphonate and similar anions is considered, along with an investigation of nitrosylarene-sulphinates. All of these approaches are considered in the

† I.U.P.A.C. rules, (C-81.2); that the radicals are named aminyl-oxides or aminoxyls, though nitroxide is widely used. Nitroxide is used throughout this thesis.

relevant chapters of this thesis, together with a discussion of the free radical halogenation of hydrocarbon solvents by simple arylsulphonylhydroxylamines and carboxylic acid amides.

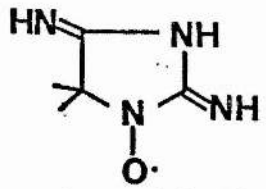
CHAPTER ONE

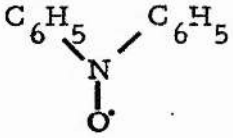
AN INTRODUCTION TO NITROXIDE CHEMISTRY

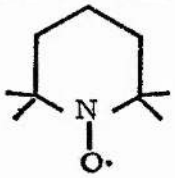
1.1 THE NITROXIDE FUNCTION

(a) The Structure, Stability and Physical Properties of the Nitroxide Function

Nitroxide radicals are molecules containing the >N-O group, derived by hydrogen atom abstraction from hydroxylamines, resulting in the group's having an unpaired electron. Although Fremy[1] isolated the first inorganic nitroxide, the first organic radical, porphyrexide, (I), was produced by Piloty[2,3]. Diphenylnitroxide[4], (II), was later isolated, and ever since radical studies have predominantly been concerned with the stable cyclic, acyclic, aliphatic and aromatic nitroxides, eg (III). The increased interest with radicals

(I) 

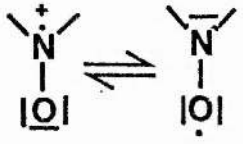
(II) 

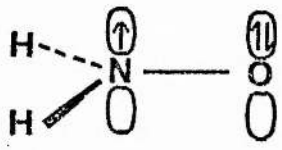
(III) 

was enhanced by the rapid development of e.s.r. spectrometry. The early work was carried out by Rassat in France and by Rozantsev in the USSR, at the beginning of the sixties. At present many nitroxides are known and many books[5,6] and reviews[7-11] have been written. These radicals are unusually stable species and investigations have outnumbered studies of other stable free radicals.

From esr. and X-ray data the structure of the nitroxide function is believed to be planar, with the unpaired electron occupying an N-O π^* orbital. The planarity of the function is justified by comparing the calculated nitrogen, hyperfinesplitting constant (hfc), for an unpaired electron in a nitrogen 2s-orbital[12], ie 552 gauss, with the

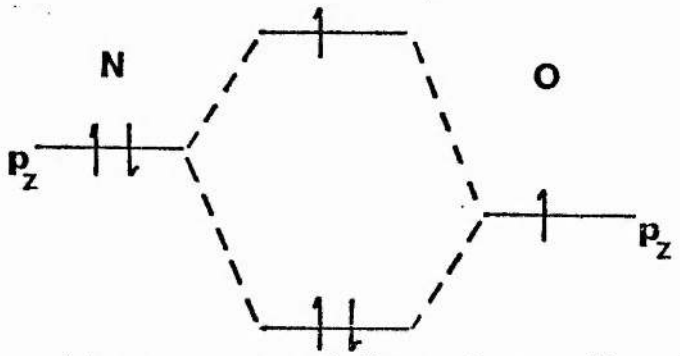
observed value of 13-15 gauss. This therefore suggests that the unpaired electron is occupying a π-orbital on the nitrogen and oxygen atom, as depicted by the two mesomeric formulae (IV) and (V). The molecular orbitals formed from the atomic orbitals of

(IV) 

 (V)

nitrogen and oxygen have two of the p_z electrons in the bonding π-orbital, and the third one in the antibonding π-orbital (See Fig. 1.1). Overall the nitrogen and oxygen atoms are connected by a $1\frac{1}{2}$-bond, which has been confirmed by the infra-red frequency[6]. The coupling

Fig. 1.1



constants observed in e.s.r. spectra indicate the coupling of the unpaired electron with the non-zero spin nuclei. An approximate measure for the spin density at nitrogen may therefore be determined. The presence of any functional groups at the nitrogen leads to the delocalisation of the unpaired electron into these groups. Hence the presence of aryl groups will lead to a reduction of spin density at the nitrogen. Substituents in the functional groups will also affect the spin density.

All stable nitroxides possess a simple single curve spectrum, which when placed in a suitable solvent changes to a triplet with a separation of approximately 10-15 gauss. With the simplest case for a free radical, the unpaired electron does not interact with the

nuclear magnetic moments, and all spins and magnetic moments of the unpaired electrons have a chaotic orientation and the same energy. When placed in a constant magnetic field the spins and the magnetic moments of the electrons orientate parallel and anti-parallel to the direction of the lines of force of the applied field. Therefore the external field splits the electrons into two groups, one of parallel orientated electrons with an energy of $\frac{1}{2}$ gβH less and a group with antiparallel orientated electrons with an energy of $\frac{1}{2}$ gβH greater than the electrons in a zero field. When an alternating magnetic field of frequency ν satisfies, $h\nu = g\beta H$, for a radical sample in a constant magnetic field, electronic transitions are induced between the two energy levels. As the lower energy level is 'populated' more highly than the upper one, energy will be absorbed in such transitions; giving rise to an e.s.r. signal.

However in the case of most free radicals, including nitroxides, the unpaired electron is present in an orbital covering several atoms. If one of these atoms has a nuclear magnetic moment then the interaction between the nuclei and the electron results in additional splitting. This causes the hyperfine splitting (h.f.s) on an e.s.r. spectrum. In the case of a nitroxide radical the unpaired electron interacts with the nuclear spin of the nitrogen atom. When placed in a constant magnetic field the nuclear spin of the nitrogen atom can adopt three values, and so each electron level is split into three sub-levels. Application of an alternating magnetic field therefore produces three electron transitions between these levels. Therefore the h.f.s. of an e.s.r. spectrum consists of three equidistant lines of equal intensity (See Fig. 1.2). Additional interactions can occur

with protons on adjoining functional groups, and with the natural isotopes ^{15}N and ^{13}C, resulting in more fine structure .

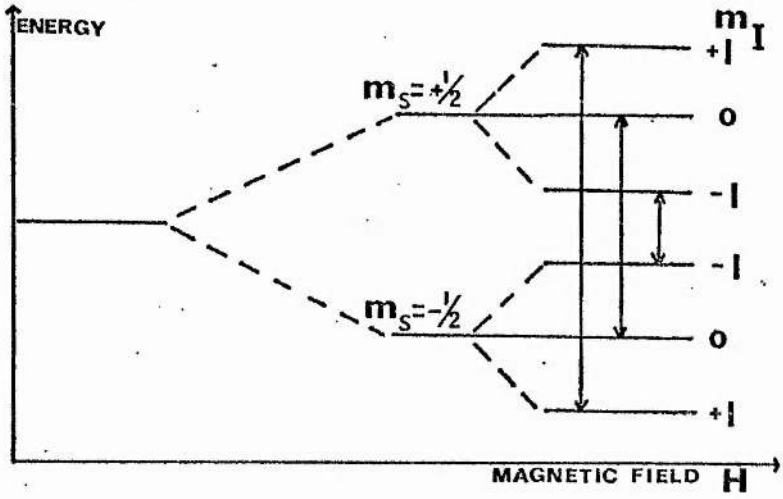


Fig. 1.2

Nitroxides have an inherently stable electronic configuration around the nitrogen and oxygen atoms, and any steric or mesomeric effects which arise from the groups attached to the nitrogen atom have little or no part in preventing dimerisation occurring at the N-O centre. No organic molecule yet prepared will dimerise at room temperature. Attaching organic groups to the nitrogen atom of nitric oxide, which is in effect the simplest nitroxide, will cause destabilisation through increased unpaired electron delocalisation. Steric and mesomeric factors are important and stop the nitroxide reacting with itself by (a) dimerisation at another centre in the molecule, and (b) by disproportionation or fragmentation. Hence stable nitroxides are only isolated when these groups do not cause the molecule to react with itself, and when there is satisfactory delocalisation of the unpaired electron over the aromatic nuclei. Nitroxides where the N-O group does not take part in the formation of a conjugated system of multiple bonds are called "nitroxyls"[5]. In this case the unpaired electron is localised on the nitrogen and

oxygen atoms to a considerably greater degree. The reason for the stability of nitroxyls is therefore less obvious. The degree of electronegativity of the atoms, other than carbon and hydrogen, in the radical is an important factor. Information on the electronic structure of the nitroxyl radicals can be obtained from an analysis of dipole moments. The dipole moment of the N-Ȯ bond in the free radical increases, as compared with the hydroxylamine. This can be explained by the interaction of the unshared electron pair of the nitrogen atom with the partially free p-orbital of the oxygen atom. The displacement of one of the electrons of the unshared pair of the nitrogen atom to the oxygen atom explains the increase in the dipole moment of the nitrogen-oxygen bond, and hence the appearance of spin density on the nitrogen atom. This argument can not be considered unambiguously since in most cases the data correlate poorly with the distribution of spin density obtained by means of e.s.r..

As we have already discussed all nitroxides exhibit an e.s.r. spectrum, and have a dipole moment; eg diphenylnitroxide has a dipole moment of 2.4 D; this suggests that electron delocalisation is over both atoms with the spin density on the nitrogen at about 44%[13]. The bond length of this radical is 1.28 Å, and can be considered between the bond lengths of N=O (1.18 Å) and N-O (1.44Å). This concept is in agreement with Pauling's[14] model for nitric oxide. In this case he considers the structure contains five bonding electrons, :N⋯O:, which consists of a σ-bond and a three electron bond between the atoms. This is supported by the small magnetic moment, the bond length and the infra-red spectrum. The bond length of 1.15 Å lies

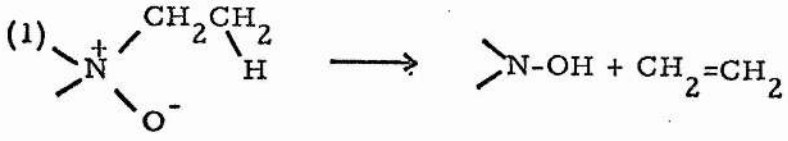
between that of N=O (1.18 Å) and :N≡O:$^{+}$ (1.06 Å), and between that for dinitrogen (1.18 Å) and dioxygen (1.21 Å). Nitroxides can therefore be considered to be analogous. They show ultra-violet absorptions at 230-325 nm due to the $\pi \longrightarrow \pi^*$ transition and at 410-570 nm for the $n \longrightarrow \pi^*$ transition. eg Ph_2NO 320-325 nm and 490-570 nm. Their characteristic infra-red frequency is 1310-1370 cm^{-1} eg Ph_2NO at 1342 cm^{-1}.

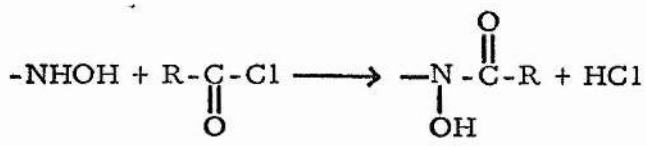
(b) The Synthesis of Nitroxides

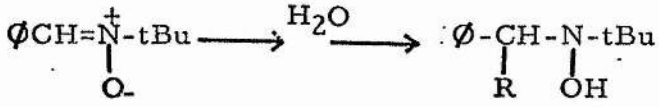
(i) from hydroxylamines

The simplest method is by the dehydrogenation of the corresponding hydroxylamine, and this generally gives the best yields of nitroxide radicals. The oxidising agents vary widely, and include, silver(I,III)oxide[4,15,16], difluorine, mercury(II) oxide[16-19], lead(IV) acetate, hydrogen peroxide[20-22], lead(IV) oxide[23,24], potassium permanganate[18] and atmospheric oxygen[7]. The oxidation takes place at room temperature, but can be accelerated by stirring and heating. Alkaline solutions of potassium ferricyanide[7,25,26] have also been used, but in excess form a complex mixture of byproducts. The presence of stabilising groups around the nitroxyl function has been the main drawback of this method, since no simple methods have been found to produce sterically hindered hydroxylamines. Methods for producing them include, the pyrolysis of the N-ethyl N-oxide of a secondary amine (1); the acylation of a primary hydroxylamine derivative. (2); addition of an organo lithium to a nitrone (3); addition of a Grignard reagent to a nitrone (4); and by addition of an aryl Grignard reagent[7,27] to nitrosobenzene (5).

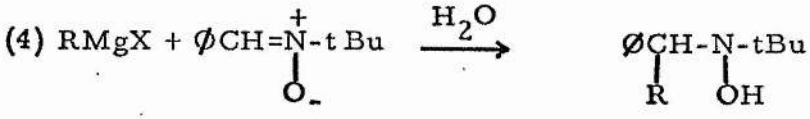
Ultra-violet irradiation has also been used with alicyclic nitroxides.

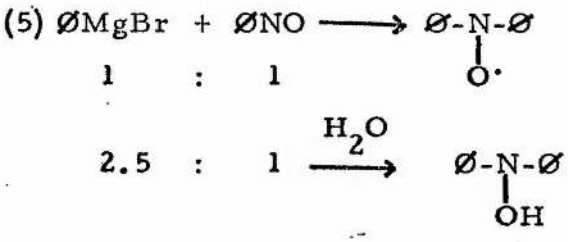
(1) 

(2) 

(3) RLi + 

R=Ø, Me, Et, n-Bu

(4) RMgX + 

(5) 

(ii) from secondary amines

Free radicals[28] always arise as intermediates in the oxidation of secondary amines, but only a few oxidising agents have become of synthetic importance. p-Nitro[29] and m-chloroperbenzoic acids[30, 31] have been widely used for the oxidation, although hydrogen peroxide[7, 32] in basic aqueous solution, or in the presence of phosphotungstic acid[33], vanadium molybdenum and tungsten salts[34-37] can also be used. Other oxidising reagents include cerium salts[7], lead (IV) oxide[7], alkaline permanganate[38], and hydroperoxides[39]. Strongly hindered secondary amines appear to go through a mechanism[40] involving a hindered hydroxylamine, which then undergoes further oxidation to an unstable nitrogen oxide, which decomposes into a

nitroxyl and hydroxyl. A large number of individual radicals have been obtained by Rassat and coworkers[9] using phosphotungstic acid. As a rule aromatic amines are not oxidised by pertungstate, and hydroperoxide in the presence of cobalt stearate[5] has been used. With pertungstic acid, di-t-alkylamines are oxidised to

Scheme 1.1 Oxidation of secondary amines by peroxide radical

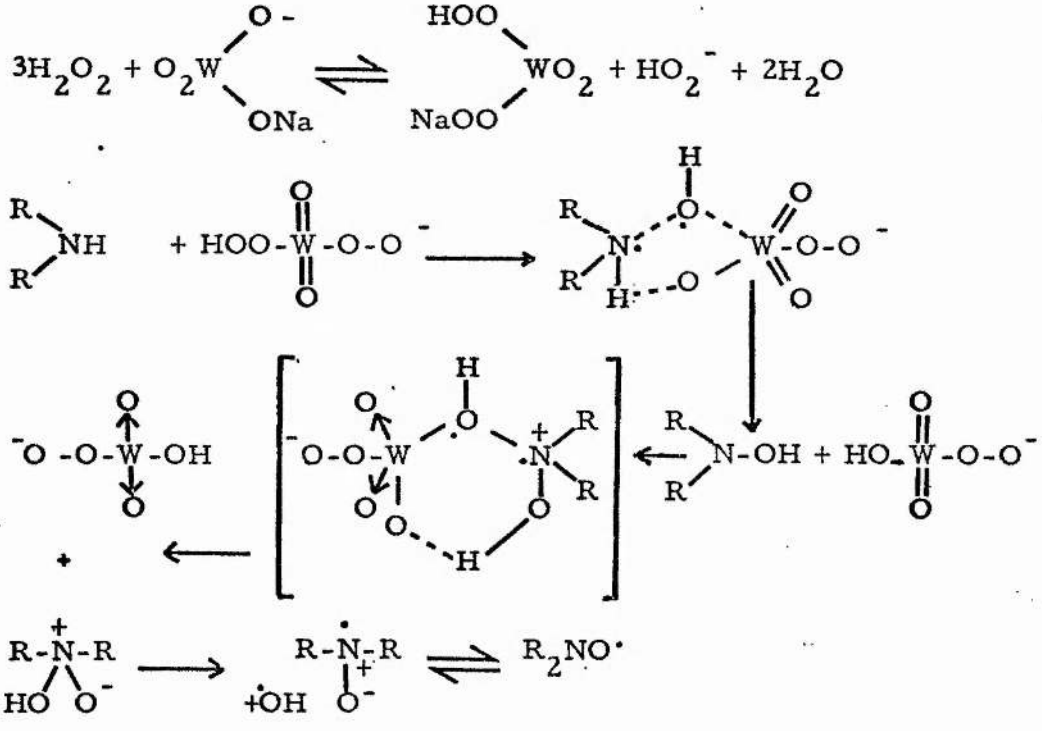
$$Ar_2NH + RO_2^{\cdot} \longrightarrow Ar_2N^{\cdot} + RO_2H$$

$$Ar_2N\cdot + Ar_2N\cdot \longrightarrow Ar_2N\text{-}NAr_2$$

$$Ar_2N\cdot + RO_2\cdot \longrightarrow Ar_2\dot{N}O + RO\cdot$$

nitroxides with hydrogen peroxide in the presence of a quaternary ammonium hydroxide and a salt of either vanadium, molybdenum[37] or tungsten. Alternatively hydrogen peroxide and phosphotungstic

Scheme 1.2 Oxidation of amines by tungstate and hydrogen peroxide



acid may be used. This was introduced by Lebedev[33], and used to produce a large number of stable radicals from heterocyclic amines.

(iii) from nitroso compounds

The number of nitroxides increased greatly following their synthesis by the photolysis of substituted nitrosobenzenes.[41,42] (6) Hence, radical addition can lead to both aromatic and aliphatic

$$RNO \xrightarrow{h\nu} (R\text{-}N{=}O)^{*} \longrightarrow R^{\cdot} + NO^{\cdot}$$

$$R^{\cdot} + RNO \longrightarrow R_2NO^{\cdot} \qquad (6)$$

nitroxides. Addition of Grignard compounds also leads to nitroxides[7]. The mixing of aliphatic or aromatic nitroso compounds with benzenesulphinic acid[43] leads to the intermediate formation of phenylsulphonylnitroxides.

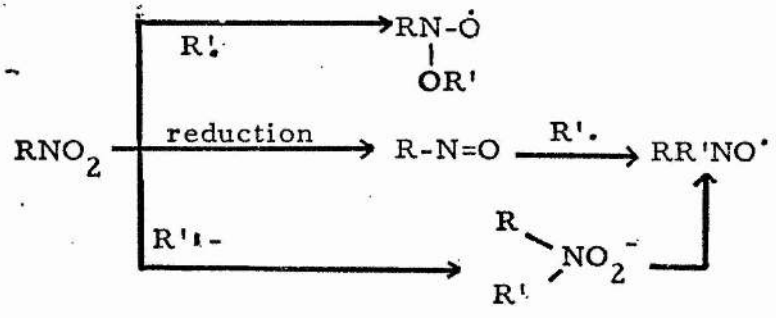
(iv) from nitro compounds

The addition of aryl or t-alkyl Grignard compounds to nitroalkanes[44-49] (7), or the addition of t-alkyl Grignard[47] compounds to aromatic nitro compounds. Radical attack at the oxygen atom give

$$t\text{-}RNO_2 + R'MgX \longrightarrow (tRR'NO_2)^{-}Mg^{+}X \xrightarrow{RMgX} tRR'\text{-}NO^{\cdot} + R^{\cdot} + MgX_2 + MgO \qquad (7)$$

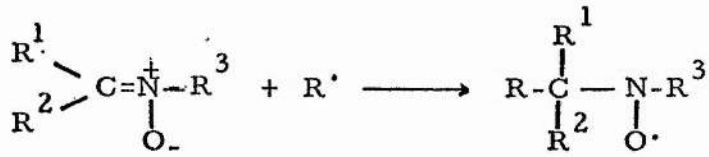
alkoxyaminyloxides. Approaches to nitroxide formation are outlined below (Scheme 1.3).

Scheme 1.3



(v) Free radical addition to nitrones

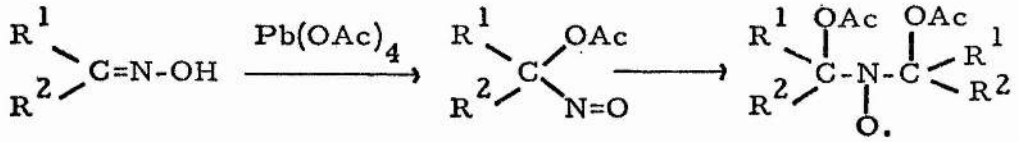
Brown[50] showed that the addition of radicals at the double bond of nitrones yielded nitroxide[51] radicals (8)

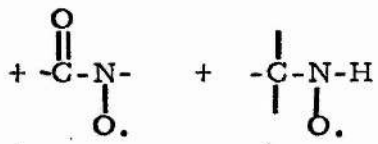


(8)

(vi) from oximes

The oxidation of oximes with lead(IV) acetate produces several nitroxides[52,53] (9) and (10).





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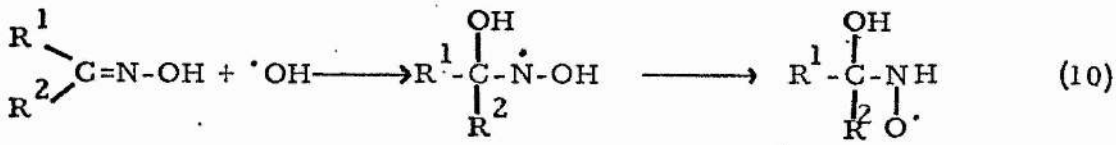


(10)

(vii)

Meyer[54,55] used the oxidation of phenol esters with nitric acid, followed by treatment with perchloric acid to produce oxides of diarylammonium salts. When reduced, the salt formed a nitroxide. More recently[56] electrochemical methods have been applied. The preparative methods outlined here are to give general approaches to the synthesis of nitroxides, and detailed study of their reactions and preparation may be found in the reviews[6,9,10].

1.2 FREMY'S SALT AND SOME RELATED COMPOUNDS

(a) Historical

Fremy[1] was the first to isolate potassium nitrosodisulphonate† (VI). The chemical development of this compound was centred around the preparation and reactions of hydroxylaminedisulphonate[58-61] salts (VII). These compounds were first reviewed by Divers and Haga[62]

(VI) $O^{\cdot}\text{-}N(SO_3^-)_2$ (VII) $KSO_3\text{-}N(OH)\text{-}SO_3K$ (VIII) $HOSO_2NSO_2OH$ (OH)

and later by Raschig[63,72], who by using an electrochemical method proposed that (VI) occurs as a dianion in solution. The potassium, barium, ammonium and lead salts are just a few examples of the hydroxylaminedisulphonates prepared by Fremy[1], from treating aqueous alkaline solutions of nitrite ion with sulphur dioxide. He classified, (VII), into a neutral and a basic salt depending on the alkali concentration, and claimed that both were derived from hydroxylaminedisulphonic acid (VIII). He postulated that, (VII), decomposes identically in both acidic and basic media. He came to this conclusion since hydroxylaminemonosulphonate, (IX), and potassium hydrogen sulphate were isolated from acidic media, and (IX) was then seen to decompose to ammonium hydrogensulphate, oxygen and hydrogen peroxide. Both ammonia and oxygen were also identified during alkaline decomposition. Oxidation of (VII) with either lead (IV) oxide or silver (I,III) oxide afforded a yellow crystalline

† See Table 1.1 for development of nomenclature

Table 1.1 Nomenclature for Fremy's salt and some related compounds

Name (date)	$HON(SO_3K)_2$	$HONH(SO_3K)$	$ON(SO_3K)_2$	$ON(SO_3K)_3$	$HN(SO_3K)_2$
Fremy (1845)	sulphazotates[a]	sulphazidates	sulphazites	metasulphazilate	sulphamidate
Claus (1871)	disulphydroxy-azates	sulphydroxyl-amminates	oxysulphazotate	trisulphoxyazoate	disulphammonates
Divers and Haga (1904)	oximidosulph-onates	oxamidosulph-onates	peroxyamido-[b] disulphonate	-	imidosulphonates[c]
Raschig (1924)	sulphazotates	-	sulphazolinates	-	imidosulphonates
Mellor (1928)	hydroxynitrilo-[d] disulphonates	hydroxynitrilo-[e] monosulphonate	peroxylamido-sulphonate	nitrilotrisulph-[f] onate	imidodisulphonate
1977	hydroxylamine-disulphonate	hydroxylamine--monosulphonate	nitrosodisulph-onate	hydroxylamine-trisulphonate	imidodisulphonate

a neutral sulphazotates $HON(SO_3K)_2$; basic sulphazotates, $KON(SO_3K)_2$

b Hantzsch and Semple called this nitroxyldisulphonate

c neutral species $HN(SO_3K)_2$; basic species $KN(SO_3K)_2$

d also potassium hydroxynitrilo-*iso*-disulphonate $KSO_3ONH(SO_3K)$ or potassium hydroxylamine-*iso*-disulphonate

e also potassium hydroxylamine-*iso*-monosulphonate NH_2OSO_3K

f potassium nitrilo-trisulphonate now refers to $N(SO_3K)_3$ (Fremy-sulphammonates)

salt (VI). Claus[58] also isolated (VI), and claimed that it decomposed to potassium hydroxylaminetrisulphonate (X), and a fixed amount of

(IX) $HONH(SO_3K)$ (X) $KSO_3ON(SO_3K)_2$ (XI) $H\cdot N(SO_3K)_2$

sulphate. Raschig[61] critisised both Fremy's and Claus' methods of making (VII) as unproductive, and preferred using bisulphite and nitrite ions.

Divers and Haga[64] showed that sodium hydroxylamine-disulphonate could be produced directly from sulphite and nitrite. The decomposition[65] of (VII) was studied, and in alkaline or acidic media only nitrous oxide was formed from the decomposition of (IX). They claimed this to be the gas observed by both Fremy and Claus as it supports combustion (Claus), and behaves like oxygen (Fremy). The reactions of alkaline hydroxylaminedisulphonates with lead acetate[62] were proved to be complex. The disodium and dipotassium salts gave no precipitate with normal lead acetate, but excess basic lead acetate gave a solid with the composition, $Pb(OH)\text{-}ON[SO_3Pb(OH)]_2.3H_2O$. This was found to decompose to sulphite and nitrite. Later papers[66-68] considered the imidodisulphonates (XI), of potassium, sodium, barium, calcium and strontium, along with their mixed ion salts. The first heavy metal salts were produced with lead, silver and mercurous ions (XII) to (XIV). They claimed that decomposition of the lead salt gave

(XII) $Pb_3N_2(SO_3)_4$ (XIII) $AgN(SO_3Ag)_2$ (XIV) $[Hg_4N(SO_3)_2]_2$

amidosulphonic acid and lead sulphate, while the silver salt (XIII)

$$4AgN(SO_3Ag)_2 \longrightarrow 2N_2 + 2SO_2 + 5Ag_2SO_4 + Ag_2S \qquad (11)$$

decomposes as in (11). Both the sodium and potassium salts of (VII) were made in substantial yields using Fremy's sulphur dioxide method, though the greater solubility of the sodium salt made isolation difficult. Both the neutral and basic salts of (VII) were shown to be from the one acid (VIII) as either formed (VI) on oxidation with lead (IV) oxide. He proposed that the decomposition[70] of (VI) proceeds via (VII) and (X). The stability of (VI) was shown to be enhanced in the presence of alkali, while the rate of decomposition to the hydroxylamine (VII) and aminedisulphonate was increased in acidic media (See (12)). Haga also made (VI) with oxidising agents such as chlorine, ozone, hydrogen peroxide, potassium ferricyanide and potassium permanganate. Some samples would spontaneously explode on drying, while other samples could be stored for periods exceeding a week. Haga could now explain the discrepancy in observations made by Fremy, Claus and Raschig. Nitrous acid, he

$$2O_2.N_2(SO_3K)_4 + H_2O \longrightarrow 2(KSO_3)_3NO + (KSO_3)_2NOH + HNO_2 \qquad (12)$$

claimed, from the decomposition would react with the hydroxylamine-disulphonate and yield both the sulphate and nitrous oxide. (Claus and Raschig). The hydroxylaminedisulphonate also produced will be reoxidised to nitrosodisulphonate by any excess lead (IV) oxide, which in turn produces more trisulphonate, until only trisulphonate[71] is present (Claus). Haga also claimed that the nitrosodisulphonate was (i) a peroxide and (ii) the nitrogen is trivalent.

Raschig[72] considered that the aqueous alkaline hydrolysis of (VI) was a two step process (see (13) and (14)). A solid state decomposition was also proposed, whereby the salt was subjected to either dilute hydrochloric or sulphuric acid, resulting in the formation of hydroxylaminedisulphonate and nitrous acid. He

$$2ON(SO_3K)_2 + H_2O \longrightarrow HO.N(SO_3K)_2 + HO.ON(SO_3K)_2 \quad (13)$$

$$2ON(SO_3K)_2 + HO.ON(SO_3K)_2 \longrightarrow HNO_2 + 2ON(SO_3K)_3 \quad (14)$$

$$4ON(SO_3K)_2 + KOH \longrightarrow 2ON(SO_3K)_3 + N_2O + K_2SO_4 + KHSO_4 \quad (15)$$

claimed that (13) and (14) does not occur if no excess alkali is present, and the overall reaction is as in (15).

(b) Stability and decomposition

As we have seen, the instability of (VI) has been reported by many workers[1, 63, 70, 73-79], and any serious kinetic study of its decomposition in aqueous solution was not approached until later[74]. The rate of decomposition in aqueous solution was shown to be pH dependent, though Murib and Ritter's claim that it was accelerated in the presence of chloride ions was later contested by Moser and Howie[80]. They showed that the spontaneous decomposition of (VI) was due to the presence of nitrite ion[70]. Manganese dioxide has also been blamed[79]. The decomposition with respect to hydronium and hydroxyl ions in aqueous media was represented as in (16). Murib

$$4ON(SO_3)_2^{2-} + 7H_2O \longrightarrow 2HON(SO_3)_2^{2-} + N_2O + 4SO_4^{2-} + 4H_3O^+ \quad (16)$$

and Ritter proposed that a degenerate branching, in which nitrous acid acts as a chain propagator, was involved, and this supported the observations of Haga[70]. The overall reaction is depicted

below (17 -19). Further studies[75, 81-83] of colour fading led to the

$$ON(SO_3)_2^{2-} + H_3O^+ \xrightarrow{K_1} HO.N(SO_3)_2^{2-} + H_2O^+ \quad (17)$$

$$H_2O + H_2O^+ \rightleftharpoons H_3O^+ + HO^\cdot \quad (18)$$

$$ON(SO_3)_2^{2-} + HO^\cdot \xrightarrow{K_2} \text{intermediates} \begin{bmatrix} N_2O, SO_4^{2-} \\ HNO_2, H_3O^+ \end{bmatrix} \quad (19)$$

comparison of the mechanism with that of diazatisation[81]. The alkaline hydrolysis of hydroxylamine disulphonates was studied by Nast[84] and coworkers, who proposed the mechanism (20) - (24).

$$2KOH + HO.N(SO_3K)_2 \longrightarrow NH_2OH + 2K_2SO_4 \quad (20)$$

$$HO.N(SO_3K)_2 + NH_2OH \longrightarrow HNO^{191} + HN(SO_3K)_2 + H_2O \quad (21)$$

$$NH_2OH + HNO \longrightarrow N_2 + 2H_2O \quad (22)$$

$$HN(SO_3K)_2 + KOH \longrightarrow H_2NSO_3K + K_2SO_4 \text{(predominates)} \quad (23)$$

$$HN(SO_3K)_2 + 3KOH \longrightarrow KNO_2 + 2K_2SO_3 + 2H_2O \quad (24)$$

The reactions with hydrogen sulphite, (25)-(29) were shown to be branched yielding about 70% imidodisulphonate and 30% amidosulphate, or 70% nitrilotrisulphonate and 30% imidodisulphonate[85].

$$HO_3S^- + SO_2 + NO_2^- \longrightarrow HO\cdot N(SO_3)_2^{2-} \quad (25)$$

$$HON(SO_3)_2^{2-} + HO_3S^- \longrightarrow N(SO_3)_3^{3-} + H_2O \quad (26)$$

$$\longrightarrow HN(SO_3)_2^{2-} + HSO_4^- \quad (27)$$

$$HO\cdot NHSO_3^- + HO_3S^- \longrightarrow HN(SO_3)_2^{2-} \quad (28)$$

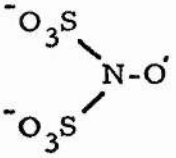
$$\longrightarrow H_2NSO_3^- + HSO_4^- \quad (29)$$

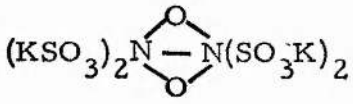
The hydrolysis[86] of hydroxylamine trisulphonate was to produce a hydroxylamine-N,O-disulphonate ion, which then hydrolyses slowly to hydroxylamine-O-sulphonate (30).

$$[(SO_3)ON(SO_3)_2]^{3-} + H_2O \longrightarrow [(SO_3)ONH(SO_3)]^{2-} \xrightarrow[\text{slow}]{H_2O} NH_2OSO_3^- + HSO_4^- + HSO_4^- \quad (30)$$

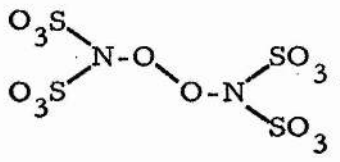
(c) Structure and physical properties

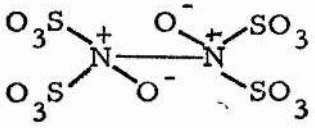
(VI) was compared to dinitrogen tetroxide[57] by Hantzsch and Semple, who proposed that the purple solution of the salt contained monomeric nitrosodisulphonate ions and that the yellow solid was a dimeric species. Magnetic studies[73, 87] have confirmed this and its radical nature has been shown in e.s.r. studies[88-95]. Hantzsch and Semple suggested a trivalent nitrogen and a monovalent oxygen atom for the molecule (XV). Raschig's original formula (XVI) involving

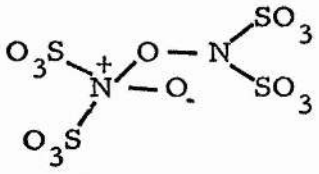
(XV) 

(XVI) 

a pentavalent nitrogen atom was rejected. No structure for the yellow solid was given, and Hantzsch discounted Sabatier's[96, 97] idea that the blue colouration of the solution was due to nitrosodisulphonic acid. These ideas were confirmed by Yamada and Tsuchida[76] from consideration of steric effects, along with visible, ultra-violet and infra-red observations. The spectral data suggested the solid to have a peroxide linkage suggesting a dimer to be present. Dimerisation would cease however if a larger cation[88, 89, 99] could be introduced. The solid state was later[80, 100] found to exist in two crystalline forms; (a) monoclinic and (b) triclinic and monomeric. The triclinic orange-brown form of (VI) has an e.s.r. spectrum at 3303 G, while the yellow-orange monoclinic form shows[100] no spectrum at all. From Yamada and Tsuchida's work[75] three structures for the dimer, (XVII), (XVIII) and (XIX) were postulated. Based on infra-red[76, 77] evidence, (XVII) and (XIX) were considered,

(XVII) 

(XVIII) 

(XIX) 

but X-ray data[80,100] allowed (XVII) and (XVIII) to be rejected. The esr. spectrum of Fremy's salt is a triplet of equal intensities with a separation of 13G and a line width[101] of 0.5G. The hyperfine splitting of the spectrum agrees with the theoretically expected interaction of the unpaired electron with the nuclear spin of the nitrogen atom. The usual esr. technique is inadequate for highly dilute solutions of the free radical, but the spectrum can now be studied by double nuclear electron resonance, hence allowing the hyperfine structure to be studied in weak magnetic fields, which is normally impossible[95,102-108]. More recently[109-110] the radiation chemistry of the radical has been investigated, and it is still used extensively for esr. studies[108,111-114]. Its decomposition in non-aqueous[115] solvents has also been looked into.

(d) Preparation

It is obviously desirable to prepare Fremy's salt in a stable state whereby it can be stored for a reasonable period of time. Instability appears to generally arise from contamination in its preparation. The majority of preparations[1,63,70,74,76,78,79,116,117,129] are carried out in three stages: (a) the preparation of the hydroxylamine-

disulphonate salt by the reaction of bisulphite and nitrite; this reaction has to be kept at low temperature to stop the formation of byproducts such as aminetrisulphonate: (b)oxidation of the hydroxylamine to the nitrosodisulphonate ion using permanganate, lead (IV) oxide or silver (I,III) oxide: (c) the solid radical is finally precipitated by adding chloride or nitrate ion. Recrystallisation is normally from alkaline or neutral solution.

This basic preparation has been modified by several chemists[78-80] and mainly concerns the isolation of the pure product after oxidation. As Moser and Howie[80] point out, the presence of excess nitrite from the synthesis of the hydroxylaminedisulphonate will destabilise the product, which is in agreement with the observations of Murib and Ritter[74]. For recrystallisation acidic solutions are not to be considered as the nitrosodisulphonate ion will decompose. Alkaline solutions will lead to the production of hydroxylamine trisulphonate, and therefore using aqueous potassium hydroxide[1,63,64,73,74,78,79,116,117a] for recrystallisation is unrealistic. The maximum stability[74] is at pH 8 which therefore must be viewed as the best pH for recrystallisation.

Sodium nitrosodisulphonate was first prepared by Raschig[72] and has more recently been produced electrochemically[118]. Both sodium and potassium hydroxylaminedisulphonate have been isolated using nitric oxide, nitrogen dioxide and sulphite[119]. Several other nitrosodisulphonates have been reported[98]. These include the tetraphenylarsonium and stibonium salts, which were first made[120] as polymeric masses. No analysis was reported until later[98]. The

caesium, rubidium and ammonium nitrosodisulphonates were prepared and analysed, along with a brown hexamminecobalt(III) salt, $[Co(NH_3)_6]_2[ON(SO_3)_2]_3$, which has still to be fully investigated. Most of these salts proved to be unstable and faded slowly over a few days. The caesium salt decomposes rapidly forming a white fused mass. No other salts of this type have been reported. Non-aqueous esr. studies have been carried out on two of these salts[100].

(e) Reactions of Fremy's salt

Fremy's radical is one of a few very selective oxidising agents and can readily oxidise phenols to quinones. The general oxidation reactions of the radical were not studied in detail until the nineteen fifties, when Teuber and coworkers produced a long series of papers[122]. These reactions have been extensively reviewed recently[122-125].

(f) Some other salts

Potassium imidodisulphonate, $HN(SO_3K)_2$, is prepared by the reaction of 100% sulphuric acid with urea[126, 117(b)] followed by heating; Potassium nitrilosulphonate, $N(SO_3K)_3$, by the action of nitrite[117(c), 127] on bisulphite; Potassium hydroxylamine trisulphonate $(KSO_3)ON(SO_3K)_2$, by the reaction of potassium nitrosodisulphonate with sulphite, followed by the addition of lead (IV) oxide[117(d), 70]; and potassium hydroxylamine-iso-disulphonate by the hydrolysis of hydroxylaminedisulphonate[117(e), 128]. A complete survey of the chemistry of these compounds and other similar compounds is given by Mellor[69].

1.3 SOME APPROACHES TO THE SYNTHESIS OF NEUTRAL ANALOGUES OF FREMY'S RADICAL

(a) from hydroxylamine disulphonate and imidodisulphonate salts

Divers and Haga[66-68] produced the first heavy metal salts of imidodisulphonates. If metal salts such as $HON(SO_3M)_2$ and $HN(SO_3M)_2$, where $M=Pb^{2+}, Ag^{+}$ etc, could be made, this would allow the production of the corresponding amines and hydroxylamines, $HON(SO_3R)_2$ and $HON(SO_3R)_2$, after the reaction of the salt with an alkyl or aryl halide. Oxidation of the hydroxylamine or amine would then lead to the nitroxide (Scheme 1.4). The reaction of Fremy's

Scheme 1.4

$$HON(SO_3)_2^{2-} + 2M^{+} \longrightarrow HON(SO_3M)_2 \xrightarrow{RX} HON(SO_3R)_2 \xrightarrow{\text{oxidation}} \dot{O}N(SO_3R)_2$$

$$H\cdot N(SO_3)_2^{2-} + 2M^{+} \longrightarrow H\cdot N(SO_3M)_2 \xrightarrow{RX} H\ N(SO_3R)_2 \nearrow$$

radical with metal ions also provides a possible route to nitroxide species. In order to explore these possibilities, the reactions of Fremy's radical and some of its derivatives with metal ions are considered in Chapter 2.

(b) N,N-bis-(arylsulphonyl)hydroxylamines

The oxidation of bis-(arylsulphonyl)hydroxylamines, $HON(SO_2Ar)_2$, may provide a more direct route to the synthesis of sulphonylnitroxides than do the compounds in (a). They appear to have been first prepared by the reaction of sulphinic acids with nitrous acid[130], or with oxides of nitrogen[131,132]. Konigs[133] also reported the action of fuming nitric acid on arenesulphinic acids as giving tris-(arylsulphonyl)amine oxides. Hinsberg[134] claimed the

preparation of bis-(phenylsulphonyl)hydroxylamine by the action of nitrous acid on benzenesulphonamide, while Piloty[135] described its preparation from the reaction of iron (III) chloride and N-(phenylsulphonyl)hydroxylamine. More recently bis-(arylsulphonyl)hydroxylamines have been obtained from the decomposition of aryl sulphones with nitric acid[136], by the reaction[137] of nitrous acid with N-(arenesulphamido)-piperidine and pyrrolidine, and by the reaction[138] of arenesulphinic acids with alkyl nitrites. Marvel and Johnson[139] have reported the isolation of N,N-bis-(1-dodecanesulphonyl)hydroxylamine by the reaction of nitrous acid on the corresponding sulphinic acid. They claim that with excess nitrous acid, and with nitric acid in glacial acetic acid, the amine oxide, $(C_{12}H_{25}SO_2)_3NO$ was the major product, and that the hydroxylamine decomposes to form amine oxide at room temperature. The reaction of arenesulphinic acids and nitrous acid has been used for both gravimetric[132] determination of aromatic sulphinic acids, and for specific titrations[140-142] of sulphinate.

Sulphinic acids provide the major route to the synthesis of N,N-bis-(arylsulphonyl)hydroxylamines. Sulphinic acids are usually prepared by the reduction of the corresponding sulphonyl halide. The reducing agents employed vary widely, and include; zinc dust[143-145] in neutral and basic aqueous or alcoholic media; stannous chloride and hydrochloric acid; sodium amalgam in benzene[146]; sodium sulphide[147]; alkaline sulphites[148]; and lithium tetrahydridoaluminate[149]. Aromatic sulphinic acids have also been prepared by Friedel-Crafts

reactions. This involves the condensation of an aromatic hydrocarbon with sulphur dioxide in the presence of aluminium trichloride[150] and hydrogen chloride. Grignard reagents provide a third means of preparing both aromatic[139] and aliphatic sulphinic acids[151, 152]. Others include diazonium[153] compounds in the presence of copper: the heating of sulphones, RSO_2R with alkaline reagents[154]; sodium ethoxide[155]; amines and phenylhydrazines[156]; alkali metals or alkali metal amides[157]; and from the cleavage of diaryl disulphones, $(ArSO_2)_2$ with piperidine[158] or potassium cyanide[159]. The reaction of thiols[160] with acrylonitrile, followed by oxidation with hydrogen peroxide and further reaction with the sodium salt[161] of a thiol, provides a route to aliphatic sulphinic acids. Methanesulphinic acid[162] has been prepared by the careful addition of water to methanesulphonyl chloride. Disulphinic acids[163] have been isolated, while more recently ethanedisulphinic[164] acid has been reported, though earlier work[165] suggested that it decomposes[166]. Aromatic sulphinic acids are more stable[152] than their aliphatic counterparts. They tend to decompose to a sulphonic acid and a disulphoxide (31)

$$3RSO_2H \longrightarrow RSO_3H + RSO_2SR + H_2O \qquad (31)$$

Decomposition is accelerated by dilute acids or on heating with water at 130°C. They are slowly oxidised to sulphonic acids when exposed to air. A more detailed discussion on their preparation and reactions is presented by Truce and Murphy[167] and Stirling[168].

(c) Secondary amines

The oxidation of secondary amines provide yet another route to the preparation of nitroxides. N,N-bis- (arylsulphonyl)imides $(ArSO_2)_2N\cdot H$, have been prepared from the reaction of arenesulphonyl chlorides with arylsulphonamides[169-171] or ammonium chloride[172]. N,N-bis(alkylsulphonyl)imides have also been isolated[173]. The reactions of imido-bis(sulphuryl chloride)[174] $HN(SO_2Cl)_2$, with amines and alcohols is also a plausible route for the synthesis of bis-imides and this is considered in Chapter 4. Very little chemistry has been reported about imido-bis(sulphuryl chloride), though some conductimetric studies have appeared.[175,176]

(d) Arenesulphonylnitroxides

So far only the synthesis of N,N-bis(arylsulphonyl)nitroxides $(ArSO_2)_2N\cdot O^{\cdot}$ has been considered. N,N-bis(arylsulphonyl)hydroxylamines have been prepared from the reaction[138] of arenesulphinic acids and alkyl nitrites and nitrosylarenesulphinates, $ArSO_2NO$, have been postulated as an intermediate[177]. A series of nitrosylarenesulphinates have been trapped by addition of a conjugated diene[178]. Other possible methods of preparing nitrosylarenesulphinates include: (i) the reactions of arenesulphinic acids, N,N-bis(arylsulphonyl)hydroxylamines and N-arylsulphonylhydroxylamines with nitrosyl chloride and nitrogen (II) oxide, and (ii) the oxidation of N-arylsulphonylhydroxylamines using the same conditions employed for the conversion of N-arylhydroxylamines to C-nitrosoarenes[179-184].

Although the reactions of nitrosyl chloride have been extensively reviewed[185], no reactions with sulphinic acids, arylsulphonamides, arylsulphonylhydroxylamines and arylsulphonylimides have been considered; all of which could lead to the formation of

arenesulphonylnitroxides. N-(phenylsulphonyl)hydroxylamine†, $C_6H_5SO_2NHOH$, was first prepared[135] by the reaction of benzenesulphonyl chloride[186, 187] and hydroxylamine, and according to Piloty[135] forms N,N-bis-(phenylsulphonyl)hydroxylamine in the presence of iron (III) chloride. Its reactions with aldehydes has been widely studied[188, 189] either to prepare the corresponding hydroxamic acid or to chromatographically separate aliphatic and aromatic aldehydes[190, 191]. Although the nitrosyl radical, NOH, has been proposed as an intermediate[192] for the reaction between N-(phenylsulphonyl)hydroxylamine and aldehydes, it has recently been observed mass spectroscopically[193]. The thermal decomposition of the sodium salt, in the presence of chlorine, has led to the isolation of nitrosylchloride, which possibly suggests that nitroxyl, NOH, is an intermediate.

(e) N-aryl-N-arylsulphonylhydroxylamines

In recent years, nitroxides which contain sulphonyl groups have been detected by esr. spectoscopy[194, 195], though not isolated. The condensation of sulphinic acids with aldehydes in the presence of a nitrogen base[196, 197], has led to a series of hydroxylamines, which after oxidation form the corresponding nitroxides, $ArSO_2CH_2N(\dot{O})C(S)NHC_6H_5$ and $(RSO_2CH_2)_2N\text{-}\dot{O}$. The latter type of nitroxides has also been obtained from the corresponding secondary amine[197]. Sulphinic acids[195] react with C-nitroso compounds to

† commonly known as Piloty's acid, and N-hydroxybenzenesulphonamide

produce e.s.r. spectra of alkyl and aryl phenylsulphonylnitroxides, when the hydroxylamine is oxidised "in situ" (32). These spectra also correspond to those obtained by the photolysis[195] of N-methyl-N-nitrosotosylamides in various hydrocarbons.

$$RNO + C_6H_5SO_2H \longrightarrow RN(OH)SO_2C_6H_5 \xrightarrow{PbO_2} R\text{-}N(O\cdot)\text{-}SO_2C_6H_5 \qquad (32)$$

The reaction of N-(phenylsulphonyl)hydroxylamine, a sulphinic acid and an aldehyde[198] leads to a hydroxylamine, which after oxidation forms a nitroxide of the form, $RSO_2CH(R')N(O\cdot)SO_2C_6H_5$. An alternative mechanism for the formation of these nitroxides from C-nitroso compounds and benzenesulphinic acid may be the addition of benzenesulphonyl radicals to[199] the C-nitroso compound. The benzenesulphonyl radicals are formed by the oxidation of the sulphinic acid. Both mechanisms may occur simultaneously. With nitrosobenzene and benzenesulphinic acid, N-phenyl-N-phenylsulphonyl-nitroxide was detected, and gave an identical e.s.r. spectrum, to that obtained from the oxidation of the resulting hydroxylamine from the reaction of benzenesulphonyl chloride and phenylhydroxylamine (33).

$$C_6H_5SO_2Cl + C_6H_5NHOH \longrightarrow C_6H_5SO_2N(OH)\text{-}C_6H_5 \xrightarrow[\text{or } Pb(OAc)_4]{PbO_2} \rightarrow C_6H_5N(O\cdot)\text{-}SO_2C_6H_5 \qquad (33)$$

An e.s.r. spectrum[195] has also been obtained when N, N-bis-(phenyl-sulphonyl)hydroxylamine is oxidised "in situ" with lead (IV) oxide, although no product was isolated. The N-aryl-N-arylsulphonyl-hydroxylamines have also been used as a means of protecting nitroso

groups[200]. Nitrosylsulphinate[201] anions, $RN(SO_2^-)O^\cdot$, have been detected with mixtures of C-nitroso compounds and alkaline sodium dithionate.

(f) E.s.r. spectra of N-aryl-N-arylsulphonylnitroxides, $RN(O^\cdot)SO_2R'$.

The nitrogen hfs is determined by the inductive and conjugative effects of the groups R and R'. The electronic effects of R and R' on a_N are explained by assuming that unpaired electron delocalisation is favoured over electron delocalisation. Nitroxides containing electron withdrawing groups attached directly to the nitroxide function show a lower a_N value. This suggests a larger spin density on the oxygen atom and a smaller spin density on the nitrogen atom. But when taking into account the inductive and conjugative electron-withdrawing ability of the arylsulphonyl group, the a_N values for sulphonylnitroxides are much larger than expected. [See Table 1.2]. Electron donating substituents in the benzenesulphonyl group increases a_N, while electron attracting substituents decrease a_N values. This agrees with studies on p-substituted phenylnitroxides[202]. The higher than expected a_N values have been explained by assuming that sulphonyl nitroxides adopt a pyramidal configuration at nitrogen[195].

Table 1.2

Nitrogen h.f.c. (a_N) and g-values of some classes of nitroxides RR'NO$^{\cdot}$

R	R^1	a_N	g-value
alkyl	alkyl	14-16	2.0060
alkyl	aryl	11-14	-
aryl	aryl	9-11	-
alkyl	CCl_3	6-7	2.0070
alkyl	acyl	7-8	2.0067
acyl	acyl	4	2.0073
alkyl	phenylsulphonyl	11-12	2.0060
phenylsulphonyl	phenylsulphonyl	10	-

1.4 INSTRUMENTATION AND MATERIALS

(a) Instrumentation

Microanalyses were carried out on a Perkin-Elmer Model 240 Elemental Analyser by the Microanalytical Laboratory of this Department. Nuclear magnetic resonance spectra were recorded on Varian EM-360, HA-100, XL-100 and CFT-20 spectrometers; ^{1}H n.m.r. were for 10% solutions with tetramethylsilane as internal reference; E.s.r. spectra on a Decca X-3 instrument using potassium nitrosodisulphonate as a calibration spectrum; i.r. spectra on a Perkin-Elmer 237 instrument using mulls of either nujol or hexachlorobuta-1,3-diene; ultra-violet spectra on a Unicam S.P. 800B spectrometer and mass spectra on an A.E.I. MS902 instrument. All mass spectra were at 70 eV unless otherwise stated. (a.u. = 1.66×10^{-27} Kg). High pressure liquid chromatography (h.p.l.c.) was carried out using a Pye-Unicam L.C.3 chromatograph with a Rikadenski-Mitsui DBE penrecorder; atomic absorption spectroscopy using a Perkin-Elmer 360 instrument with a Perkin-Elmer 56 recorder, and g.l.c. using a Pye series 104 chromatograph with a 2% Neo-pentylglycolsuccinate column. Melting points were determined in open capillaries and are uncorrected.

(b) Materials

Ethanol, propan-1-ol, methylene chloride, acetonitrile and carbon tetrachloride were dried over flamed-out molecular sieves. Diethyl ether, for the sodium arenesulphinate preparations

was repeatedly refluxed over calcium hydride and stored over the same reagent, otherwise it was dried over sodium wire, as was any other solvent . All other chemicals were commercial products unless stated otherwise, and were used as received.

(c) Abbreviations

s	:	singlet
d	:	doublet
t	:	triplet
q	:	quartet
m	:	multiplet
br	:	broad
d	:	(after melting point): with decomposition
v.w	:	very weak
h	:	hours
h.p.l.c.	:	high pressure liquid chromatography
D.M.S.O.	:	dimethylsulphoxide
T.H.F.	:	tetrahydrofuran
tr	:	trace

1.5 REFERENCES

1. M.E. Fremy, Ann. Chim. Phys., 1845, 15, 408
2. O. Piloty and B.G. Schwerin, Ber., 1901, 34, 1870
3. O. Piloty and B.G. Schwerin, ibid., 1901, 34, 2354
4. H. Wieland and M. Offenbacher, ibid., 1914, 47, 2111
5. E.G. Rozantsev, "Free Nitroxyl Radicals", New York-London, Plenum Press, 1970, and references therein
6. A.R.A.Forrester, J.M. Hay and R.H. Thomson, "Organic Chemistry of Stable Free Radicals", Chapter 5 London-New York; Academic Press, 1968, and references therein
7. E.G. Rozantsev and V.D. Sholle, Synthesis, 1971, 190
8. E.G. Rozantsev and V.D. Sholle, ibid., 1971, 401
9. G. Sosnovsky and D.J. Rawlinson, Intra-Science Chem. Reports, 1967, 1(2), 109 and references therein
10. H.G. Aurich and W. Weiss, Organic Syntheses, 1975, 59, 66
11. E.G. Rozantsev and V.D Scholle, Russian Chemical Reviews, 1971, 40, 233
12. P.W. Atkins and M.C.R. Symons, "The Structure of Inorganic Radicals", Elsevier, London, 1967, Table 2.1, p.21
13. E. Janzen, Topics in Stereochemistry, 1971, 6, 177
14. L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, New York, 1960, p. 343
15. A. Calder, A.R. Forrester and G. McConnachie, J.C.S. Perkin I, 1974, 2198

16. W.D. Blackley and R.R. Reinhard, J. Amer. Chem. Soc., 1965, 87, 802

17. S.P. Makarov, A. Ya. Yakubovich, S.S. Dubov and A.N. Medvedev, Zhur. Uses. Khim. Obshch. im. Mendeleva, 1965, 10, 106; CA, 62, 16034g

18. S.P. Makarov, A. Ya. Yakubovich, S.S. Dubov and A.N. Medvedev, Dokl. Akad. Nauk. USSR, 1965, 160, 1319

19. P.A.S. Smith and S.E. Gloyer, J. Org. Chem., 1975, 40, 2504; 2508

20. A.B. Shapiro, A.L. Bucharchenko, A.A. Medzhidov and E.G. Rozantsev, Zh. Strukt. Khim., 1966, 7, 187

21. A.B. Shapiro and E.G. Rozantsev, Bull. Acad. Sci. USSR, 1966, 1593

22. A.B. Shapiro, A.A. Medzhidov and E.G. Rozantsev, J. Org. Chem. USSR, 1966, 2, 1838

23. E.G. Rozantsev and V.A. Golakev, Bull. Acad. Sci. USSR, 1966, 852

24. R.Ramasseul and A. Rassat, Bull. Soc. Chim., 1970, 12, 4330

25. A.R. Forrester and S.P. Hepburn, J.C.S. Perkin I, 1974, 2208

26. F.H. Banfield and J. Kenyon, J. Chem. Soc., 1926, 1612

27. A.R. Forrester and S.P. Hepburn, J.Chem. Soc.(C), 1970, 1277

28. J.R. Thomas, J. Amer. Chem. Soc., 1960, 82, 5955

29. G.L. Chaplet-Letourneux, H. Lemaire and A. Rassat, Bull. Soc. Chim. France, 1965, 3283

30. A.S. Waggoner, T.J. Kingzett, B. Rottschaefer and O.H. Griffith, Chem. Phys. Lipids, 1969, 3, 245

31. J.F.W. Keana, S.B. Keana and D. Beetham, J. Amer. Chem. Soc., 1967, 89, 3055

32. A. Hudson and H.A. Hussain, J. Chem. Soc. (B), 1967, 1299; 1968, 251; 1968, 953; 1968, 1346

33. O.L. Lebedev, M.L. Khidekel and G.A.Razuraev, Dokl. Akad. Nauk. SSSR, 1961, 140, 1327

34. E.G. Rozantsev and M.B. Neiman, Tetrahedron, 1964, 20, 131

35. E.G. Rozantsev and L.A. Krinitzkaya, ibid., 1965, 21 491

36. E.G. Rozantsev and A.B. Shapiro, Bull. Acad. Sci. USSR, 1964, 1043

37. F. Chauveau, Bull. Soc. Chim. France, 1960, 819

38. R.M. Dupeyne and A. Rassat, Tetrahedron Lett., 1975, 22 1839

39. G.M. Coppinger and J.D. Swalen, J. Amer. Chem. Soc., 1961, 83, 4900

40. A. Hoffmann, A. Fieldman, E. Gelbhum and W. Hodgson, J. Amer. Chem. Soc., 1964, 86, 639

41. K. Murayama, R. Tanikaya and R. Gotto, Bull. Chem. Soc. Japan, 1964, 37, 1893

42. E.T. Strom, A.L. Bluhm and J. Weinstein, J. Org. Chem., 1967, 32, 3853

43. Th.A.J.W. Wajer, H.W. Geluk, J.B.F.N. Engberts and Th.J. de Boer, Rec. Trav. Chim. Pays-Bas, 1970, 89, 696

44. H. Lemaine, A. Rassat and A.M. Ravet, Bull. Soc. Chim. France, 1963, 1980

45. H. Lemaire, Y. Marechal, R. Ramasseul and A. Rassat, ibid., 1965, 372

46. R. Briere and A. Rassat, ibid., 1965, 378

47. G.L. Chaplet-Letourneux, H. Lemaire and A. Rassat, ibid., 1965,444

48. A.K. Hoffmann and A. Henderson, J. Amer. Chem. Soc., 1961, 83, 4671

49. A.K. Hoffmann, W.G. Hodgson and W.H. Jura, ibid., 1961, 83, 4675

50. R.F.C. Brown, L. Subrahamanyon and C.P. Whittle, Aust. J. Chem., 1967, 20, 339

51. A.L. Bluhm and J. Weinstein, J. Amer. Chem. Soc., 1970, 92, 1444

52. J.W. Hartgernik, J.B.F.N. Engberts, Th.A.J. Wager and Th. J. de Boer, Rec. Trav. Chim. Pays-Bas, 1969, 88, 481

53. H. Bethoux, H. Lemaire and A. Rassat, Bull. Soc. Chim. France, 1964, 1985

54. K.H. Meyer and H.G. Bilbroth, Ber., 1919, 52, 1476

55. K.H. Meyer and W. Reppe, ibid., 1921, 54, 327

56. G. Cauquis, P.J. Grossi, A. Rassat and D. Serve, Tetrahedron Lett., 1973, 21, 1863

57. A. Hantzsch and W. Semple, Chem. Ber., 1895, 28, 2744

58. A. Claus, Ann. Chem., 1871, 158, 205

59. A. Claus, ibid., 1871, 158, 336

60. A. Claus, Ber., 1871, 4, 508

61. F. Raschig, Ann. Chem., 1887, 241, 161; 223

62. E. Divers and T. Haga, J. Chem. Soc., 1894, 65, 523

63. F. Raschig, "Swelwefel-and Stickstoff-Studien", Verlag Chemie, Leipzig-Berlin,1924

64. E. Divers and T. Haga, J. Chem. Soc., 1887, 51, 659

65. E. Divers and T. Haga, ibid., 1889, 55, 760

66. E. Divers and T. Haga, ibid., 1892, 61, 976; 986

67. E. Divers and T. Haga, ibid., 1896, 69, 1629

68. E. Divers and T. Haga, ibid., 1896, 69, 1610

69. J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans Green and Co. Ltd., 1928, p. 647 for detailed discussion

70. T. Haga, J. Chem. Soc., 1904, 85, 78

71. T. Haga, ibid., 1906, 89, 240

72. F. Raschig, Chem. Zenta, 1924, II, 446

73. R.W. Asmussen, Z. Anorg. Chem., 1933, 212, 317

74. J.H. Murib and D.M. Ritter, J. Amer. Chem. Soc., 1952, 74, 3394

75. J.C.M. Li and D.M. Ritter, ibid., 1953, 75, 5823; 5831

76. S. Yamada and R. Tsuchida, Bull. Chem. Soc. Japan, 1959, 32, 721

77. W.P. Griffith, J. Lewis and G. Wilkinson, J. Inorg. Nucl. Chem., 1958, 7, 38

78. H.J. Teuber and G. Jellink, Ber., 1952, 85, 95

79. R.P. Singh, Can. J. Chem., 1966, 44, 1994

80. W. Moser and R.A. Howie, J. Chem. Soc. A, 1968, 3039

81. J.C.M. Li and D.M. Ritter, J. Amer. Chem. Soc., 1953, 75, 3024

82. J. H. Murib and D.M. Ritter, ibid., 1953, 75, 2534

83. H. Gehlen and J. Germak, Z. Anorg. u. Allgem. Chem., 1954, 275, 113

84. R. Nast, N. Katalin and E. Grzinwok, ibid., 1952, 267, 304

85. F. Seel, E. Degener, H. Knorre, E. Gollinck, and M. Magnus, ibid., 1959, 229, 122

86. J.P. Candlin and R.G. Wilkins, J. Chem. Soc., 1961, 3625

87. H. Katz, Z. Physik, 1933, 87, 238

88. S.I. Weissmann, T.R. Tuttle and E. de Boer, J. Phys. Chem., 1957, 61, 28

89. J.J. Windle and A.K. Wiersema, J. Chem. Phys., 1963, 39, 1139

90. Y.H. Tchao and J. Herve, Compt. rend., 1959, 248, 3696

91. Y.H. Tchao and J. Herve, ibid., 1959, 249, 53

92. J.P. Lloyd and G.E. Pake, Phys. Rev., 1954, 94, 579

93. G.E. Pake, J. Townsend and S.I. Weissmann, Phys. Rev., 1952, 85, 682

94. W. Muller-Warmuth and P. Parikh, Z. Naturforsch, 1960, 15, 86

95. Z. Luz, B.L. Silver and C. Eden, J. Chem. Phys., 1966, 44, 4421

96. P. Sabatier, Compt. rend., 1896, 122, 1417, 1537

97. P. Sabatier, ibid., 1896, 123, 255

98. D.L. Filmore and B.J. Wilson, Inorg. Chem., 1968, 7, 1592

99. M.P. Eastman, G.V. Bruno, and J.H. Feed, J. Chem.Phys., 1970, 52, 2511

100. R.A. Howie, L.S.D. Glasser and W. Moser, J. Chem. Soc.A, 1968, 3043

101. J. Townsend, S.I. Weissmann and G.E. Pake, Phys. Rev., 1953, 89, 606

102. B. Elschner, R. Neubert and G. Weiderhald, Z. Physik. Chem. (Leipzig), 1959, 210, 21

103. W. Muller-Warmuth, Z. Naturfursch, 1960, 159, 927

104. R.E. Richards and J.W. White, Proc. Roy.Soc. Ser. A, 1962, 269, 287

105. M.T. Jones, J. Chem. Phys., 1963, 38, 2893

106. R. Kado, Mem. Coll. Sci. Univ. Kyoto Soc.A, 1967, 31, 8192

107. F. Shizuo and S. Kayoko, Bull. Chem. Soc. Japan, 1969, 42

108. J.B. Howell and D.C. McClain, J. Phys. Chem., 1969, 73, 4405

109. W.T. Rakintzis and G. Stein, J. Phys. Chem., 1966, 70, 727

110. P.J. Hannick, H. Shields and T. Grangwer, J. Chem. Phys., 1972, 57, 5029

111. R.G. Kooser and W.V. Volland, J. Chem. Phys., 1969, 73, 5243

112. D.C. McClain, J. Magn. Resonance, 1970, 3, 281; Chem. Abs. ,74, 178t

113. B.L. Bales, Chem. Phys. Letts., 1971, 10, 361

114. M. Decorps, F. Genoud and M.C. Schouler, Mol. Phys., 1973, 26, 237

115. B.J. Wilson, J.H. Hayes and J.A. Durbin, Inorg. Chem., 1976, 15, 1702

116. G. Harvey and R.G.W. Hollingshead, Chem. Ind., 1953, 244

117. W.G. Palmer, "Experimental Inorganic Chemistry", Cambridge Univ. Press 1954, (a) 282, (b) 352, (c) 353, (d) 383, (e) 286

118. P.A. Wehrli and F. Prigott, Org. Syntheses, 1972, 52, 83

119. J.F. Quinn and C. Osuch, U.S. Patent, 2,812,238 1957

120. T.L. Chu, G.E. Pake, D.E. Paul, J. Townsend, and S.I. Weissmann, J. Phys. Chem., 1953, 57, 504

121. B. Smaller and E. Yascutiz, J. Chem. Phys., 1953, 21, 1905

122. H. Zimmer, D.C. Lankin and S.W. Morgan, Chem. Rev., 1971, 71, 229 and references therein

123. L.F. Fieser and M. Fieser, "Reagents for Organic Chemistry', New York, N.Y., 1968, 1, 940; 2, 347

124. H. Musso, Angew. Chem. Int. Ed. (Eng.),, 1963, 2, 723

125. H. Ishii, J. Soc. Org. Synth. Chem. Japan, 1972, 30, 922 Chem. Abs., 78, 83441d

126. P. Baumgarten, Ber., 1936, 69, 1929

127. H. Sisler and L.F. Audrieth, J. Amer. Chem. Soc., 1938,60, 1947

128. F. Raschig, Ber., 1923, 56, 206

129. C. Salt and M.L. Thomlinson, Chem. Ind. (London), 1961, 549

130. R. Otto and H. Ostrop, Ann. Chem., 1867, 141, 370

131. R. Otto and V. Gruber, ibid., 1868, 145, 19

132. W. Konigs, Ber., 1878, 11, 616

133. W. Konigs, ibid., 1878, 11, 1588

134. O. Hinsberg, ibid., 1894, 27, 598

135. O. Piloty, ibid., 1896, 29, 1560

136. H.R. Henze and N.E. Artman, J. Org. Chem., 1957, 22, 1410

137. P.A.S. Smith and H.G. Pars, ibid., 1959, 24, 1325

138. G. Kresze and W. Kort, Ber., 1961, 94, 2624

139. C.S. Marvel and R.S. Johnson, J. Org. Chem., 1948, 13, 822

140. B. Linsberg, Acta Chem. Scand., 1963, 17, 378

141. B. Linsberg, ibid., 1963, 17, 384

142. J.P. Danehy and V.J. Elia, Anal. Chem., 1972, 44, 1281

143. F.C. Whitmore, F.H. Hamilton and N. Thurman, J. Amer. Chem. Soc., 1923, 45, 1067

144. M.S. Kharasch, E.M. May and F.R. Mayo, J. Org. Chem., 1938, 3, 175

145. H. Gilman, E W. Smith and H.J. Oatfield, J. Amer. Chem. Soc., 1934, 56, 1412

146. S. Gabriel and A. Deutsh, Ber., 1880, 13, 388

147. V. Migrdichian, "Organic Syntheses", Reinhold, New York, 1957, 2, 1701

148. S. Smiles and C.M. Bere, Organic Syntheses, Coll. Vol. I, 1932, 7; J. Chem. Soc., 1924, 125, 2361

149. L. Field and F.A.Grunwald, J. Org. Chem., 1951, 16, 946

150. S. Smiles and R. Le Rossignal, J. Chem. Soc., 1908, 93, 745

151. H.G. Houlton and H.V. Tartar, J. Amer. Chem. Soc., 1938, 60, 544

152. P. Allen, J. Org. Chem., 1942, 7, 23

153. H.R. Todd and R.L. Shriner, J. Amer. Chem. Soc., 1934, 56, 1382

154. M.S. Kharasch and R. Swindler, J. Org. Chem., 1954, 19, 1704

155. G.W. Fenton and C.K. Ingold, J. Chem. Soc., 1930, 705

156. E. Fromm and H. Landmann, Ber., 1923, 56, 2290

157. W. Bradley, J. Chem. Soc., 1938, 458

158. H.J. Backer, Rec. Trav. Chim., 1951, 70, 257

159. W. Ziegler and R. Connor, J. Amer. Chem. Soc., 1940, 62, 2596

160. C.D. Hurd and L.L. Gershbein, ibid., 1947, 69, 2328

161. W.E. Truce and J.F.E. Roberts, J. Org. Chem., 1963, 28, 593

162. F. Wudl, D.A. Lightner and D.J. Cram, J. Amer. Chem. Soc., 1967, 89, 4099

163. E. Wellisch, E. Gipstein and O.J. Sweeting, J. Org. Chem., 1962, 27, 1810

164. W.H. Mueller and M.B. Dines, Chem. Comm., 1969, 1205

165. R. Otto and R.C. Cassanova, J. Prakt. Chem., 1887, 36, 436

166. E.P. Kohler, Am. Chem. J., 1897, 19, 745

167. W.E. Truce and A.M. Murphy, Chem. Rev., 1951, 48, 69 and references therein

168. C.J.M. Stirling, Int. J. Sulphur Chem. (B), 1971, 6, 277-320

169. N.N. Dykanov, Zhur. Obshei Khim, 1959, 29, 3602

170. N.N. Dykanov and A.I. Roshchenko, J. Org. Chem. USSR, 1, 260

171. G. Hann and V.E.B. Fahberghist, Chemische und Pharmazeutische Fabriken; Chem. Abs., 52, 7532i Ger. (East) 9132

172. F. Runge, H. Engelbrecht and G. Preusser, Chem. Ber., 1953, 86, 1571

173. B. Helferich and H. Fleshig, Ber., 1942, 75, 532

174. R. Appel, M. Becke-Goehring, M. Eisenhauser and J. Hautenstein, Ber., 1962, 95, 625

175. R.C. Paul, P. Kapoor, R. Kapoor and R.D. Verma, Indian J. Chem., 1975, 13, 619

176. R.C. Paul, P. Kapoor, R. Kapoor and R.D. Verma, ibid., 1975, 13, 1184

177. J. Hamer "1,4-Cycloaddition Reactions", Academic Press, 1967, 435

178. G. Kretze and W. Kort, Ber., 1961, 94, 2624

179. O. Wichterle, V. Greger, A. Dubansky and V. Seidl, Coll. Czech. Chem. Comm., 1959, 24, 1158

180. C.S. Marvel and O. Kamm., J. Amer. Chem. Soc., 1919, 41, 276

181. G.H. Coleman, C. McCloskey and F.A. Stewart, Organic Syntheses, Coll. Vol. 3, 1955, 668

182. T. Emery and J.B. Neilands, J. Org. Chem., 1962, 27, 1075

183. E. Bamberger, Ber., 1894, 27, 1555

184. O. Piloty and I. Ruff, Ber., 1897, 30, 1656

185. L.J. Beckham, W.A. Fessler and M.A. Kize, Chem. Rev., 1951, 48, 319

186. E. Hug, Bull. Soc. Chim., 1934, 1, 990

187. H.F. Whalen and L.W. Jones, J. Amer. Chem. Soc., 1925, 47, 1353

188. P.A.S. Smith and G.E. Hein, ibid., 1960, 82, 573

189. A. Hassner, E. Wiederkehr and A.J. Kascheres, J. Org. Chem., 1970, 35, 1962

190. H. Struck, Mikrochim. Acta, 1956, 1277; Chem.Abs., 50, 8395c

191. E. Bayer, K.H. Reucher and R. Heide, Chem. Ber., 1957, 90, 1929

192. O. Baudisch, Science, 1940, 92, 336; Chem. Abs., 35, 44[3]

193. F. Steel and C. Bliefert, Z. Anorg. Allg. Chem., 1974, 406, 273

194. J.J. Zeilstra and J.B.F.N. Engberts, J. Amer. Chem. Soc., 1975, 97, 7091

195. Th.A.J.W. Wajer, H.W. Geluk, J.B.F.N. Engberts and Th.J. de Boer, Rec. Trav. Chim. Pays-Bas, 1970, 89, 696

196. H. Meijer, R.M. Tel, J. Strating and J.B.F.N. Engberts, ibid., 1973, 92, 72

197. G. Rawson and J.B.F.N. Engberts, Tetrahedron, 1970, 26, 5653

198. H. Hellmann and K. Teichmann, Chem. Ber., 1956, 89, 1134

199. M. McMillan and W.A. Waters, J. Chem. Soc. B, 1966, 422

200. A. Darchen and C. Moinet, Chem. Comm., 1976, 20, 820

201. D. Mulvey and W.A. Waters, J.C.S. Perkin II, 1974, 772

202. Th.A.J.W. Wajer, A. Mackor, Th.J. de Boer and J.D.W. Van Voost, Tetrahedron Lett., 1967, 1941

CHAPTER TWO

AN INVESTIGATION OF HEAVY METAL SALTS OF THE HYDROXYLAMINEDISULPHONATE AND IMIDODISULPHONATE IONS

2.1 PREPARATION OF SALTS AND ANALYTICAL METHODS

Potassium hydroxylaminedisulphonate, potassium imidodisulphonate, potassium hydroxylaminetrisulphonate, potassium nitrilotrisulphonate and potassium hydroxylamine-iso-disulphonate were prepared as described in the relevant chapters of Palmer's[1] book. Fremy's salt was prepared as by Moser and Howie[2].

Standard solutions of the salts above and of silver nitrate, lead (II) nitrate, mercury (II) nitrate, mercury (I) nitrate and thallium (I) nitrate were made up. Suitable quantities of each solution were taken for the stoichiometry required and mixed together. Any precipitate was filtered, weighed and dried. The metal content of the product was analysed by atomic absorption spectroscopy, which generally involved digesting a known weight of the solid in aqua-regia and making up to a suitable volume. Comparison of this solution with a known concentration of standard solutions of the metal ions allows the determination of the metal content. The sulphur content of the product was determined[3] by duplicate gravimetric analysis for both sulphate[3a] and sulphite[3b]. The filtrate was analysed in a similar manner. The equations for the overall reactions were established by analysis of all the products. The results shown in Table 2.1 support within experimental error

the overall reactions. A solution of Fremy's salt was prepared and its concentration determined iodometrically (1) and (2).

$$H_3O^+ + ON(SO_3)_2^{2-} + I^- \longrightarrow \tfrac{1}{2}I_2 + HON(SO_3)_2^{2-} + H_2O \qquad (1)$$

$$\tfrac{1}{2}I_2 + S_2O_3^{2-} \longrightarrow \tfrac{1}{2}S_4O_6^{2-} + I^- \qquad (2)$$

2.2 REACTIONS OF POTASSIUM HYDROXYLAMINEDISULPHONATE WITH SOME METAL IONS

(a) Silver Nitrate

Solutions of potassium hydroxylaminedisulphonate (P.H.D.S.) (10.087 mmol) and silver nitrate (10.087 mmol) were mixed together and allowed to stand in the absence of light during one week; gas evolution was observed during mixing. The dark deposit (1.0073 g, 9 mmol, 92.5%) produced was found to contain between 95.5 and 98.2% silver, and contained no sulphate or sulphite ions. The filtrate contained sulphate ions (19 mmol, 94.2%) but no sulphite ions.

(b) Lead (II) Nitrate

Solutions of P.H.D.S. (9.71 mmol) and lead (II) nitrate (9.71 mmol) were mixed together and after stirring during 24 h. offered a white solid (2.8339 g) which was filtered and dried. Found; Pb, 68.8%. No nitrogen was present in the product and gravimetric analysis for sulphate suggested a sulphur content of 11.1%. O_4PbS requires; Pb, 68.3; S, 10.6%. The filtrate contained sulphate (56.27×10^{-4} mol) and sulphite ions (40.19×10^{-4} mol).

(c) Mercury (II) Nitrate

Solutions of mercury (II) nitrate (2.0 mmol) and P.H.D.S. (1.0 mmol) were mixed together at pH 6.8 (phosphate buffer) and yielded a white precipitate (0.3815 g). Found: Hg, 67.9; S, 11.2%. No nitrogen was present. $HgSO_4$ requires; Hg, 64.1; S, 10.3%. The filtrate was found to contain the excess mercury (II) ions (1.4 mmol), sulphate (0.5 mmol) and sulphite (0.5 mmol) ions. Molar ratio S:Hg 1:1.

(d) Thallium (I) Nitrate

Solutions of thallium (I) nitrate (9.8 mmol) and P.H.D.S. (9.8 mmol) were mixed and stirred during 3 days. No product was precipitated.

(e) Mercury (I) Nitrate

Solutions of mercury (I) nitrate (1 mmol) and P.H.D.S. (1.0 mmol) were mixed and stirred during 3 days. No product was obtained.

2.3 REACTIONS OF POTASSIUM IMIDODISULPHONATE WITH SOME METAL IONS AND SOME RELATED REACTIONS

(a) potassium imidodisulphonate

Direct addition of solutions containing (i) silver, (ii) mercury (II), (iii) mercury (I) and (iv) thallium (I) ions to an equimolar solution of potassium imidodisulphonate yielded no product on standing during 3 weeks. When either a very dilute solution of lead (II) acetate

(3.25 g in 600 ml) or a lead (II) nitrate solution was gradually added to a stirred solution of the imidodisulphonate (0.04M, 250 ml), a white flocculent precipitate was produced of $HOPbN[SO_3Pb(OH)]_2$.

Found: Pb, 74.7; S, 7.2; H, 0.3; N, 1.4%. Calculated:

Pb, 73.4; S, 7.6; H, 0.4; N, 1.6%.

Addition of aqueous potassium hydroxide (0.56 g, 10 mmol) to a solution of potassium imidodisulphonate (2.53 g, 10 mmol) yielded the tripotassium salt, $KN(SO_3K)_2$ (2.71 g, 9.3 mmol, 63.2%). An aqueous solution of the tripotassium salt (0.6 g, 2.1 mmol) was slowly added to a stirred solution of silver nitrate (0.74 g, 4.1 mmol). A sandy brown precipitate was formed.

Found: Ag, 49.7; S, 14.6; N, 3.3; K, 9.1%. $KAg_2NS_2O_6$ requires:

Ag, 50.3; S, 14.9; N, 3.3; K, 9.1%.

The trisilver (I) salt (68%) was prepared by mixing the imidodisulphonate and silver nitrate solutions in a molar ratio of 1:3 respectively.

Found: Ag, 64.6; S, 13.3; N, 2.6%. $Ag_3NS_2O_6$ requires:

Ag, 65.1; S, 12.9; N, 2.8%.

(b) <u>potassium nitrilotrisulphonate</u>

Equimolar solutions of (i) silver nitrate, (ii) mercury (II) nitrate, (iii) mercury (I) nitrate and (iv) thallium (I) nitrate were added to a solution of potassium nitrilotrisulphonate (3g, 8.08 mmol). No precipitate was formed. Lead (II) nitrate however produced a dense white precipitate immediately on mixing.

Found: Pb, 68.5; S, 10.8%. O_4PbS requires: Pb, 68.3; S, 10.6%.

(c) potassium hydroxylaminetrisulphonate

Addition of solutions of the trisulphonate in equimolar quantities to the following ions in aqueous solution yielded no precipitated product. (i) Ag^{+}, (ii) Pb^{2+}, (iii) Hg^{2+}, (iv) Hg_2^{2+} and (v) Tl^{+}. Slow evaporation of a solution containing silver nitrate (0.22 g, 1.29 mmol) and the trisulphonate (0.5 g, 1.29 mmol) in water (100 ml) failed to yield any silver salt of the trisulphonate. Potassium hydroxylaminetrisulphonate crystallised out first. Similar results were obtained for potassium hydroxylamine-iso-disulphonate.

2.4 REACTIONS OF FREMY'S SALT WITH SOME METAL IONS

(a) Silver nitrate

A solution of potassium nitrosodisulphonate (23.95 mmol) became colourless after 90 minutes upon adding a solution of silver nitrate (11.97 mmol) and a grey deposit (1.2903 g) was produced on standing during two days in the absence of light. No gases appeared to be evolved during that time. After filtering and drying the product contained 95-98.2% silver (1.29 g, 11.9 mmol, 100%) and no nitrogen or sulphur. The filtrate was found to contain only sulphate ions (45.2 mmol, 94.4%).

(b) Lead (II) nitrate

A solution of Fremy's salt (23.95 mmol) showed complete loss of colour after 1 h. when mixed with an aqueous solution of lead (II) nitrate (11.97 mmol) and produced a white precipitate

(3.461 g). Found: Pb, 65.2; S, 10.2%. No nitrogen was present. O_4PbS requires: Pb, 68.3; S, 10.6%. The filtrate was found to contain both sulphate (27.2 mmol) and sulphite ions (5.818 mmol) corresponding to a molar ratio of 4.68:1 respectively.

(c) Mercury (II) nitrate

A solution of Fremy's salt (23.95 mmol) was colourless after 1 h. when added to an aqueous solution of mercury (II) nitrate (11.98 mmol), and formed a white precipitate (3.09 g) and gave an identical analysis to the solid formed in the reaction of mercury (II) nitrate and potassium hydroxylaminedisulphonate. No gases appeared to be evolved during the reaction. The filtrate contained both sulphate (28.7 mmol) and sulphite (5.4 mmol) ions; molar ratio $SO_4^{2-}:SO_3^{2-}$ 5.31:1.

(d) Thallium (I) nitrate

No precipitate was produced on adding an equimolar solution of thallium (I) nitrate to a solution of Fremy's salt. Colour fading of the solution was complete after 12h. Identical results were obtained for solution mixtures in the molar ratios 1:2, 1:3 and 1:4 for the metal ion and Fremy's salt respectively.

2.5 SOME OTHER RELATED REACTIONS

(a) Benzyl bromide (3.4 g, 0.02 mol) was added dropwise to a stirred suspension of potassium nitrosodisulphonate (2.7 g, 0.01 mol) in acetonitrile (50 ml) during 1 h. Fremy's salt was recovered unchanged after stirring during 3 h.. A similar result

was obtained with gentle refluxing.

(b) Benzyl bromide (6.8 g, 0.04 mol) was added dropwise to a stirred suspension of potassium hydroxylaminedisulphonate (5.38 g, 0.02 mol) in acetonitrile (50 ml) during 15 minutes. The hydroxylamine (92%) was recovered unchanged after (i) stirring during 2h. and (ii) refluxing for 2h.. Evaporation of the solvent afforded benzyl bromide (87%) in each case.

(c) A solution of ethyl iodide (1.56 g, 0.01 mol) in benzene (10 ml) was slowly added to a stirred suspension of the disilver (I) salt of potassium imidodisulphonate, $Ag_2KN(SO_3)_2$, (2.15 g, 0.005 mol), in benzene (50 ml). Filtration of the suspension after stirring during 48 h. afforded unchanged silver salt (2.05 g, 95%), identical (microanalysis and gravimetric analysis) with earlier samples. Ethyl iodide was recovered (1.2 g, 77%) and identified by comparison (^{1}H n.m.r.) with an authentic sample. [^{1}H n.m.r.; δ 1.9 (t, 3H) and 3.2 (q, 2H) p.p.m.]. Identical results were obtained when ethyl iodide was added to a suspension of the trisilver (I) salt, $Ag_3N(SO_3)_2$ in the molar ratio 3:1 respectively. When refluxed in excess 1-bromooctane during 48 h. both starting materials were recovered unchanged.

(d) A solution of chlorotrimethylsilane (2.17 g, 0.02 mol), in acetonitrile or dimethylsulphoxide (50 ml) was gradually added to a stirred suspension of potassium hydroxylaminedisulphonate (2.7 g, 0.01 mol) in the same solvent (100 ml). Filtration of the mixture after stirring during 48 h. afforded unchanged hydroxylaminedisulphonate (2.3 g, 85%). Similar results were obtained

Table 2.1

Reactions of potassium hydroxylaminedisulphonate and Fremy's

Reaction	IN		OUT	
			product	
	g(mmol) metal ion	g(mmol) sulphur	g(mmol) metal ion	g(mmol) sulphur
Ag^{+} + $HON(SO_3K)_2$	1.1(10.087)	0.647(20.17)	1.007(9.327) (metal)	NONE
Pb^{2+} + $HON(SO_3K)_2$	2.0197(9.71)	0.6214(19.42)	1.9497(9.37)	0.3143(9.82) as SO_4^{2-}
Hg^{2+} + $HON(SO_3K)_2$	0.40(2.0)	0.064(2.0)	0.297(1.4)	0.3929(1.22) as SO_4^{2-}
Ag^{+} + $ON(SO_3K)_2$	1.298(11.97)	1.5328(47.9)	1.29(11.9) (metal)	NONE
Pb^{2+} + $ON(SO_3K)_2$	2.489(11.97)	1.5328(47.9)	2.3639(11.37)	0.353(11.0) as SO_4^{2-}
Hg^{2+} + $ON(SO_3K)_2$	2.396(11.98)	1.5328(47.9)	1.981(9.9)	0.32(10.0) as SO_4^{2-}
Pb^{2+} + $N(SO_3K)_2$	1.657(7.966)	0.776(24.24)	1.6287(7.83)	0.2753(8.6) as SO_4^{2-}

salt with various metal ions

OUT		Δ (IN - OUT)	
filtrate			
g(mmol) metal ion	g(mmol) sulphur	g(mmol) metal ion	g(mmol) sulphur
NONE	0.608(19.0) as SO_4^{2-}	0.0927(0.86)	0.037(1.56)
NONE	0.1801(5.63) as SO_4^{2-} 0.1286(4.02) as SO_3^{2-}	0.06998(0.34)	0.00151(0.047)
0.16(0.8)	0.017(0.53) as SO_4^{2-} 0.018(0.56) as SO_3^{2-}	-0.057(-0.2)	0.02(0.6)
NONE	1.449(45.2) as SO_4^{2-}	0.0025(0.02)	0.0837(2.6)
NONE	0.87(27.2) as SO_4^{2-} 0.186(5.8) as SO_3^{2-}	0.1251(0.6)	0.1225(3.8)
NONE	0.918(28.7) as SO_4^{2-} 0.172(5.4) as SO_3^{2-}	0.415(2.08)	0.1228(3.8)
NONE	0.2488(7.77) as SO_4^{2-} 0.2216(6.93) as SO_3^{2-}	0.0283(0.136)	0.0339(1.05)

with potassium imidodisulphonate (2.54 g, 0.01 mol). Yield = 92%.

(e) Reaction of mercury (II) nitrate with sulphite ion in aqueous solution

A saturated solution of mercury (II) nitrate (1.2 g, 0.004 mol), was prepared and the solution was filtered to remove any undissolved solid. A solution of sodium sulphite (0.1006 M) was added dropwise until a dense white precipitate was formed. After filtering and drying the precipitated product contained: Hg, 80.2; S, 8.21%. $Hg_3(SO_3)_2$ requires: Hg, 79.0%, S, 8.4%. Further addition of the sulphite solution yielded an increasing quantity of metallic mercury as the sulphite solution was added. Any attempt to carry out this reaction on a larger scale proved fruitless due to the large quantity of solution required and the small amount of product precipitated.

Solutions of mercury (II) chloride and acetate did not produce a precipitate on addition of an aqueous sodium sulphite solution.

2.6 RESULTS AND DISCUSSION

Aqueous solutions of potassium hydroxylaminedisulphonate and potassium imidodisulphonate were added to aqueous solutions of (i) silver nitrate, (ii) lead (II) nitrate, (iii) mercury (II) nitrate, (iv), mercury (I) nitrate and (v) thallium (I) nitrate in the hope of producing heavy metal hydroxylaminedisulphonates and imidodisulphonates. (3) and (4) eg. Ag^+.

$$HON(SO_3K)_2 + 2Ag^+ \longrightarrow HON(SO_3Ag)_2 + 2K^+ \quad (3)$$

$$HN(SO_3K)_2 + 2Ag^+ \longrightarrow HN(SO_3Ag)_2 + 2K^+ \quad (4)$$

Potassium imidodisulphonate fails to produce a precipitate with silver, mercury (II), mercury (I) and thallium (I) ions. The salt however does react with lead (II) ions and with dilute solutions of lead (II) acetate to form the same product, $Pb(OH)N[Pb(OH)SO_3]_2$, which is in agreement with Divers and Haga[4]. Equations (5) and (6).

$$3Pb(NO_3)_2 + 3H_2O + 4NaN(SO_3Na)_2 \longrightarrow (PbOH)_3N(SO_3)_2 + 3HN(SO_3Na)_2 + 6NaNO_3 \quad (5)$$

$$3Pb(C_2H_3O_2)_2 + 3H_2O + HN(SO_3Na)_2 \longrightarrow (PbOH)_3N(SO_3)_2 + 2NaC_2H_3O_2 + 4C_2H_4O_2 \quad (6)$$

No simple lead imidodisulphonate, $HN(SO_3)_2Pb$, could be isolated from the reactions considered. Divers and Haga claimed that addition of lead (II) acetate or nitrate to a solution of trisodium imidodisulphonate gives a basic salt, which when treated with nitric acid predominantly passes into solution, while the undissolved part remains unchanged. They proceeded to treat the basic salt with dilute sulphuric acid to make "lead hydroimidodisulphonate", $HN(SO_3)_2Pb$; but any attempt to isolate the salt from solution resulted in decomposition to amidosulphonic acid and lead sulphate. Divers and Haga also reported[4] the isolation of the silver imidodisulphonates, disilver potassium imidodisulphonate, $KAg_2N(SO_3)_2$ and trisilver imidodisulphonate, $Ag_3N(SO_3)_2$, by successive replacement of the potassium ions on addition of aqueous silver nitrate to tripotassium

imidodisulphonate (7); these observations were confirmed, though

$$AgNO_3 + KN(SO_3K)_2 \longrightarrow K_2AgN(SO_3)_2 \xrightarrow{AgNO_3}$$

$$KAg_2N(SO_3)_2 \xrightarrow{AgNO_3} Ag_3N(SO_3)_2 \qquad (7)$$

the position of the metal ions for $Ag_2KN(SO_3)_2$ can not be specified until the crystal structure of the compound has been determined. Simple mercury (II) imidodisulphonates, $HN(SO_3)_2Hg$ do not appear to exist although complex mercury(II) salts have been reported[5]. Mercury (I) salts similarly do not form the corresponding simple imidodisulphonate in aqueous solution, but a salt with the composition $[Hg_4N(SO_3)_2]_2O6H_2O$ has been reported[5]. (8)

$$8HgNO_3 + H_2O + 2HN(SO_3Na)_2 \longrightarrow [Hg_4N(SO_3)_2]_2O + 4NaNO_3 + 4HNO_3 \qquad (8)$$

$$Hg_2{=}N{=}(HgSO_3)_2$$
$$O \qquad\qquad 6H_2O$$
$$Hg_2{=}N{=}(HgSO_3)_2$$

Potassium hydroxylaminedisulphonate, $HON(SO_3K)_2$, decomposes in the presence of silver, mercury (II) and lead (II) ions to form the metal or metal sulphate and, sulphate and sulphite ions. Silver ions appear to be reduced to the metal when an equimolar solution of silver and hydroxylaminedisulphonate ions are mixed together. The metal appears as a dark grey solid. Two moles of sulphate ions were found in the filtrate, suggesting a reaction according to equation (9). Gas evolution was observed.

$$4H_2O + Ag^+ + HON(SO_3)_2^{2-} \longrightarrow Ag\ (s) + 2SO_4^{2-} + \tfrac{1}{2}N_2 + 3H_3O^+ \qquad (9)$$

Decomposition in the presence of lead (II) ions proceeds by a different route producing lead (II) sulphate along with sulphate and sulphite ions in solution. Gas evolution was not observed (10).

$$5H_2O + 2Pb^{2+} + 2HON(SO_3)_2^{2-} \longrightarrow 2PbSO_4 + SO_3^{2-} + SO_4^{2-} + N_2 + 4H_3O^+ \qquad (10)$$

Mercury (II) sulphate appears to be produced when the hydroxylamine-disulphonate ion is mixed with mercury (II) ions. Although the analytical figures may suggest this, some doubt is cast on this conclusion since mercury (II) sulphate is extensively hydrolysed in aqueous media and forms an acidic solution and a precipitate of the basic sulphate, $Hg_3O_2(SO_4)$. The product has a mercury to sulphur ratio of 1:1, but is unlikely to be mercury (II) sulphite, $HgSO_3$, as this type of sulphite is unknown. The mercury sulphites that do exist[6] are; mercuric sodium sulphite, $Hg(SO_3Na)_2$; mercuric oxysulphite, $Hg_2(SO_3HgO)_2$; mercurosic sulphite, $Hg(SO_3Hg)_2$ and hypomercurosic sulphite, $Hg(SO_3)_2Hg_3$; which all have mercury to sulphur ratios different to that of the product.

In an attempt to study this product an aqueous solution of sodium sulphite was gradually added to a very dilute solution of mercury (II) nitrate. Only very dilute solutions could be used due to the insolubility of mercury (II) nitrate. On adding a few drops of the sulphite solution a dense white precipitate of mercury oxysulphite[6]

was formed (11). On adding more sulphite the solution darkened

$$4Hg(NO_3)_2 + 2Na_2SO_3 + 2H_2O \longrightarrow 4NaNO_3 + 4HNO_3 + (OHg_2SO_3)_2 \quad (11)$$

momentarily and then became white again due to the formation of mercurosic sulphite (12).

$$(OHg_2SO_3)_2 + 6Na_2SO_3 + 2H_2O \longrightarrow 4NaOH + 4Hg(SO_3Na)_2$$

$$2H_3O^+ + Hg(SO_3Na)_2 + 2Hg(NO_3)_2 \longrightarrow 2NaNO_3 + Hg(SO_3)_2Hg_2 + 2H_2O \quad (12)$$

The formation of mercurosic sulphite is in agreement with earlier work[6]. The compound is most likely to contain both mercury (I) and mercury (II) as the sulphite decomposes in the presence of hydrochloric acid yielding mercury (I) and mercury (II) chloride. On further addition of sulphite hypomercurosic sulphite is formed which then decomposes to mercury and mercury (I) sulphate (13)-(15). This is seen by a continued darkening of the solution.

$$2Hg(SO_3)_2Hg_2 + 2Na_2SO_3 \longrightarrow Hg(SO_3)_2Hg_3 + 2Hg(SO_3Na)_2 \quad (13)$$

$$Hg(SO_3)_2Hg_3 + 2Na_2SO_3 \longrightarrow 2Hg + 2Hg(SO_3Na)_2 \quad (14)$$

$$Hg(SO_3)_2Hg_3 \longrightarrow 2Hg + Hg_2SO_4 + SO_2 \quad (15)$$

The salt, $Hg_3(SO_3)_2$, which was isolated would indicate that the earlier observations were correct, and that no simple mercury (II) sulphite exists. The product from the reaction of mercury (II) ions and potassium hydroxylaminedisulphonate may possibly be a mixture of some of these mercury salts, as no other possible single product agrees with the data obtained. If mercury (II) sulphate is produced the reaction should be analogous to that of lead (II) nitrate and potassium hydroxylaminedisulphonate (16).

$$5H_2O + 2Hg^{2+} + 2HON(SO_3)_2^{2-} \longrightarrow 2HgSO_4 + SO_3^{2-} + SO_4^{2-} + N_2 + 4H_3O^+ \quad (16)$$

Sulphate and sulphite ions were produced. No solid product was precipitated with thallium (I) and mercury (I) ions.

Many salts of the hydroxylaminedisulphonate ion have been prepared[4] predominantly with alkali and alkaline earth elements. The only heavy metal salt produced was $(HOPb)_3NS_2O_7$, from the reaction of basic lead acetate and the trisodium salt of the hydroxylaminedisulphonate anion. The reactions considered above suggest that metal hydroxylaminedisulphonates, such as $HON(SO_3Ag)_2$ and $HON(SO_3)_2Pb$, are far too unstable to be isolated as such, but may appear as intermediates and decompose immediately.

Fremy[7] first isolated salts of the nitrilotrisulphonate ion (sulphammonates) by passing sulphur dioxide into concentrated solutions of ammonium nitrite mixed with a large excess of ammonia, and reported its decomposition to sulphate. Other alkali metal salts were also considered, but reactions with other metal ions were not considered. Silver, thallium (I), mercury (II) and mercury (I) ions have no affect on the salt while lead (II) ions precipitate lead (II) sulphate and produce sulphate and sulphite ions in solution.

Both potassium hydroxylaminetrisulphonate, $KSO_3ON(SO_3K)_2$, and potassium hydroxylamine-iso-disulphonate, $KSO_3ONH(SO_3K)$, were unaffected by any of the metal ions and slow evaporation of a mixture failed to crystallise the expectedly less soluble heavy metal salt.

Fremy's salt was prepared[2] and used immediately. In the presence of silver ions colour fading was complete in approximately 90 minutes depositing silver metal and forming sulphate ions in solution. The stoichiometry of the reaction is represented below (17). No gas evolution was observed in the

$$4ON(SO_3)_2^{2-} + 2Ag^+ + 15H_2O \longrightarrow 2Ag\,(s) + 8SO_4^{2-} + 10H_3O^+ + N_2O + N_2 \qquad (17)$$

reaction, (cf reaction of potassium hydroxylaminedisulphonate and silver ions), but it is apparent that the reaction probably occurs via potassium hydroxylaminedisulphonate which is formed by the decomposition of Fremy's salt (18) and then reacts as in (9).

$$4ON(SO_3)_2^{2-} + 7H_2O \longrightarrow 2HON(SO_3)_2^{2-} + 4SO_4^{2-} + N_2O + 4H_3O^+ \qquad (18)$$

The presence of silver ions also appear to enhance the colour fading and therefore the decomposition of the nitrosodisulphonate anion since the usual decomposition time is about 500 h.[8].

Similar results were obtained for both lead (II) and mercury (II) ions in aqueous solution producing lead (II) sulphate and probably mercury (II) sulphate respectively. Both sulphate and sulphite ions were detected in the filtrate for each reaction (19) and (20).

$$4ON(SO_3)_2^{2-} + 2Pb^{2+} + 12H_2O \longrightarrow 2PbSO_4 + 5SO_4^{2-} + SO_3^{2-} + N_2 + N_2O + 8H_3O^+ \qquad (19)$$

$$4ON(SO_3)_2^{2-} + 2Hg^{2+} + 12H_2O \longrightarrow 2HgSO_4 + 5SO_4^{2-} + SO_3^{2-} + N_2 + N_2O + 8H_3O^+ \qquad (20)$$

Thallium (I) and mercury (I) ions precipitated no product. Solutions

of Fremy's salt in the presence of metal ions therefore decompose to the corresponding hydroxylamine at a rate which is indicated by the solution's loss of colour and show colour fading rates to $Pb^{2+} \triangleq Hg^{2+} > Ag^{+} > Tl^{+} \gg K^{+} \triangleq Cd^{2+}$. The hydroxylamine then decomposes as described earlier. The rate of decomposition[8] of Fremy's salt in aqueous solution depends upon the pH and upon the other substances present in the solution. All the metal ion salt solutions except mercury (II) nitrate at the concentrations employed are neutral, and Fremy's salt is most stable at pH 8, so this could be a contributary factor to the relatively faster rate of decomposition observed in the presence of mercury (II) ions. There certainly are no nitrite[2] or chloride[9] ions present to any extent in the metal ion solutions, and therefore they may be ruled out as a possible factor contributing to the faster rate of decomposition in the presence of the metal ions. The production of a water-insoluble product is not a necessary requirement for a fast rate of decomposition, but it is perhaps significant that each of the metals found here to promote fast decomposition of $ON(SO_3)_2^{-2}$ has at least two oxidation states accessible (albeit only transiently in some instances) in aqueous solution so that one- or two-electron redox reactions involving the metal are possible: by contrast with cadmium which has but a single oxidation state accessible in aqueous solution, the rate of decomposition of $ON(SO_3)_2^{-2}$ is essentially unchanged from that of the pure potassium salt, and no insoluble product results. The hypothesis that at least two oxidation states of the cation are necessary for fast decomposition

rationalises adequately the observation that derivatives of $ON(SO_3)_2^{2-}$ have hitherto been described only of Group I and Group II metals, and further suggests that other simple stable derivatives will be accessible only of metal ions such as Sc^{3+}, Y^{3+}, La^{3+}, Zn^{2+} and Cd^{2+}.

Heavy metal hydroxylaminedisulphonates can not therefore be synthesised from the reaction with alkyl or aryl halides to form the corresponding N,N-bis-(arylsulphonate)hydroxylamine $HON(SO_3R)_2$, which when oxidised could possibly lead to the analogous nitroxide radical. The two silver salts, $Ag_2KN(SO_3)_2$ and $Ag_3N(SO_3)_2$ could provide a possible route to suitable amines. Ethyl iodide failed to react with these salts. No compound $HN(SO_3Et)_2$ was formed, and this is probably due to the insolubility of the silver salts in the solvent used. Similarly under more vigorous conditions 1-bromooctane (b.p. 197-200°) failed to react with $Ag_3N(SO_3)_2$. Both benzyl bromide and chlorotrimethylsilane failed to react with potassium hydroxylaminedisulphonate in the solvents employed.

Since heavy metal salts of hydroxylaminedisulphonates and imidodisulphonates appear to be either unobtainable or too unreactive in the conditions employed, this possible route for the synthesis of suitable hydroxylamines and amines for nitroxide production can not be utilised.

2.7 REFERENCES

1. W.G. Palmer "Experimental Inorganic Chemistry", Cambridge University Press 1954
2. W. Moser and R.A. Howie, J. Chem. Soc. A, 1968, 3039
3. A.I. Vogel, 'A Textbook of Quantitative Inorganic Analysis', Longmans, 3rd Edition , (a) 573 (b) 574
4. E. Divers and T. Haga, J. Chem. Soc., 1892, 61, 976; 61, 986
5. E. Divers and T. Haga, ibid., 1896, 69, 1629
6. E. Divers and T. Shimidzu, J. Chem. Soc., 1886, 49, 533
7. M.E. Fremy, Ann. Chim. Phys., 1845, 15, 408
8. J.H. Murib and D.M. Ritter, J. Amer. Chem. Soc., 1952, 74, 3394
9. G. Harvey, and R.G.W. Hollingshead, Chem. Ind., 1953, 244

CHAPTER THREE

THE SYNTHESIS AND REACTIONS OF N,N-BIS-(ARYLSULPHONYL)HYDROXYLAMINES

3.1 SODIUM ARENESULPHINATES

(a) The preparation of sodium arenesulphinates

Sodium benzene and sodium toluene-p-sulphinate, were commercial products. However other arenesulphinates were not easily available and were prepared by the reduction of the corresponding sulphonyl chloride by several methods to assess the most efficient reducing agent. Both benzenesulphonyl and toluene-p-sulphonyl chloride were reduced using sodium amalgam[1,2], sodium sulphite[3], sodium sulphide[4], zinc dust[5,6] in propan-1-ol and lithium tetrahydridoaluminate[7]. Details are outlined in Table 3.1. The preparations produce sodium chloride as a by-product, hence there is contamination of the product, and analytically pure samples were difficult to obtain. The salts were therefore used directly to produce N,N-bis-(arylsulphonyl)hydroxylamines. Of the reducing agents employed, zinc dust and lithium tetrahydridoaluminate were found to be the most successful. Zinc dust in propanol was chosen in preference due to its convenience.

Sodium p-chlorobenzenesulphinate and sodium p-methoxybenzenesulphinate were therefore prepared from the corresponding arenesulphonyl chloride by zinc reduction, in yields of 91% and 98% respectively. No conditions were found under which

Table 3.1

Microanalytical data for sodium arenesulphinates from various reductions of arenesulphonyl chlorides $pXC_6H_4SO_2Cl$

Reducing Agent	X = H		X = CH_3-	
	Yield	Microanalysis Calculated Found Empirical formula	Yield	Microanalysis Calculated Found Empirical formula
Sodium amalgam in benzene	31.6	C, 43.39; H, 3.07% C, 27.75; H, 1.90% $C_6H_5SO_2Na \cdot 1.63NaCl$		-
Sodium sulphite aqueous	45.0	C, 32.07; H, 2.87% $C_6H_5SO_2Na \cdot 1NaCl$	32.0	C, 47.18; H, 3.74% C, 35.31; H, 3.96% $p\text{-}CH_3C_6H_4SO_2Na \cdot NaCl$
Sodium sulphide aqueous	No apparent reduction			
Zinc dust, in propanol	87.0	C, 34.96; H, 2.60% $C_6H_4SO_2Na \cdot 0.75NaCl$	91.0	C, 35.04; H, 4.06% $p\text{-}CH_3C_6H_4SO_2Na \cdot NaCl$
Lithium tetrahydroaluminate in ether		-	93.0	C, 44.02; H, 3.96% $p\text{-}CH_3C_6H_4SO_2Na \cdot 0.2NaCl$

Table 3.2

Mass Spectrum of the sulphone from the reduction of p-chlorobenzenesulphonyl chloride

m/e	77	111	159	286
I(%)	4.5	54.8	100	12.3
Ion	$C_6H_5^+$	$^{35}ClC_6H_4^+$	$^{35}ClC_6H_4SO^+$	$(^{35}ClC_6H_4)_2SO_2^+$

Table 3.3

Mass spectrum of the sulphone from the reduction of p-methoxybenzenesulphonyl chloride

m/e	107	155	171	188
I(%)	28.1	19.2	36.8	100
Ion	$MeOC_6H_4^+$	$MeOC_6H_4SO^+$	$MeOC_6H_4SO_2^+$	$MeOC_6H_4SO_3H^+$

m/e	214	230
I(%)	1.8	19.3
Ion	$C_6H_4SO_2C_6H_4^+$	$OC_6H_4SO_2C_6H_4^+$

p-nitrobenzenesulphonyl chloride could be selectively reduced to the sulphinate, without simultaneous reduction of the nitro group. Sodium p-fluorobenzenesulphinate was prepared[8] from fluorobenzene. Small quantities of diarylsulphones were identified mass spectroscopically in the reductions of p-chlorobenzenesulphonyl chloride and p-methoxybenzenesulphonyl chloride. [See Table 3.2 and Table 3.3]. All the other reduction products exhibit ions up to $ArSO_3H^+$.

(b) The Preparation of N-(phenylsulphonyl)hydroxylamine

Benzenesulphonyl chloride, (35.4 g, 0.20 mol), was added dropwise to a solution of hydroxylamine hydrochloride, (13.9 g, 0.2 mol), in ethanol, (150 ml), through which ammonia was bubbled. When the reaction was complete, passage of ammonia was continued for a further 10 minutes, before removal of the ammonium chloride by filtration. Evaporation of the solvent yielded a product, which was recrystallised from acetonitrile, (12.1 g, 0.07 mol; 35%; mp = 124-126°).

Found: C, 41.5; H, 4.6; N, 8.9 %. $C_6H_7NO_3S$ requires: C, 41.8; H, 4.1; N, 8.1%.

Higher yields of the hydroxylamine, (ca 60%), were obtained when triethylamine was used instead of ammonia.

(c) The preparation of sodium benzenesulphinate from N-(phenylsulphonyl)hydroxylamine

An aqueous solution of the hydroxylamine, (6.92 g, 0.04 mol), was stirred with a sodium hydroxide solution, (3.2 g, 0.08 mol), at

room temperature, and yielded unchanged starting material. No sodium benzenesulphinate was found[9].

3.2 N,N-BIS-(ARYLSULPHONYL)HYDROXYLAMINES

(a) The preparation of N,N-bis-(arylsulphonyl)hydroxylamines

The arenesulphinate was dissolved in distilled water and any undissolved sulphones removed by filtration. The pure sulphinate was dried in a low oven (40°), after evaporation of the solvent. Typically, the sodium arenesulphinate, (0.02 mol), and sodium nitrite, (0.69 g, 0.01 mol), were dissolved in distilled water, (50 ml), and cooled in ice. Dropwise addition of cold concentrated hydrochloric acid to the stirred solution yielded the product as a dense white precipitate. The product was filtered off, washed with water and dried over calcium chloride in vacuo. Yields, microanalytical data and melting points (uncorrected) are recorded in Table 3.4. The p-fluoro derivative was too unstable for accurate microanalysis or for melting point determination. The compounds were stored at -30°.

A white solid was obtained from the filtered solution of sodium p-chlorobenzenesulphinate, which had a mass peak at m/e = 286 (12.3%) corresponding to $(^{35}ClC_6H_4)_2SO_2^+$, as observed in Table 3.2. Microanalysis of the compound gave: C, 49.1; H, 2.7%; and

$C_{12}H_8Cl_2O_2S$ requires C, 50.1; H, 2.8%,

and a mp = 145-147° (lit = 148°).

Table 3.4

Microanalytical data, melting points and yields of N,N-bis-(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2N.OH$

X	Found (%) C	H	N	Calculated (%) C	H	N	Mp(°)	Yield (%)
H	45.9	3.4	4.2	45.9	3.5	4.5	125	86
CH_3	49.0	4.3	3.8	49.2	4.4	4.1	126	50
Cl	36.3	2.4	3.3	37.7	2.4	3.7	128	91
CH_3O	41.8	4.2	3.4	45.0	4.1	3.7	74-75	61
F	unstable			41.0	2.6	4.0	dec.	47

Table 3.5

Preparation, microanalysis, melting points and yields of N,N,O-tris-arylsulphonyl)hydroxylamines $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$

X	Mol of $(pXC_6H_4SO_2)_2N\cdot OH$ (x 10^{-3})	Mol of PbO_2 (x 10^{-3})	Found (%) C	H	N	Calculated (%) C	H	N	Mp (°)	Yield (%)
H	5.0	7.2	47.6	3.3	3.0	47.4	4.0	3.1	88-91	72
CH_3	3.0	8.4	50.8	4.6	2.9	50.9	4.3	2.8	183-184	71
Cl	2.6	20.0	38.6	2.9	2.2	38.8	2.2	2.5	132-135	52
CH_3O	1.6	8.4	46.4	4.1	2.4	46.4	3.9	2.6	107-108	50
F	5.2	20.0	43.0	2.7	2.4	42.6	2.4	2.8	123-125	65

Table 3.6

Oxidations of N,N-bis-(p-tolylsulphonyl)hydroxylamine

Oxidant/solvent	Found (%) C	H	N	Calculated (%) C	H	N	mp(°)
silver (I,III) oxide/CH_2Cl_2	50.9	4.4	2.6	50.9	4.3	2.8	179-183
silver (I,III) oxide/C_6H_6	50.9	4.4	2.5				181-184
lead (IV) oxide/C_6H_6	51.2	4.2	2.6				178-182
lead (IV) acetate/CH_2Cl_2	50.8	4.2	2.7				178-182
activated[10] manganese (IV) oxide/CH_2Cl_2	50.8	4.5	2.7				181-183

(b) Reaction of N-(phenylsulphonyl)hydroxylamine with benzenesulphonyl chloride

The hydroxylamine, (2.4 g, 0.02 mole), and benzenesulphonyl chloride, (3.5 g, 0.02 mol), in ethanol, (150 ml), were stirred at room temperature, and triethylamine (2.01 g, 0.02 mol) was gradually added. Filtration of the triethylamine hydrochloride after stirring during 48 h. was followed by evaporation of the solvent. This yielded crude N,N-bis-(phenyl sulphonyl)hydroxylamine, which was recrystallised from toluene. Mp and microanalysis were identical with samples obtained earlier (Yield 64%).

3.3 THE OXIDATION OF N,N-BIS-(ARYLSULPHONYL)HYDROXYLAMINES

(a) The oxidation of N,N-bis-(arylsulphonyl)hydroxylamines with lead (IV) oxide

In a typical oxidation the hydroxylamine was stirred during 24 h with an excess of lead (IV) oxide in methylene chloride (100 ml). The mixture was then centrifuged, and evaporation of the solvent from the supernatant yielded the crude tris-(arylsulphonyl)hydroxylamine. The products were recrystallised twice from toluene. The solid residue was washed with water and gave a positive test for nitrate, but a test for nitrite was negative. A blank oxidation of hydroxylammonium chloride in methylene chloride gave a positive test for nitrate but no nitrite. Table 3.5 records the stoichiometries employed, yields, melting points and microanalytical data.

(b) Other oxidations of N,N-bis-(p-tolylsulphonyl)hydroxylamine

The hydroxylamine was stirred with excess of different oxidants in different solvents during 14 days. After centrifuging and removal of the solvent, the resulting solid was recrystallised twice from toluene. A list of oxidants with the melting points and microanalytical data of the product is given in Table 3.6 . The following reagents gave only unchanged starting material: (i) lead (IV) oxide in aqueous potassium carbonate solution; (ii) silver (I,III) oxide in aqueous potassium carbonate solution; (iii) m-chloroperbenzoic acid in diethyl ether. Use of selenium (IV) oxide in methylene chloride gave only an intractable oil, from which no homogeneous product could be isolated.

Silver (I,III) oxide was prepared by holding an aqueous solution of sodium hydroxide (3.6 g) and potassium persulphate (3.7 g) at 90° for 20 minutes, followed by addition of a silver nitrate solution (2.5 g). After a further 20 minutes at 90° the product was filtered off and dried in vacuo over phosphorus pentoxide in the dark, until required.

(c) Other oxidations of N,N-bis-(p-chlorobenzenesulphonyl)hydroxylamine

Reaction of the hydroxylamine during 14 days with the following oxidants gave tris-(p-chlorobenzenesulphonyl)hydroxylamine. Identical microanalysis, melting point and mixed melting points were observed with that obtained by lead (IV) oxide oxidation in methylene chloride. (i) silver (I,III) oxide in methylene chloride; (ii) silver

(I,III) oxide in benzene; (iii) lead (IV) oxide in benzene.

3.4 THE DECOMPOSITION OF N,N-BIS-(ARYLSULPHONYL) HYDROXYLAMINES $(p\text{-}XC_6H_4SO_2)_2N.OH$

Aliquots (0.1 g) of each compound were placed in ampoules, which were subsequently evacuated and allowed to stand at room temperature during 24 h . Dry air was admitted, followed after a further 24 h by moist, ambient air. Any change was monitored at each step. Gas evolution was monitored by a manometer.

(a) X=H

The compound is stable in dry air. mp = 124-125°. Found: C, 45.8; H, 3.3; N, 4.4%. Calculated: C, 45.9; H, 3.5; N, 4.5%. In moist air nitrogen oxides are evolved, and extraction with water removed benzenesulphonic acid (mp = 62-64°), leaving tris-(phenylsulphonyl)hydroxylamine, mp = 88-90°, after recrystallisation from toluene. Found: C, 47.6; H, 3.3; N, 3.1%. Calculated: C, 47.4; H, 4.0; N, 3.1%.

(b) X=p-CH_3 and p-Cl

No decomposition was observed, mp 125-126 and 127-128° respectively. X=p-CH_3; Found: C, 49.1; H, 4.3; N, 4.0%. p-Cl, Found: C, 37.3; H, 2.4; N, 3.2%.

(c) X=p-CH_3O

The compound is stable in dry air, (melting point and analysis unchanged), but in moist air decomposition occurs without the evolution of nitrogen oxides to give an intractable black tar.

(d) X=p-F

The compound is stable in dry air, but in the presence of moisture decomposes very rapidly with evolution of nitrogen oxides. Extraction of the residue with water removed p-fluorobenzenesulphonic acid. Recrystallisation from benzene gave mp = 84-85° (lit. 87°). Conversion to the sodium salt with sodium hydroxide solution gave: C, 35.0; H, 2.5%; $C_6H_4FNaO_3S$ requires: C, 36.4; H, 2.1%. The remaining solid proved to be tris(p-fluorobenzenesulphonyl)hydroxylamine (mp = 120-123°).
Found; C, 42.9; H, 2.3; N, 2.7%: Calculated: C, 42.6; H, 2.4; N, 2.8%.

3.5 DECOMPOSITION OF TRIS-(ARYLSULPHONYL)HYDROXYLAMINES $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$

The same procedure used for N,N-bis-(arylsulphonyl)hydroxylamines was employed. All compounds were stable in dry air, giving identical melting points and microanalyses as before. When X = H, p-CH_3 and p-CH_3O, exposure to moist air after 21 days caused no change. When X=p-Cl and p-F, exposure to moist air over a period of weeks caused slow evolution of nitrogen oxides and an accumulation of sulphonic acid $p\text{-}X\cdot C_6H_4SO_3H$.

3.6 SOME OTHER RELATED REACTIONS

(a) Reaction of N-(phenylsulphonyl)hydroxylamine with iron (III) chloride

The hydroxylamine (3.46 g, 0.02 mol), and iron (III) chloride (3.25 g, 0.02 mol), were stirred in aqueous solution[11] during 15 h .

After centrifuging and removal of the solvent the hydroxylamine was recovered unchanged, mp = 124-126°, with no depression on mixing.

(b) Reaction of benzenesulphinic acid with fuming nitric acid

A solution of sodium benzenesulphinate, (4.0 g, 0.024 mol), in water (100 ml), was treated with concentrated hydrochloric acid, (0.02 mol), at 0°. The resulting precipitate of benzenesulphinic acid was filtered off and dried over calcium chloride. It was then stirred during 18 h. with fuming nitric acid, (s.g., 1.51, 10 ml). Filtration of the resulting solid, followed by recrystallisation from toluene yielded tris-(phenylsulphonyl)hydroxylamine, (2.10 g, 0.0046 mol, 58%). mp = 88-89°.

Found: C, 47.5; H, 3.4; N, 3.1%. Calculated: C, 47.4; H, 4.0; N, 3.1%.

(c) Reaction of toluene-p-sulphinic acid with excess nitrous acid

A solution of sodium toluene-p-sulphinate tetrahydrate (2.5 g, 0.01 mol) in water (50 ml) was treated at 0° with concentrated hydrochloric acid, (3 ml); toluene-p-sulphinic acid was filtered off, washed and added to a solution of sodium nitrite, (1.38 g, 0.02 mol), in water (200 ml), to which concentrated hydrochloric acid (6 ml), was then added at 0°. The mixture was stirred during 24 h. N,N-bis-(p-tolylsulphonyl)hydroxylamine (1.0 g, 0.0029 mol, 58%) was filtered off and recrystallised from toluene (mp = 125-126°) Found: C, 49.2; H, 4.1; N, 3.9%. No tris-(p-tolylsulphonyl)hydroxylamine was obtained.

(d) Reaction of benzenesulphonamide with nitrous acid

(i) Benzenesulphonamide (3.14 g, 0.02 mol), and sodium nitrite, (2.07 g, 0.03 mol), were dissolved in water, (100 ml), and concentrated hydrochloric acid, (9 ml), was slowly added. Nitrogen oxides were evolved. After 1 h. the solid product was removed by filtration; a quantitative recovery of unchanged sulphonamide was obtained. (mp = 154-156°). Found: C, 45.6; H, 4.7; N, 8.8%. $C_6H_7NO_2S$ requires: C, 45.6; H, 4.5; N, 8.9%.

(ii) A reaction involving two moles of sulphonamide and three moles of nitrous acid in ethanol also gave unchanged sulphonamide (95%). Identical mp and analysis to (i).

(iii) A 1:1 molar ratio, after stirring during 24 h. at room temperature in ethanol gave unchanged sulphonamide, and diphenyldisulphone, $(C_6H_5SO_2)_2$, was detected mass spectroscopically.

(e) Reaction of benzenesulphonamide with nitric acid

Aliquots, (3.1 g, 0.02 mol), of benzenesulphonamide were treated during 24 h. with nitric acid as follows; (i) 10 ml concentrated nitric acid plus 10 ml water; (ii) 10 ml concentrated nitric acid; (iii) 10 ml fuming nitric acid. A quantitative recovery of the sulphonamide was achieved in each case. No bis or tris-(phenylsulphonyl)hydroxylamine was formed.

(f) Reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with nitric acid

The hydroxylamine (1.6 g, 0.005 mol), was dissolved in glacial acetic acid, (150 ml), and concentrated nitric acid, (8.3 ml),

was added dropwise and the mixture held at 45° during 45 minutes. Nitrous fumes were observed. After 10 h. at room temperature, the product, tris-(p-tolylsulphonyl)hydroxylamine, (0.8g, 0.0016 mol, 48%), was filtered off and recrystallised in toluene. mp=178-182°. Found: C, 50.8; H, 4.4; N, 2.9%.

Evaporation of the filtrate yielded toluene-p-sulphonic acid (0.4 g, 0.0023 mol). mp = 102-103 (lit. 104-5°), which was converted to the sodium salt by addition of a sodium hydroxide solution.

Found: C, 42.9; H, 3.5% . Calculated: C, 43.3; H, 3.6%.

(g) Reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with excess nitrous acid

To an aqueous suspension (100 ml) of the hydroxylamine (1.7 g, 5×10^{-3} mol) and sodium nitrite,(1.38 g, 0.02 mol), was added concentrated hydrochloric acid, (6 ml). The solution was stirred during 3 h. The solid product, (1. 5 g, 4.4×10^{-3} mol, 88%) was filtered, washed and dried. It gave an identical microanalysis and melting point to the starting material.

(h) Reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with toluene-p-sulphinic acid

(i) Toluene-p-sulphinic acid, (1.2 g, 8×10^{-3} mol), in glacial acetic acid, (75 ml), was added dropwise to a solution of the hydroxylamine, (2.0 g, 6×10^{-3} mol) in glacial acetic acid (150 ml). The mixture was warmed to 60° and held for 5 h . Nitrogen oxides were evolved. After a further 24 h at room temperature the solvent was removed and the solid product recrystallised from

toluene and identified as toluene-p-sulphonic acid, mp = 103°, (lit[12], 104-106°) mass spectroscopically. No tris-(p-tolylsulphonyl)-hydroxylamine or amine[9] was found.

(ii) An identical experiment was carried out under dry dinitrogen. No oxides of nitrogen were evolved. The bis-(p-tolylsulphonyl)hydroxylamine was recovered quantitatively. Identical mp and microanalysis with previous samples. Similar results were obtained for N, N-bis-(phenylsulphonyl)hydroxylamine.

(i) Reaction of N, N-bis-(p-tolylsulphonyl)hydroxylamine with toluene-p-sulphonyl chloride

Toluene-p-sulphonyl chloride (1.37 g, 7.2×10^{-3} mol), in glacial acetic acid (75 ml) was stirred into a solution of the hydroxylamine (2.45 g, 7.2×10^{-3} mol) and pyridine (0.57 g, 7.2×10^{-3} mol) in glacial acetic acid (75 ml). After 24 h. at room temperature, the mixture was reduced to small volume and extracted with benzene (2 x 100 ml). The benzene layer was washed well with water, dried over anhydrous sodium sulphate for 24 h. and evaporated to yield an oil which crystallised slowly. Extraction with ether gave unchanged toluene-p-sulphonyl chloride (mp = 69-71°). Recrystallisation of the residue from toluene gave tris-(p-tolylsulphonyl)hydroxylamine, (0.52 g, 1.1×10^{-3} mol, 15%). Found: C, 50.9; H, 4.1; N, 2.8%. mp = 182-184°.

(j) The reaction of N, N-bis-(p-tolylsulphonyl)hydroxylamine with sulphur dioxide

The hydroxylamine, (0.85 g, 0.0025 mol), was placed in a pyrex tube and liquid sulphur dioxide was condensed onto the solid

using a card-ice trap. During 2 days the gas evaporated and yielded a white solid which had a mass spectrum showing only $CH_3C_6H_4SO_2^+$ (m/e = 155) fragments. After drying the compound (mp = 114-116°d), gave

Found: C, 45.29; H, 4.32; N, 3.66%. $C_{14}H_{15}NS_3O_5$ requires: C, 45.02; H, 4.05; N, 3.75%.

(k) Reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with lead (IV) oxide in cyclohexene

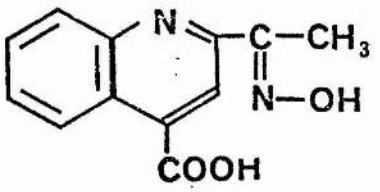
The hydroxylamine, (1.7 g, 0.005 mol), was stirred in cyclohexene (150 ml, 1.48 mol), with an excess of lead (IV) oxide during 24 h. The mixture was centrifuged and the solvent evaporated. The remaining oil was extracted with acetone. Evaporation of these extracts yielded, N,N-bis-(p-tolylsulphonyl)-hydroxylamine, (1.4 g, 0.0041 mol, 82%), but no N,N,O-tris-(p-tolylsulphonyl)hydroxylamine. The residual oil contained no aromatic protons (n.m.r.), no p-$CH_3C_6H_4SO_2$ fragments (mass spectrum), and was scarcely volatile in an oil-pump vacuum. No such hydrocarbon was formed in a control reaction, in the absence of the hydroxylamine.

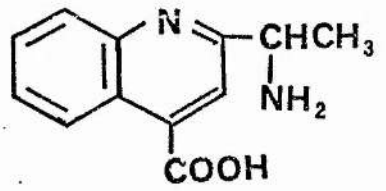
3.7 SPECTRAL DATA

(a) Infra-red Spectra

The infra-red spectra of both bis- and tris-(arylsulphonyl)-hydroxylamines are consistent with the constitutions postulated. All the spectra, (nujol mull and hexachlorobuta-1,3-diene) contain a strong band at 1080 cm^{-1}, identified as υ(N-O) by analogy with

2-(1-hydroxyiminoethyl)-4-quinoline carboxylic acid (I), which contains a strong band at 1040 cm^{-1}, whereas 2-(1-aminoethyl)-4-quinoline carboxylic acid (II) does not[13]. The main difference

(I) 

(II) 

between the spectra of the two series is the presence of ∂(O-H) only in the bis series, and of ∂(S-O) only in the tris series (See Table 3.7).

(b) N.M.R. Spectra

The proton spectra (C_6D_6) of the bis-derivatives are entirely as expected; no hydroxyl protons were observed. In the spectra of the tris-derivatives, two methyl resonances in the intensity ratio of 2:1 are observed at δ 3.01 when X = p-CH_3O-, separated by 2.3Hz and each having $\partial_{\frac{1}{2}}$ = 0.6 Hz. When X=p-CH_3, only a single methyl resonance could be resolved at δ 1.77 having $\partial_{\frac{1}{2}}$ = 2.0 Hz. This absorption seems unlikely to conceal two unresolved methyl resonances since in the analogous bis-hydroxylamine compound $\partial_{\frac{1}{2}}$ for the methyl resonance is also 2.0Hz at δ 1.73. When X=p-F, two resonances, with an intensity ratio of 2:1 were observed in the ^{19}F spectrum (proton decoupled), at -100.90 (1F) and -101.02 (2F) p.p.m. (CCl_3F), with a separation of 11.00Hz. When X=H, p-CH_3 and p-Cl four resonances are present associated with the aryl ring in the ^{13}C spectrum, (proton decoupled), of the bis

hydroxylamines (D.M.S.O.). While the analogous tris derivatives show a further four resonances associated with the aryl ring connected to oxygen. (See Table 3.8 and 3.9). For X=p-CH_3 two methyl resonances are observed at 21.11 p.p.m. and 20.72 p.p.m.: X=H and p-Cl the two resonances associated with each carbon atom of the aryl rings are shown. Tris-(p-tolylsulphonyl)imide shows four resonances associated with the ring and one methyl resonance at 21.11 p.p.m.

(c) E.S.R. Spectra

Millimolar solutions of the tris-hydroxylamines in benzene were carefully degassed in suitable tubes and then sealed. Each hydroxylamine, except X=p-CH_3O, gave a typical triplet signal associated with a nitroxide radical. When X=p-F each line showed further splitting of 0.6 gauss due to fluorine coupling with the nitrogen atom. a_N values are shown in Table 3.10, and the spectra in Fig. 3.1 and Fig. 3.2 .

(d) Mass Spectra

All the bis-hydroxylamines show molecular ion peaks at 70 eV (See Table 3.11). The tris-hydroxylamines show very similar fragmentation, but molecular ion peaks only become apparent at 20 eV, each having intensities $<0.1\%$.

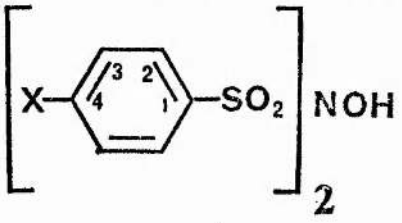
Table 3.7

Diagnostic infra-red frequencies in $(p\text{-}XC_6H_4SO_2)_2NOH$ and $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4\ X\text{-}p$

X		H	CH_3	Cl	CH_3O	F
$(p\text{-}XC_6H_4SO_2)_2NOH$	∂ (OH)cm^{-1}	3300	3280	3200	3440	3400
$(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4\cdot X\text{-}p$	∂ (S-O)cm^{-1}	850	815	825	850	815

Table 3.8

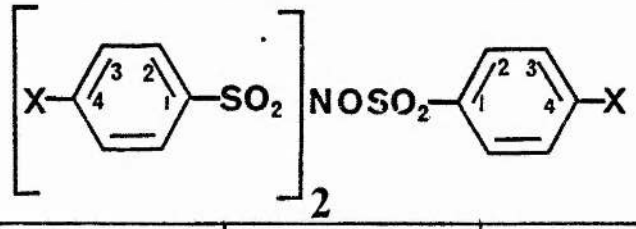
^{13}C n.m.r. spectra of N, N-bis-(arylsulphonyl)hydroxylamines



Carbon atom	C_1	C_2	C_3	C_4	X (ppm)
X					
H	139.95	129.06	128.62	134.63	-
CH_3	138.90	128.77	128.28	144.77	$\delta(CH_3)$21.19
Cl	133.07	129.34	127.74	140.15	-
MeO	127.15	131.13	114.21	163.96	$\delta(CH_3)$55.83
F	132.79 (J=10.6Hz)	128.07 (J=8.5Hz)	114.70 (J=21.7Hz)	162.31 (J=245.1Hz)	-

Table 3.9

^{13}C n.m.r. spectra of N, N, O-tris-(arylsulphonyl)hydroxylamines



Carbon Atom / X	C_1	C_2	C_3	C_4	X (p.p.m.)
H	136.28 136.40	129.53 128.31	128.31 125.83	134.44 147.16	
CH_3	138.01 -	129.86 129.07	129.77 128.14	146.00 145.09	$\delta(CH_3)$ 21.11 (422.3Hz) 20.72 (414.4Hz)
Cl	130.24 131.18	129.78 128.99	127.79 127.53	146.94 154.37	
CH_3O	163.93 -	131.10 127.08	114.22 112.82	- 125.92	$\delta(CH_3)$ 55.85 55.17
F	129.8 133.6	132.20 127.97	116.63 114.48	166.66 -	
		10.3Hz 8.3Hz	23.7Hz 21.5Hz	255.3Hz	
$(p\text{-}CH_3C_6H_4SO_2)_3N$	141.11	128.70	127.33	142.38	$\delta(CH_3)$=21.11

Table 3.10

Nitrogen h.f.c. (a_N) for N, N, O-tris-(arylsulphonyl)hydroxylamines

$(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$

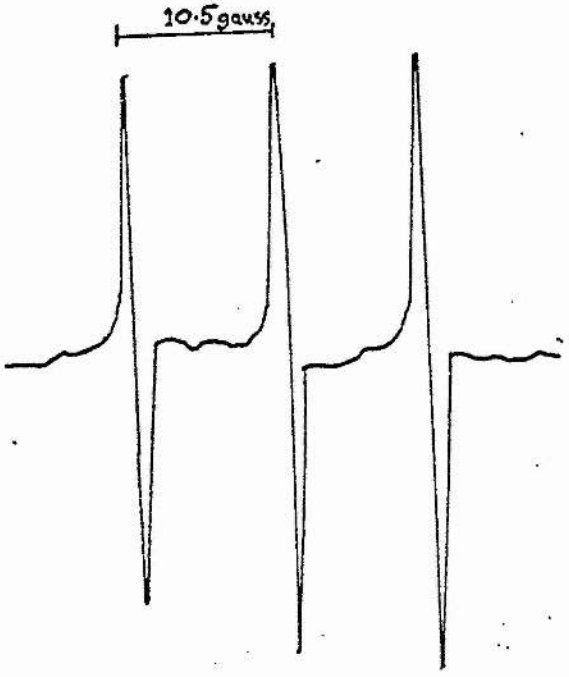
X	a_N(gauss)	Signal (gauss)
H	12.0	3309, 3320, 3333
CH_3	11.0	3310, 3321, 3332
Cl	10.5	3310, 3321, 3331
MeO	-	
F	10.5	3333, 3343, 3354

Table 3.11

Mass Spectra (70 eV) of N, N-bis-(arylsulphonyl)hydroxylamines

Ion	X(I%)	H	CH_3	Cl	F	MeO
M^+		297(1)	341 (0.5)		349 (0.5)	373 (1)
M^+-16(0)			325 (1.4)			
M^+-32			309 (1.4)			
M^+-48			293 (4.1)			
$(XC_6H_4SO_2)_2N^+$				364 (1.5)	332 (3.3)	
$(XC_6H_4SO_2)NSO_2C_6H_4^+$				329 (4.9)		
$(C_6H_4SO_2)_2N^+$				294 (1.6)		
$XC_6H_4SO_3H^+$				192(12.1)	176(39.2)	188(71.5)
M^+-64(SO_2)		249 (6.6)				
M^+-128($2SO_2$)		185 (1.6)				
M^+-129		184 (1.3)				
$XC_6H_4SO_2^+$		141 (3.3)	155(15.9)	175(28.0)	159(83.3)	171(100)
$XC_6H_4SO^+$		125(40.0)	139 (4.2)	159(42.9)	143(62.5)	155(40.0)
$XC_6H_4S^+$		109(24.3)	123(21.5)	143(65.8)	127 (6.7)	139(43.8)
$XC_6H_4^+$		77(100)	91(100)	111(100)	95(100)	107(63.8)

(a) N,N,O-tris-(p-chlorobenzenesulphonyl)-hydroxylamine in benzene



(b) N,N,O-tris-(phenylsulphonyl)-hydroxylamine in benzene

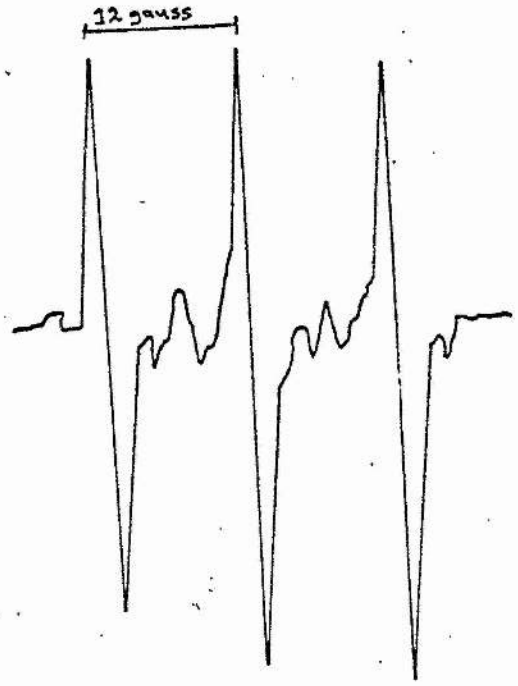
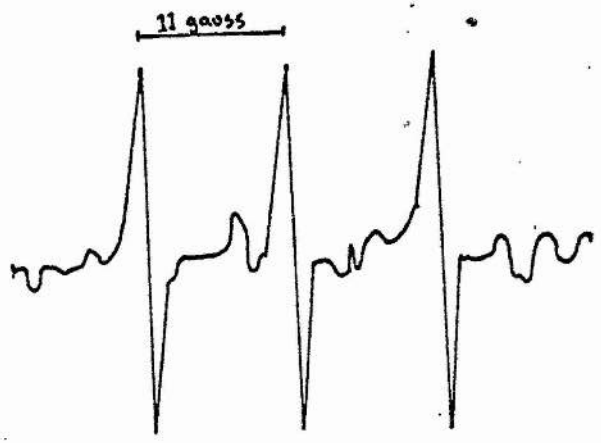


Fig. 3.1 E.S.R. Spectra of N,N,O-tris-(arylsulphonyl)hydroxylamines

(a) N,N,O-tris-(p-tolylsulphonyl)hydroxylamine in benzene



(b) N,N,O-tris-(p-fluorobenzenesulphonyl)-hydroxylamine in benzene

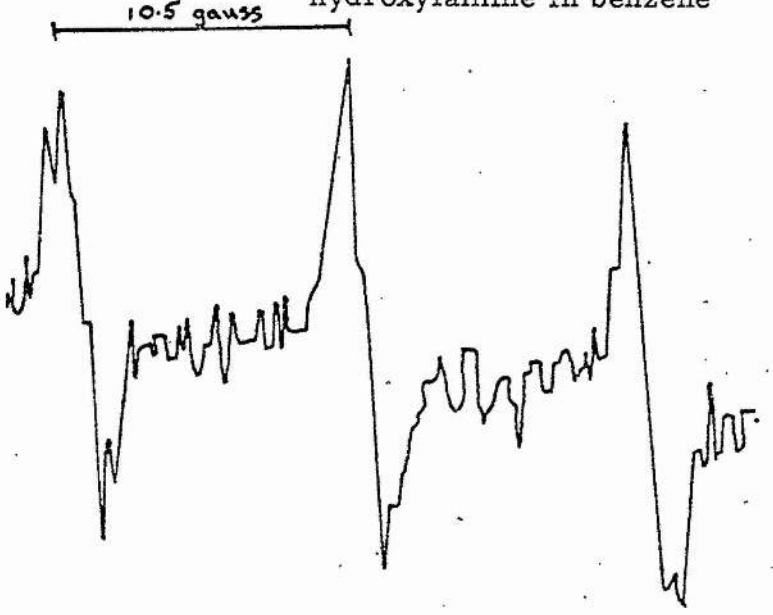


Fig. 3.2 E.S.R. Spectra of N,N,O-tris-(arylsulphonyl)hydroxylamines

3.8 THE PREPARATION AND OXIDATION OF SODIUM ALKYLSULPHINATES

(a) sodium methylsulphinate

Methane sulphonyl chloride was reduced in propanol by zinc dust. A white solid corresponding to $CH_3SO_2Na \cdot O.53NaCl$ was isolated in 81% yield. Found: C, 9.02; H, 2.35%. CH_3NaO_2S requires: C, 11.77; H, 2.96%.

(b) sodium n-butylsulphinate

Acrylonitrile, (60 ml), was slowly added to a stirred ice-cold mixture of n-butanethiol, (48.8ml), and sodium methoxide (1.2g) and during the addition the temperature was kept below 45°. After addition was complete the mixture was stirred during 3 h . Distillation at 14 mm yielded β -butanemercaptopropionitrile (27 g, 42%) at 125-128° [14,15]. The product was confirmed by mass spectrometry. Hydrogen peroxide (101 ml), was then slowly added to a stirred ice-cold solution of the alkanemercaptopropionitrile, (26g), in glacial acetic acid, (6.18 g). After addition was complete the mixture was heated on a steam bath for 4 h . Vacuum distillation removed the acetic acid, hydrogen peroxide and water at 33-40° and the remaining solid (26 g, 84%) gave; C, 47.8; H, 7.7; N, 8.2%: $C_7H_{13}NO_2S$ requires C, 48.0; H, 7.5; N, 8.0%.

A solution of sodium isopropylthiol, (26 g) in ethanol (250 ml) was added to a stirred solution of n-butane-β-sulphonylpropionitrile (26g), in ethanol (150 ml) during 20 minutes. Evaporation of the solvent after refluxing for 5h. afforded a white solid, which after recrystallisation from water gave: C, 32.9; H, 5.9%. $C_4H_9NaO_2S$ requires C, 33.3; H, 6.3%.

(c) Oxidation of sodium methylsulphinate and sodium n-butylsulphinate

The sodium sulphinate (0.02 mol), was dissolved in an ice-cold solution of sodium nitrite (0.01 mol), and concentrated hydrochloric acid (3 ml) was slowly added. No precipitate was formed, but nitrogen oxides were evolved. Evaporation of the solvent gave the corresponding sulphonic acid. Distillation of the crude methane sulphonic acid at 8 mm (bp = 164-166°) yielded the pure acid. n-Butylsulphonic acid was identified mass spectroscopically [M^+ = 138 (2.1%)]. Oxidation with fuming nitric acid also yielded the alkylsulphonic acid.

(d) Some other related reactions

Attempts to prepare sodium isopropyl and n-propylsulphinates by the reaction[16] of the corresponding alkyl bromide with magnesium and sulphur dioxide, in the presence of iodine proved unsuccessful. The reduction of diethylsulphamoyl chloride, Et_2NSO_2Cl, with zinc dust in propanol afforded a white salt. C, 11.9; H, 2.9; N. 3.9%, corresponding to $C_4H_{10}NO_2SNa \cdot 4.2NaCl$. No bis-hydroxylamine was isolated on addition of nitrous acid.

3.9 RESULTS AND DISCUSSION

Arenesulphinic acids react with aqueous nitrous acid to give N,N-bis-(arylsulphonyl)hydroxylamines, equation (1).

$$2XC_6H_4SO_2H + HNO_2 \longrightarrow (XC_6H_4SO_2)_2NOH + H_2O \qquad (1)$$

(X = H, p-CH_3, p-Cl, p-CH_3O, p-F)

These hydroxylamines are white crystalline solids, stable in dry air. Microanalyses, yields and melting points are recorded in Table 3.4. The yield is essentially independent of the quantity of sodium nitrite used, provided that at least the stoichiometric quantity is present. The hydroxylamines are also produced in reasonable yields, (c.a. 64%), from the reaction of N-(arylsulphonyl)-hydroxylamines and arenesulphonyl chlorides in the presence of a base. N,N-bis-(alkylsulphonyl)hydroxylamines, $(RSO_2)_2NOH$ appear to be too unstable to isolate when $R=CH_3$ or $n\text{-}C_4H_9$, but when $R=C_{12}H_{25}$ the bis-hydroxylamine[17] is more stable and has been isolated. Evidence for the N,N-substitution is provided by the infra-red spectra which all contain δ(O-H).

A number of methods for the reduction of arenesulphonyl chlorides have been recorded[2-7]. The most satisfactory is the use of zinc dust in propan-1-ol[5], this gave yields ranging from 87% when X=H to 98% when X=p-CH_3O. When X=p-Cl or p-CH_3O small quantities of diarylsulphone were also produced during the reduction, possibly according to (2).

$$ArSO_2Na + ArSO_2Cl \longrightarrow NaCl + SO_2 + Ar_2SO_2 \qquad (2)$$

Sodium alkylsulphinates were also produced by zinc reduction. A wide variety of oxidising agents were tested in the hope of effecting oxidation of the bis-(arylsulphonyl)hydroxylamine to the corresponding nitroxyls (3).

$$(p\text{-}XC_6H_4SO_2)_2NOH \longrightarrow (p\text{-}XC_6H_4SO_2)_2NO^{\cdot} \qquad (3)$$

In methylene chloride, lead (IV) oxide reacted with each of the bis-hydroxylamines to yield, N,N,O-tris-(arylsulphonyl)hydroxylamines and nitrate. Two of the bis-(arylsulphonyl)hydroxylamines, having X=p-CH_3 and p-Cl, were reacted with a number of oxidants [See Table 3.12]. When X=p-CH_3, the same tris-(arylsulphonyl)-hydroxylamine was obtained when the oxidising agent was silver (I,III) oxide, AgO, in either methylene chloride or benzene, lead (IV) oxide in benzene, lead (IV) acetate in methylene chloride or manganese (IV) oxide in methylene chloride. Aqueous lead (IV) oxide or silver (I,III) oxide, excess nitrous acid and m-chloroperbenzoic acid had no action on this bis-compound. When X=p-Cl, the tris species was also produced by the action of lead (IV) oxide in benzene and silver (I,III) oxide in either benzene or methylene chloride.

Two plausible routes from $(ArSO_2)_2NOH$ to $(ArSO_2)_2NOSO_2Ar$ are outlined in Scheme 3.1. The failure of certain oxidants to generate N,N,O-tris-(arylsulphonyl)hydroxylamines allows route A to be ruled out. Nitrous acid reacts rapidly with hydroxylamine to yield dinitrogen oxide[18], and lead(IV) oxide, silver (I,III) oxide and m-chloroperbenzoic acid all oxidise hydroxylamine to nitrate under conditions which they fail to convert N,N-bis-(arylsulphonyl)-hydroxylamines into the tris derivatives. Excess nitrous acid will not convert toluene-p-sulphinic acid or N,N-bis-(p-tolylsulphonyl)-hydroxylamine to the tris species. This observation contrasts with that of Marvel and Johnson[17] who reported that either excess nitrous

Table 3.12

Formation of tris-(arylsulphonyl)hydroxylamines by oxidation of N,N-bis-(arylsulphonyl)hydroxylamines

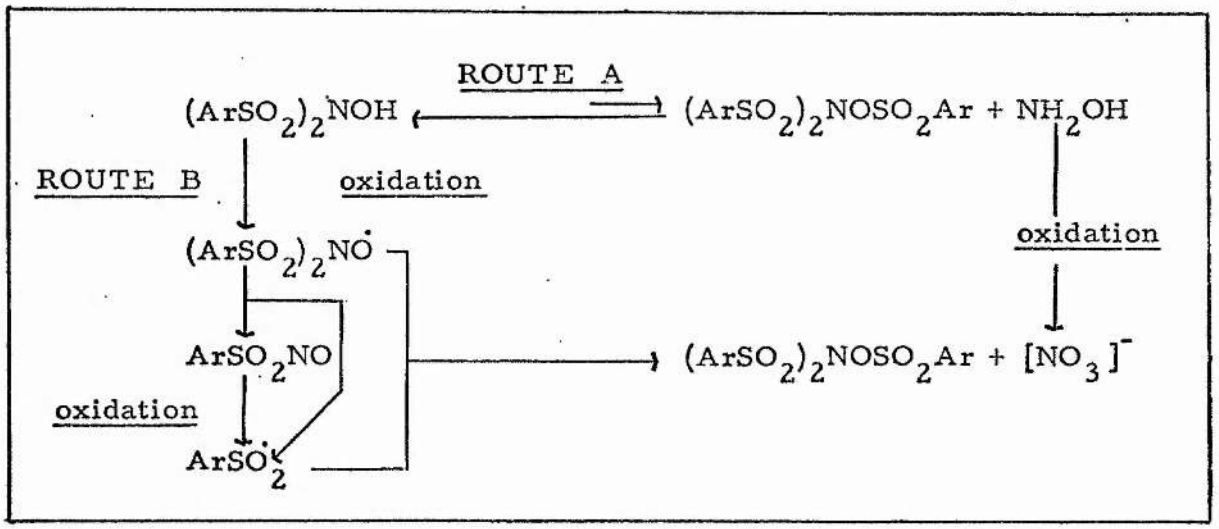
(+, formed; -, not formed)

Oxidant	X = H	p-CH_3	p-Cl	p-MeO	p-F
PbO_2-CH_2Cl_2	+	+	+	+	+
AgO-CH_2Cl_2		+	+		
PbO_2-C_6H_6		+	+		
AgO-C_6H_6		+	+		
$Pb(O_2CMe)_4$-CH_2Cl_2		+			
MnO_2-CH_2Cl_2		+			
PbO_2-$K_2[CO_3]$(aq)		-			
AgO-$K_2[CO_3]$ (aq)		-			
$Na[NO_3]$-HCl (aq)		-			
SeO_2-CH_2Cl_2		a			
HNO_3-$MeCO_2H$		+[b]			
m-$ClC_6H_4CO_3H$-Et_2O		-			

a - No homogenous product isolated

b - Evaporation of the filtrate, after removal of the product, yielded toluene-p-sulphonic acid

Scheme 3.1



Possible routes to the formation of N, N, O-tris-(arylsulphonyl)-hydroxylamines from N, N-bis-(arylsulphonyl)hydroxylamines

or nitric acid will convert N,N-bis-(1-dodecanesulphonyl)hydroxylamine to the amine oxide, $(C_{12}H_{25}SO_2)_3NO$. The alternative route B involves a reversal of the spin-trapping reaction to give an N,N-bis-(arylsulphonyl)nitroxide and a nitrosylarenesulphinate as possible intermediates. Some support for this route is drawn from e.s.r. observations for benzene solutions of the tris-hydroxylamines give a typical nitroxide triplet signal, with hyperfine splitting constants (a_N) of 10.5-12.0 gauss. The h.f.c. previously[19] observed for N,N-bis-(phenylsulphonyl)nitroxide, from the oxidation 'in situ' of N,N-bis-(phenylsulphonyl)hydroxylamine was 10 gauss. No spectrum was observed for X=p-CH_3O. The substituents in the aryl rings appear to have very little effect on the a_N values, and this is probably due to the dominant electron withdrawing ability of the arylsulphonyl groups. The tris-hydroxylamines, which are microanalytically pure samples appear to contain a small amount of the corresponding nitroxide radical, for when they are dissolved in a suitable solvent, (e.g. benzene) the observed e.s.r. signals are weak in relatively strong solutions. Also suggestive of the intermediacy of radicals is the observation that in cyclohexene, the conversion of $(RSO_2)_2NOH$ to $(RSO_2)_2NOSO_2R$ by lead (IV) oxide is suppressed in favour of oligomerisation of the cyclohexene. Arylsulphonyl radicals were not detected although toluene-p-sulphonyl radicals have previously[20,21] been observed by e.s.r.

The tris-derivatives are believed to be N,N,O-trisubstituted hydroxylamines rather than N,N,N-trisubstituted amine oxides as

described by earlier workers[9,22-24] on the grounds of their infra-red spectra which all contain ν(S-O) and their n.m.r. spectra which all show evidence of two types of benzenoid group, when X=p-CH_3O (^{1}H n.m.r.), X=p-F (^{19}F n.m.r.), X=H, p-Cl and p-CH_3 (^{13}C n.m.r.). The amine oxide structure may also be discounted on theoretical grounds. The nitrilotrisulphonate ion, $N[SO_3]_3^{-3}$, is found to be planar at nitrogen[25] with an S···S distance of 2.96 Å, approximately equal to the 2.90 Å expected[26] in the hard-atom approximation, and it may be supposed that $N(SO_3R)_3$ would be similar although with a shorter N-S and hence shorter S···S distance. If the NS_3 fragment is planar largely because of S···S repulsions, then an increase in the coordination number of the nitrogen, as in the formation of the amine oxide $(RSO_2)_3NO$, which would be accompanied by a change in the geometry of the nitrogen atom from trigonal planar to approximately tetrahedral, will only increase the steric compression of the sulphur atoms and consequently increase the total potential energy.

It is probable that the nitrogen atom even in a bis- or tris-(arylsulphonyl)hydroxylamine has almost planar geometry. In Fremy's radical di-anion, $ON(SO_3)_2^{-2}$, the ONS_2 fragment is planar[27] with O-N and N-S distances of 1.28 Å and 1.66 Å respectively, the distances and hence the angles, assuming the hard atom approximation[26], in species such as $(ArSO_2)_2NOH$ and $(ArSO_2)_2NOSO_2Ar$ can be estimated from those in Fremy's anion, and from those in the related pair of molecules, N,N-bis-(trifluoromethyl)nitroxide,

$(CF_3)_2NO^{\cdot}$, and N,N-bis-(trifluoromethyl)hydroxylamine, $(CF_3)_2NOH$. In $(CF_3)_2NO^{\cdot}$ the C-N and N-O distances are[28] 1.441 and 1.26 Å respectively, while in $(CF_3)_2NOH$ these distances are[29] 1.435 and 1.399 Å respectively; if a roughly similar change in the N-O distance occurs in the sulphur species, that in the bis and tris-(arylsulphonyl)hydroxylamines may be expected to be ca. 1.41 Å, with an N-S distance of ca. 1.65 Å. Assuming hard-atom non-bonded distances of 2.90 Å for S···S and 2.58 Å for S···O, the SNS and SNO angles are expected to be 123 and 114.7°, giving a sum of angles at nitrogen of 352.4°, much larger than the 331.8° observed[30] in trimethylamine.

It is therefore to be expected that reaction of a bis-(arylsulphonyl)hydroxylamine with an arenesulphonyl chloride would give for steric reasons an O- rather than an N- derivative; in accord with this, reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with toluene-p-sulphonyl chloride is found to give N,N,O-tris-(p-tolylsulphonyl)hydroxylamine. This has also been confirmed[31] by reduction of the tris-hydroxylamine $(RSO_2)_2NOSO_2R^1$, where $R=p\text{-}CH_3\text{-}C_6H_4$ and $R^1=C_6H_5$, forming only bis-(p-tolylsulphonyl)-imide, and therefore the phenylsulphonyl and toluene-p-sulphonyl groups do not occupy equivalent positions in the molecule, ie. invalidates the amine oxide structure.

Konigs[24] reported that the reaction of fuming nitric acid on benzenesulphinic acid gave the tris species, although he regarded it as a trisubstituted amine oxide; this observation has been confirmed. The claim by Hinsberg[32] to have obtained N,N-bis-(phenylsulphonyl)hydroxylamine by the action of nitrous acid on

benzenesulphonamide could not be substantiated. In contrast to carboxylic acid amides, benzenesulphonamide is remarkably inert towards nitrous acid, and under most reaction conditions is recovered unchanged; the only product identified was diphenyldisulphone, $(PhSO_2)_2$, which may have been produced by dimerisation of benzenesulphonyl radicals. Similarly Piloty's[11] report that N-(phenylsulphonyl)hydroxylamine reacts with iron (III) chloride to form the bis-derivative could not be confirmed; no reaction was observed. It should be noted that the m.p. recorded by Piloty (110°C) is substantially below the figure observed during these investigations (125°), as it is also the value he reported for the tris-derivative.

It appears that any nitrogen containing oxidant will generate N,N-bis-(arylsulphonyl)hydroxylamines from arenesulphinic acids, and that the bis-compounds either do not react at all with oxidising agents or give the corresponding tris-compound, which represents a fairly deep potential trap in the energy hypersurface of this system. Thus a mild reducing agent such as nitrous acid must be used if only the bis-species is required; nitric acid with an arenesulphinic acid yields the tris-compound directly.

The reaction of toluene-p-sulphinic acid with N,N-bis-(p-tolylsulphonyl)hydroxylamine in glacial acetic acid was reported by von Meyer[9] to give tris-(p-tolylsulphonyl)amine, according to equation (4).

$$p\text{-}CH_3C_6H_4SO_2H + (p\text{-}CH_3C_6H_4SO_2)_2NOH \longrightarrow (p\text{-}CH_3C_6H_4SO_2)_3N + H_2O \qquad (4)$$

Reinvestigation of this reaction under von Meyer's conditions, in air, produced copious evolution of nitrogen oxides, giving toluene-p-sulphonic acid as the sole solid product. Under dry dinitrogen, however, no nitrogen oxides were lost and the bis-compound was recovered unchanged. It is possible that in von Meyer's experiment, part either of the arenesulphinic acid or of the bis-compound was oxidised by the nitrogen oxides to tris-(p-tolylsulphonyl)hydroxylamine; certainly the m.p. he quoted for the material he described as an amine, 184°, is very similar to that found in this work for the tris-substituted hydroxylamine, 183-184°.

Although all the bis-(arylsulphonyl)hydroxylamines studied here are stable in dry air, only those having X=p-CH_3 and p-Cl are stable in moisture. When X=p-F or H, moisture causes the evolution of nitrogen oxides, leaving the corresponding arylsulphonic acid and tris-(arylsulphonyl)hydroxylamine, while when X=p-CH_3O no nitrogen oxides were evolved and the sole product was a black tar. The rate of decomposition when X=p-F was so fast that accurate microanalysis was not possible: the fast decomposition when X=p-CH_3O may account for its rather poor microanalytical data. It is reasonable to suppose that the initial step in the decomposition is hydrolysis of an N-S bond; for hydrolysis of sulphonyl derivatives Hammett's ρ is positive[33], and the σ_p constants suggest that the rates of hydrolysis should decrease in the order $Cl > F > H > CH_3 > CH_3O$. However, the order of decomposition rates observed is $F > CH_3O > H > CH_3 \simeq Cl$. The decomposition

of N,N-bis-(arylsulphonyl)hydroxylamines to form the corresponding tris derivative is in agreement with the decomposition observed[17] for N,N-bis-(1-dodecanesulphonyl)hydroxylamine. For the tris-derivatives the order is $F \triangleq Cl \geqslant H \triangleq CH_3 \triangleq CH_3O$, decomposition of the halogeno-species giving nitrogen oxides and the arene-sulphonic acid.

Any attempt to isolate N,N-bis-(alkylsulphonyl)hydroxylamines proved fruitless; yielding the corresponding alkylsulphonic acid only. This seems to suggest that lower members of the N,N-bis-(alkyl-sulphonyl)hydroxylamines, $(RSO_2)_2NOH$, when $R=CH_3$ or $n\text{-}C_4H_9$-, are very unstable and either decompose directly to the sulphonic acid or via the tris-hydroxylamine with analogy to the decomposition of bis-(arylsulphonyl)hydroxylamines and tris-(arylsulphonyl)hydroxyl-amines.

3.10 References

1. E. Hug, Bull. Soc. Chim. France, 1934, 990
2. S. Gabriel and A. Deutsch, Ber., 1880, 13, 388
3. S. Smiles and C.M. Bere, Organic Syntheses Coll. Vol. I, 1932, 7
4. V. Midrdichian, 'Organic Syntheses', Reinhold, New York, 1957, 2, 1701
5. H. Gilman, E.W. Smith, and H.J. Oatfield, J. Amer. Chem. Soc., 1934, 56, 1412
6. F.C. Whitmore and F. H. Hamilton, Org. Syntheses II, 89

7. L. Field and F.A. Gunwald, J. Org. Chem., 1951, 16, 946

8. R.M. Hann, J. Amer. Chem. Soc., 1935, 57, 2167

9. E. von Meyer, J. Prakt. Chem., 1901, 63, 175

10. J. Attenburrow, A.F.B. Cameron, J.M. Chapman, R.M.Evans, B.A.Hems, A.B.A. Jansen and T. Walker, J. Chem. Soc., 1952, 1094

11. O. Piloty, Ber., 1896, 29, 1560

12. A.F. Holleman and P. Caland, Ber., 1911, 44, 2505

13. Thermodynamic Research Centre Data Project, Infra-red Spectral Data Vol. I (Texas A and M University, College Station, Texas) 1974

14. C.D. Hurd and L.L. Gershbein, J. Amer. Chem. Soc., 1947, 69, 2328

15. W.E. Truce and F.E. Roberts, J. Org. Chem., 1963, 28, 593

16. H.G. Houlton and H.V. Tartar, J. Amer. Chem. Soc., 1938, 60, 544

17. C.S. Marvel and R.S. Johnson, J. Org. Chem., 1948, 13, 822

18. R. Nast and I. Foppl, Z. Anorg. Chem., 1950, 263, 310

19. Th.A.J.W. Wajer , H.W. Geluk, J.B.F.N. Engberts and Th.J. de Boer, Rec. Trav. Chim. Pays-Bas, 1970, 89, 696

20. A.G. Davies, B. P. Roberts and B.R.S. Sanderson, J.C.S. Perkin II, 1973, 626

21. M. McMillan and W.A. Waters, J. Chem. Soc. (B), 1966, 422

22. R. Otto and H. Ostrop, Ann. Chem., 1867, 141, 370

23. W. Konigs, Ber., 1878, 11, 616

24. W. Konigs, ibid., 1878, 11, 1588

25. J.V. Tillak and C.H.L. Kennard, J. Chem. Soc. (A), 1970, 1637

26. C. Glidewell, Inorg. Chim. Acta, 1975, 12, 219

27. R.A. Howie, L.S.D. Glasser and W. Moser, J. Chem. Soc. (A), 1968, 3043

28. C. Glidewell, D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick and S.M. Williamson, J. Chem. Soc. (A), 1971, 478

29. C. Glidewell, C.J. Marsden, A.G. Robiette and G.M. Sheldrick, J.C.S. Dalton, 1972, 1735

30. B. Beagley and T.G. Hewitt, Trans. Faraday Soc., 1968, 64, 2561

31. W.V. Farrar, J. Chem. Soc., 1960, 3063

32. O. Hinsberg, Ber., 1894, 27, 598

33. H.H. Jaffe, Chem. Rev., 1953, 53, 191

CHAPTER FOUR

THE SYNTHESIS AND REACTIONS OF N,N-BIS-(ARYLSULPHONYL)IMIDES

4.1 THE PREPARATION OF N,N-BIS-(ARYLSULPHONYL)IMIDES

(a) Reaction of Arylsulphonamides with Arenesulphonyl Chlorides

The N,N-bis-(arylsulphonyl)imides, $(p\text{-}XC_6H_4SO_2)_2NH$, when X=H or p-$CH_3$, were synthesised by refluxing equimolar quantities of the corresponding arylsulphonamide and arenesulphonyl chloride in xylene for 30 minutes, followed by addition of a mole of potassium carbonate. The potassium salt of the imide was extracted from the remaining residue with hot ethanol and the solution filtered. The white solid product, after evaporation of the solvent, was dissolved in distilled water (ca 150 ml) and concentrated hydrochloric acid slowly added to precipitate the imide. After recrystallisation from acetone the pure product was dried. Microanalytical data, yields and melting points are given in Table 4.1 . These two imides were also prepared using sodium hydroxide.[1] When X=p-Cl or p-MeO, the bis-imide was prepared by the addition of the arenesulphonyl chloride to a solution of ammonium chloride[2] in acetone and water. The mass spectra of the imides are shown in Table 4.2 .

(b) Reaction of Imido-bis-(sulphuryl chloride) with amines and alcohols

(i) Imido-bis-(sulphuryl chloride) was prepared from phosphorus pentachloride[3], sulphamic acid and chlorosulphonic acid in yields up

to 70%. The product exhibited a molecular ion peak in its mass spectrum at m/e 213 (1%), $HN(SO_2{}^{35}Cl)_2$ mp = 37°.

(ii) Preparation of N,N-bis-(piperidinesulphonyl)imide

Piperidine (6.80 g, 0.081 mol), was added slowly to a stirred solution of imido-bis-(sulphuryl chloride), (4.28 g, 0.02 mol) in benzene (75 ml). The solution was refluxed during 15 minutes, cooled and filtered, and the solvent evaporated. The crude product was heated with water (50 ml) on the steam bath, filtered and dried. Yield, 70%; mp = 139-140°. Found: C, 38.3; H, 7.0; N, 13.1%. $C_{10}H_{21}N_3O_4S_2$ requires: C, 38.6; H, 6.8; N, 13.5%. The ^1H n.m.r. spectrum (C_6D_6) contained δ 1.28 (m, 12H) and 3.28 (t, 8H) p.p.m.

(iii) Preparation of N,N-bis-(diethylaminosulphonyl)imide

A solution of redistilled dry diethylamine, (7.4 g, 0.101 mol) in benzene (50 ml) was slowly added to a stirred ice-cold solution of imido-bis-(sulphuryl chloride), (5.4 g, 0.0254 mol) in benzene (75 ml) during 20 minutes; the mixture was protected from atmospheric moisture at all times by a constant flow of dry dinitrogen. When addition was complete the mixture was refluxed during 50 minutes and after cooling to room temperature was stirred during 48 h., followed by filtration to remove any diethylamine hydrochloride. After stirring during a further 48 h. the mixture was thoroughly washed with water (5 x 500 ml), and the organic layer dried over anhydrous sodium sulphate. Evaporation of the solvent afforded a pale yellow solid (2.1 g) which on recrystallisation from acetone gave the product.

Table 4.1

Microanalytical data, yields and melting points for N, N-bis-(arylsulphonyl)imides $(p\text{-}XC_6H_4SO_2)_2NH$

X	Found (%) C	H	N	Calculated (%) C	H	N	mp (°)	Yield (%)
H	48.3	3.7	4.6	48.5	3.7	4.7	156-157	61
CH_3	51.6	4.5	4.2	51.7	4.7	4.3	169-170	77
Cl	39.8	2.2	3.5	39.4	2.5	3.8	185-190	48
MeO	46.8	4.6	4.0	47.1	4.2	3.9	142-144	23

Table 4.2

Mass Spectra of N, N-bis-(arylsulphonyl)imides $(p\text{-}XC_6H_4SO_2)_2NH$

Ion^+	X =	H m/e	I(%)	CH_3 m/e	I(%)	Cl m/e	I(%)	MeO m/e	I(%)
M		297	1.0	325	6.8	365	2.5	357	1.5
$XC_6H_4SO_2NHC_6H_4X$		233	7.8	261	3.2	301	1.3	293	3.1
$XC_6H_4NHC_6H_4X$		168	1.0	197	5.0	-	-	229	2.7
$XC_6H_4SO_2$		141	26.3	155	24.5	175	53.3	171	100
XC_6H_4SO		125	1.0	139	5.4	159	63.0	155	76.1
XC_6H_4S		109	1.0	123	14.1	-	-	139	47.2
XC_6H_4		77	100	91	100	111	100	107	48.2
[$XC_6H_4SO_2C_6H_4X$		-	-	-	-	286	9.8	-	-]

Yield 1.9 g (26%); mp = 50-52°. Found: C, 33.3; H, 7.7; N, 14.4%. $C_8H_{21}O_4N_3S_2$ requires: C, 33.4; H, 7.4; N, 14.6%. The ^1H n.m.r. spectrum (C_6D_6) contained δ0.94(t) and 3.17 (q) p.p.m. in the intensity ratio 3:2 respectively.

(iv) Reaction of Imido-bis-(sulphuryl chloride) with pyrrolidine

A similar procedure was followed as for piperidine. Evaporation of the solvent yielded an oil which would not crystallise after standing for 2 weeks at 0°. The ^1H n.m.r. spectrum (C_6D_6) of the oil contained δ2.41 (br.s. 8H) and 3.83 (br.s. 8H). The oil gave a positive test for chloride when an aqueous sample was added to silver nitrate solution; and was therefore dissolved in benzene and thoroughly washed with water again. After drying over anhydrous sodium sulphate during 24 h. and evaporation of the solvent, a white solid (0.4 g) was isolated. Found: C, 36.5; H, 7.0; N, 10.3%. $C_8H_{17}N_3O_4S_2$ requires: C, 33.9; H, 6.0; N, 14.8%. The ^1H n.m.r. was identical to that observed for the oil. A similar oil was obtained when two moles of butyl lithium[4] were added to one mole of imido-bis-(sulphuryl chloride).

(v) Reaction of Imido-bis-(sulphuryl chloride) with alcohols

The alcohols ROH, when R=$(CH_3)_2CH$-, $C_6H_5CH_2$-, C_2H_5 and n-C_4H_9-, were added to a solution of imido-bis-(sulphuryl chloride) in varying solvents and under varying reaction conditions in the presence of a base. All the reactions produced viscous oils which would not crystallise. Only the starting materials were obtained when sodium alkoxides were used in place of a base. See Table 4.3 for details.

Table 4.3

The reaction conditions for the reaction of Imido-bis-(sulphuryl chloride) with alcohols (ROH)

R-	base or alkoxide	solvent	reaction conditions	Product
$(CH_3)_2CH$	pyridine	60-80 petrol	reflux	oil
	no base	$CHCl_3$	reflux	oil
	pyridine	C_6H_6	reflux	oil
	no base	C_6H_6	reflux	oil
	pyridine	C_6H_6	0^o stir	oil
	alkoxide	ether	0^o stir	no reaction
$C_6H_5CH_2$-	pyridine	60-80 petrol	reflux	oil
	pyridine	$CHCl_3$	reflux	oil
	1, 6 lutidine	C_6H_6	reflux	oil
	pyridine	C_6H_6	0^o	oil
C_2H_5-	1, 6 lutidine	C_6H_6	0^o	oil
	alkoxide	$CH_3C_6H_5$	-10^o	no reaction
n-C_4H_9-	pyridine	no solvent	0^o	oil

Table 4.4

Diagnostic Infra-red frequencies for N, N-bis-(arylsulphonyl)imides

$(p\text{-}XC_6H_4SO_2)_2NH$

	X =	H	CH_3	Cl	MeO
$\nu(N\text{-}H)_{str}$ cm^{-1}		3120	3170	3270	3180
$\nu(N\text{-}H)_{def}$ cm^{-1}		1580	1595	1570	1585

(c) Some other Imides

(i) N,N-bis-(methylsulphonyl)imide

Methylsulphonamide was prepared by slow addition of methanesulphonyl chloride, (8 ml, 0.1 mol) during 20 minutes to benzene (50 ml), through which ammonia was bubbled. When addition was complete, passage of ammonia was continued for a further 5 minutes. Removal of the solvent was followed by extraction of the residue with ether (3 x 100 ml). Evaporation of the combined extracts yielded the crude sulphonamide, which was recrystallised from acetone and water. Yield 6 g (64%); mp = 86-88°.

N,N-bis-(methylsulphonyl)imide was prepared[5] from the reaction of methylsulphonamide with methanesulphonyl chloride.

(ii) N,N-bis-(sulphonylamine)imide

Triammonium imidodisulphonate[6], $NH_4 \cdot N(SO_3NH_4)_2$, was converted to N,N-bis-(sulphonylamine)imide, $HN(SO_2NH_2)_2$ by refluxing with acetic anhydride. Found H, 3.2; N, 24.1%. $H_5N_3O_4S_2$ requires: H, 2.9; N, 24.0%.

4.2 ATTEMPTED OXIDATION OF BIS-SULPHONYLIMIDES

No oxidation was observed during 1 week for the following (a) N,N-bis-(p-tolylsulphonyl)imide with $H_2O_2/Na_2[WO_4](aqu)$[7-9]; m-$ClC_6H_4CO_3H$-Et_2O[10-12]; $K[MnO_4]$-acetone; lead (IV) oxide-acetone; $Ce^{3+}/H_2O_2(aqu)$[7]; H_2O_2/MeOH[7] and $Fe^{+2}/H_2O_2(aqu)$[7].

(b) N,N-bis-(phenylsulphonyl)imide with, $H_2O_2/Na_2[WO_4]$(aqu) and m-$ClC_6H_4CO_3H$-Et_2O.

(c) N,N-bis-(p-chlorobenzenesulphonyl)imide with, $H_2O_2/Na_2[WO_4]$(aqu).

(d) N,N-bis-(piperidinesulphonyl)imide with $H_2O_2/Na_2[WO_4]$ (aqu); m-$ClC_6H_4CO_3H$-Et_2O and lead (IV) oxide-acetone.

(e) N,N bis-(methylsulphonyl)imide with $H_2O_2/Na_2[WO_4]$ (aqu) and lead (IV) oxide-acetone.

(f) N,N-bis-(diethylaminosulphonyl)imide with $H_2O_2/Na_2[WO_4]$ (aqu), m-$ClC_6H_4CO_3H$-Et_2O, lead (IV) oxide-benzene and H_2O_2 (aqu).

(g) N,N-bis-(sulphonylamine)imide with $H_2O_2/Na_2[WO_4]$ (aqu).

4.3 SOME RELATED REACTIONS

(a) Reaction of N,N-bis-(p-tolylsulphonyl)imide with nitrosyl chloride

The imide, (0.8 g, 0.0025 mol), in benzene (150 ml) was recovered quantitatively on addition of excess nitrosyl chloride.

mp = 168-169° Found: C, 51.7; H, 4.7; N, 4.3%
Calculated: C, 51.7; H, 4.6; N, 4.5%.

For further details and discussion see Chapter 5.

(b) Reaction of N,N-bis-(p-tolylsulphonyl)imide with nitrogen (II) oxide and nitrogen (IV) oxide

The imide (0.3 g, 0.001 mol), in benzene (150 ml) which was under a continuous flow of dry dinitrogen, afforded unchanged imide on addition of excess nitrogen (II) oxide. Identical m.p. and micro-analysis to previous samples. Similar results were obtained with nitrogen (IV) oxide.

(c) Reaction of sodium-bis-(p-tolylsulphonyl)imide with silver nitrate

An aqueous solution of the sodium salt, (4.0 g, 0.012 mol) was slowly added to a stirred solution of silver nitrate, (2 g, 0.012 mol) during 15 minutes. The solution was filtered and the white product dried. Found: C, 37.4; H, 3.2; N, 3.2%. $C_{14}H_{14}NAgO_4S_2$ requires: C, 38.9; H, 3.3; N, 3.2%.

(d) Reaction of silver-bis-(p-tolylsulphonyl)imide with toluene-p-sulphonyl chloride

Tris-(p-tolylsulphonyl)imide was prepared[13] from silver-bis-(p-tolylsulphonyl)imide and toluene-p-sulphonyl chloride. Yield, 69%. mp = 222-225° (lit.[13] 230°). Found: C, 52.0; H, 4.4; N, 2.8% $C_{21}H_{21}NO_6S_3$ requires: C; 52.6; H, 4.4; N, 2.9%.

(e) Reaction of N,N-bis-(p-tolylsulphonyl)imide with halogens

(i) N,N-bis-(p-tolylsulphonyl)imide (1.6 g, 0.005 mol), was dissolved in benzene (100 ml) and an excess of dichlorine was bubbled in. Evaporation of the volatiles gave a product, (31.4 g, 33%, mp = 132-140°) whose mass spectrum gave ion clusters up to m/e = 288 ($C_6H_6^{35}Cl_6$), which is identical to the product produced from the chlorine/benzene/N,N bis-(p-tolylsulphonyl)hydroxylamine reaction, (See Chapter 6).

(ii) Reaction of sodium bis-(p-tolylsulphonyl)imide with diiodine and dichlorine

The sodium salt (3.3 g, 0.005 mol) suspended in either diethyl ether or carbon tetrachloride (150 ml); these solvents were used for

diiodine (1.25 g, 0.005 mol) and dichlorine (excess) respectively. After stirring during 12 h. filtration yielded unchanged imide. Yields 85 and 87% respectively.

4.4 SPECTRAL DATA

(a) Infra-red Spectra

The infra-red spectra of the N,N-bis-(arylsulphonyl)imides are consistent with the constitutions postulated; all showing strong bands for ν(N-H) at ca 3170 cm^{-1}. Diagnostic frequencies are given in Table 4.4. N,N-bis-(piperidinesulphonyl)imide and N,N-bis-(diethylaminosulphonyl)imide show $\nu(N\text{-}H)_{str}$ bands at 3200 and 3150 cm^{-1} respectively.

(b) N.M.R. Spectra

The proton spectra (C_3D_6O) of N,N-bis-(arylsulphonyl)imides are entirely as expected. When X=H and p-Cl a singlet resonance is observed for the nitrogen proton at δ 9.7 and 6.5 p.p.m. respectively. When X=p-CH_3 and p-CH_3O the methyl resonances occur at δ 2.43 and 2.95 p.p.m. respectively. The spectrum of N,N-bis-(piperidinesulphonyl)imide contains a multiplet (12H) at δ 1.28 p.p.m. corresponding to the β and γ proton resonances of the piperidine ring and a triplet (8H) at δ 3.28 p.p.m. for the α-protons. N,N-bis-(diethylaminosulphonyl)imide exhibits a spectrum containing a triplet and quartet in the intensity ratio 3:2 as expected.

4.5 RESULTS AND DISCUSSION

Arenesulphonyl chlorides react with arylsulphonamides in the presence of potassium carbonate, or alkaline ammonium chloride to produce alkali salts of bis-(arylsulphonyl)imides; which on acidification yield the corresponding N, N-bis-(arylsulphonyl)imide. Equation (1) and (2). These imides are stable in both moist and dry

$$p\text{-}XC_6H_4SO_2NH_2 + p\text{-}XC_6H_4SO_2Cl + K_2CO_3 \xrightarrow{\text{xylene}} (p\text{-}XC_6H_4SO_2)_2NK + KCl + CO_2 + H_2O \quad (1)$$

$$(p\text{-}XC_6H_4SO_2)_2NK + HCl \longrightarrow (p\text{-}XC_6H_4SO_2)_2NH + KCl \quad (2)$$

$X = H,\ p\text{-}CH_3$

air. Microanalyses, yields and melting points are recorded in Table 4.1. Although N, N-bis-(piperidinesulphonyl)imide and N, N-bis-(diethylaminosulphonyl)imide were readily prepared (3) and (4) the analogous pyrrolidine compound proved difficult to isolate. The ^1H n.m.r. of the oily and solid product did however show resonances corresponding to the α-protons (δ 3.83 p.p.m.) and the β-protons (δ 2.41 p.p.m.) of the pyrrolidine ring. No imides $(ROSO_2)_2NH$,

$$HN(SO_2Cl)_2 + 4C_5H_{10}NH \longrightarrow HN(SO_2NC_5H_{10})_2 + 2C_5H_{10}NH_2^+Cl^- \quad (3)$$

$$HN(SO_2Cl)_2 + 4(C_2H_5)_2NH \longrightarrow HN(SO_2N(C_2H_5)_2)_2 + 2(C_2H_5)_2NH_2^+Cl^- \quad (4)$$

could be isolated from the reaction of imido-bis-(sulphuryl chloride) with alcohols under the conditions employed. These reactions warrant further investigation since they lead directly to the neutral analogues of the imidodisulphonate ion, $HN(SO_3)_2^{-2}$. Evidence of the

N,N-disubstitution is provided by the infra-red spectra which all contain δ(N-H) (See Table 4.4).

Silver-bis-(p-tolylsulphonyl)imide reacts with toluene-p-sulphonyl chloride (5) under fairly vigorous conditions to yield the tris-imide,

$$(p\text{-}CH_3C_6H_4SO_2)_2NAg + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow[175^o]{vacuo} (p\text{-}CH_3C_6H_4SO_2)_3N + AgCl \qquad (5)$$

$(p\text{-}CH_3C_6H_4SO_2)_3N$. The tris-imide would be expected to be planar with analogy to the nitrilotrisulphonate ion, $N(SO_3)_3^{-3}$. (See discussion in Chapter 3).

A wide range of oxidising agents were tried in the hope of effecting oxidation of the bis-(sulphonyl)imides to the corresponding nitroxyls (6), since these reagents[7-12] have been previously used to

$$(p\text{-}XC_6H_4SO_2)_2NH \longrightarrow (p\text{-}XC_6H_4SO_2)_2NO^{\bullet} \qquad (6)$$

oxidise secondary amines to nitroxide radicals. Hydrogen peroxide in methanol[7] or in the presence of sodium tungstate[7-9], ceric salts[7] and iron (II) salts[7]; m-chloroperbenzoic acid[10-12] in diethyl ether; potassium permanganate in acetone[15]; lead (IV) oxide in acetone or benzene were all unsuccessful.

The initial step in the oxidation of $(RSO_2)_2NOH$ by a range of reagents was postulated in Chapter 3, to be loss of a hydrogen atom to yield the radical $(RSO_2)_2NO^{\bullet}$, part of which dissociates to give $RSO_2^{\bullet}$, (and RSO_2NO); subsequent cross-combination of the radicals yields the product $(RSO_2)_2NOSO_2R$. The occurrence of the first step

is supported by the failure of the corresponding bis-(arylsulphonyl)-imide, $(RSO_2)_2NH$ to undergo oxidation by any of the reagents which oxidise $(RSO_2)_2NOH$. N,N-bis-(arylsulphonyl)imides do not react with nitrosyl chloride, nitrogen (II) oxide and nitrogen (IV) oxide. No N-nitrosation is observed. The imides appear to initiate free radical chlorination of the solvent when the hydrocarbon is either benzene or cyclohexane; no reaction is observed in carbon tetrachloride. This reaction is considered in detail in Chapter 6.

The sodium salts of diarylamines, Ar_2NNa, react with dichlorine[14], potassium permanganate[15]-acetone, lead (IV) oxide[15] in benzene and silver (I,III) oxide to form the corresponding tetra-arylhydrazine Ar_2NNAr_2. Sodium-bis-(p-tolylsulphonyl)imide did not react with diiodine or dichlorine to form the analogous compound $(ArSO_2)_2NN(SO_2Ar)_2$.

4.6 REFERENCES

1. N.N. Dykhanov, Zhur. Obskei. Khim., 1959, 29, 3602
2. F. Runge, H. Engelbrecht, and G. Preusser, Chem. Ber., 1953, 86, 1571
3. R. Appel, M. Becke-Goehring, M. Eisenhauser and J. Hautenstein, Chem. Ber., 1962, 95, 625
4. H. Gilman, J.A. Beel, C.G. Brannen, M.W. Bullock, G.E. Dunn and L.S. Miller, Organic Reactions Vol. VI, 352; J. Amer. Chem. Soc., 1949, 71, 1499

5. B. Helferich and H. Flechsig, Ber., 1942, 75B, 532

6. H.H. Sisler and L.F. Audrieth, Inorganic Synthesis II, 179

7. E.G. Rozantsev and V.D. Scholle, Synthesis, 1971, 190

8. J. Chaplet-Letourneaux, H. Leamaire and A. Rassat, Bull. Chim. Soc. Fr., 1965, 3283

9. R. Briere, H. Lemaire and A. Rassat, Bull. Chim. Soc. Fr., 1965, 3273

10. A.S. Waggoner, T.J. Kingzett, S. Rottschaefer and O.H. Griffith, Chem. Phys. Lipids, 1969, 3, 245

11. J.F.W. Keana, S.B. Keana and D. Betham, J. Amer. Chem. Soc., 1967, 89, 3055

12. K. Tokumaru, H. Sakuragi and O. Simamura, Tetrahedron Lett., 1964, 3945

13. H. Steller and H. Hausmann, Chem. Ber., 1957, 90, 2728

14. F.D. Chattaway and H. Ingle, J. Chem. Soc., 1895, 67, 1090

15. H. Wieland et al, Ber., 1906, 39 , 1499; 1907, 40, 4271; 1912, 45, 2600; 1920, 53, 1320.

CHAPTER FIVE

THE REACTIONS OF ARYLSULPHONYLHYDROXYLAMINES WITH NITROSYL CHLORIDE, NITROGEN (II) OXIDE; AND SOME OTHER RELATED REACTIONS

5.1 SOME REACTIONS WITH NITROSYL CHLORIDE

(a) Reaction of nitrosyl chloride with sodium toluene-p-sulphinate

(i) A solution of nitrosyl chloride, (0.89 g, 13.7 mmol), in diethyl ether (100 ml) was added during 0.5 h. to a suspension of sodium toluene-p-sulphinate (2.42 g, 13.7 mmol); after 24 h. the mixture was filtered. The residue contained sodium nitrate, nitrite and chloride, and unreacted sodium toluene-p-sulphinate, which was characterised by reaction with aqueous nitrous acid to yield N,N-bis-(p-tolylsulphonyl)hydroxylamine (1.02 g, 3.0 mmol, 43.8%, mp 123°). Evaporation of the filtrate yielded toluene-p-sulphonyl chloride, (1.2 g, 6.3 mmol, 46.0%), which after recrystallisation from ether had mp and mixed mp 70°.

(ii) Sodium toluene-p-sulphinate (1.78 g, 0.01 mol) in diethyl ether (150 ml) was treated with an excess of gaseous nitrosyl chloride. Removal of the volatiles gave toluene-p-sulphonyl chloride (1.85 g, 0.097 mol, 97%, mp 70-71°).

(b) Reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with nitrosyl chloride

(i) A solution of nitrosyl chloride (0.159 g, 2.4 mmol) in ether (100 ml) was added to a suspension of N,N-bis-(p-tolylsulphonyl)hydroxylamine (0.82 g, 2.4 mmol) in ether (100 ml).

After stirring during 24 h. the mixture was evaporated, and extraction of the solid residue with ether (5 x 100 ml), left un changed N,N-bis-(p-tolylsulphonyl)hydroxylamine (0.31 g, 0.91 mmol, 38%, mp 124-125°). Evaporation of the ether extracts gave toluene-p-sulphonyl chloride, (0.39 g, 2.0 mmol, 42%, mp 70-71°).

(ii) With excess gaseous nitrosyl chloride N,N-bis-(p-tolylsulphonyl)hydroxylamine (1.02 g, 3.0 mmol) yielded toluene-p-sulphonyl chloride (1.14 g, 6.0 mmol, 100%).

(c) Reaction of nitrosyl chloride with other arylsulphonyl compounds

The products of the reactions of other arylsulphonyl compounds with an excess of gaseous nitrosyl chloride (in ether or benzene) are summarised in Table 5.1.

5.2 SOME REACTIONS WITH NITROGEN(II) OXIDE

Typically, the substrate was dissolved in diethyl ether or benzene and an excess of the gas bubbled in, the apparatus being flushed with dry dinitrogen meanwhile. Subsequent removal of excess nitrogen (II) oxide with dinitrogen, followed by evaporation of the volatiles, afforded the products which are summarised in Table 5.1.

Table 5.1

Products from reactions of arylsulphonyl species with excess nitrosyl chloride or nitrogen (II) oxide

Substrate	NOCl-Ether (Yield %)	NO-ether/benzene (Yield %)
p-$CH_3C_6H_4SO_2Na$	p-$CH_3C_6H_4SO_2Cl$ (97)	p-$CH_3C_6H_4SO_2Na$ (87) p-$CH_3C_6H_4SO_3H$ (6.3)
p-$CH_3C_6H_4SO_2H$	p-$CH_3C_6H_4SO_2Cl$ (93)	p-$CH_3C_6H_4SO_2H$ (70) $(p\text{-}CH_3C_6H_4SO_2)_2$ [a] (1.5)
p-$CH_3C_6H_4SO_3Na$	p-$CH_3C_6H_4SO_3Na$ (100)	-
p-$CH_3C_6H_4SO_2NH_2$	p-$CH_3C_6H_4SO_2Cl$ (94)	-
$(p\text{-}CH_3C_6H_4SO_2)_2NH$	$(p\text{-}CH_3C_6H_4SO_2)_2NH$ (100)	$(p\text{-}CH_3C_6H_4SO_2)_2NH$ (100)
$C_6H_5SO_2NHOH$	$C_6H_5SO_2Cl$ (85)	$C_6H_5SO_2NHOH$ (12) $C_6H_5SO_3H$ [b] (57) $(C_6H_5SO_2)_2$ (tr)
$(C_6H_5SO_2)_2NOH$	$C_6H_5SO_2Cl$ (92)	$C_6H_5SO_3H$ (93)
$(p\text{-}CH_3C_6H_4SO_2)_2NOH$	p-$CH_3C_6H_4SO_2Cl$ (100)	p-$CH_3C_6H_4SO_3H$ (99)
$(C_6H_5SO_2)_2NOSO_2C_6H_5$	$(C_6H_5SO_2)_2NOSO_2C_6H_5$ (100)	-
$(p\text{-}CH_3C_6H_4SO_2)_2NOSO_2C_6H_4CH_3\text{-}p$	$(p\text{-}CH_3C_6H_4SO_2)_2NOSO_2C_6H_4CH_3\text{-}p$ (100)	p-$CH_3C_6H_4SO_3H$ (83)

a Identified by mp 209°C (lit.[1]: 210-212°) and by mass spectrometry

b Identified by microanalysis of sodium salt

5.3 OXIDATION OF N-PHENYLSULPHONYLHYDROXYLAMINE

(a) Nitrosyl Chloride

Nitrosyl chloride (0.159 g, 2.4 mmol) and N-phenylsulphonylhydroxylamine (0.42 g, 2.4 mmol), were mixed in diethyl ether (100 ml). Oxides of nitrogen were evolved. After 24 h. the mixture was evaporated to yield benzenesulphonyl chloride (0.42 g, 2.4 mmol, 100%).

(b) Dichlorine[2]

A solution of dichlorine (0.142 g, 2.0 mmol) in carbon tetrachloride (50 ml) was added to a solution of N-phenylsulphonylhydroxylamine (0.84 g, 4.8 mmol) in the same solvent (50 ml). After 24 h. removal of the solvent yielded benzenesulphonyl chloride (0.42 g, 2.2 mmol, 46%), and unreacted starting material (0.30 g, 1.7 mmol, 35%). Use of excess chlorine with ether as solvent gave benzenesulphonyl chloride (90%). No chloroethyl ethers were detected. Found: C, 41.1; H, 2.8%. $C_6H_5ClO_2S$ requires: C, 40.8; H, 2.9%.

(c) Nitrogen (II) Oxide

N-Phenylsulphonylhydroxylamine (1.73 g, 0.01 mol) in benzene (100 ml) was treated with an excess of gaseous nitrogen (II) oxide. After evaporation of the volatiles, benzene extraction of the residue gave unchanged N-phenylsulphonylhydroxylamine (0.20 g, 1.2 mmol, 12%), leaving benzenesulphonic acid (0.90 g, 5.7 mmol, 57%) contaminated with a small amount of diphenyl disulphone, which was identified mass spectroscopically.

(d) Nitrous Acid[3]

To a stirred aqueous solution containing N-phenylsulphonylhydroxylamine (1.73 g, 0.01 mol) and sodium nitrite (0.69 g, 0.01 mol) was added concentrated hydrochloric acid (3 ml). Subsequent filtration and evaporation yielded benzenesulphonic acid (1.3 g, 8.2 mmol, 82%), which on conversion to the sodium salt gave: C, 39.7; H, 2.7%. $C_6H_5NaO_3S$ requires: C, 40.0; H, 2.8%.

(e) Nitric Acid[4]

N-Phenylsulphonylhydroxylamine (1.73 g, 0.01 mol), was stirred in glacial acetic acid (100 ml) with an excess of concentrated nitric acid. Oxides of nitrogen were evolved and after removal of the volatiles, benzenesulphonic acid (76%) was isolated. Identical microanalysis for the sodium salt as previously obtained.

(f) Acid Sodium Dichromate[5]

N-Phenylsulphonylhydroxylamine (1.73 g, 0.01 mol) was dissolved in 98% sulphuric acid (2 ml). Ice-cold aqueous sodium dichromate (0.57 g, 2.2 mmol in 25 ml) was added and the solution stirred during 24 h. The mixture was extracted with benzene (4 x 25 ml), and evaporation of the combined benzene extracts yielded benzenesulphonic acid, (1.22 g, 7.7 mmol, 77%), whose sodium salt analyses as for (d).

(g) Periodic Acid[6] and Sodium Hypochlorite[7]

Reactions as in (f) with excess (55%) aqueous periodic acid or sodium hypochlorite solution gave benzenesulphonic acid in

yields of 76% and 68% respectively. Sodium salts analyse as previously.

(h) Metal Oxides[4]

N-Phenylsulphonylhydroxylamine (1.73 g, 0.01 mol), was stirred at room temperature during 24 h. with an excess of lead (IV) oxide suspended in benzene. After centrifuging, evaporation of the solvent yielded N, N, O-tris-(phenylsulphonyl)-hydroxylamine, (0.77 g, 1.7 mmol, 51%, mp and mixed mp[4] 88-90°). Identical microanalysis with previous samples. With mercury (II) oxide[8], silver (I,III) oxide or manganese (IV) oxide under similar conditions, no oxidation of the N-phenylsulphonylhydroxylamine occurred (mp 124-126°).

5.4 SOME OTHER REACTIONS

(a) Reaction of benzenesulphonamide with peroxomonosulphuric acid[9]

Equimolar quantities (0.05 mol) of benzenesulphonamide and the freshly prepared peroxoacid were stirred together at 0° during 1 h. . The mixture was filtered and the product was washed and dried, affording unchanged benzenesulphonamide (90%).

(b) Reaction of toluene-p-sulphonyl chloride with silver nitrite

Toluene-p-sulphonyl chloride (2.0 g, 0.0105 mol) was stirred during 24 h. with an excess of silver nitrite suspended in benzene (150 ml). Filtration and removal of the solvent yielded an

oil (1.8 g, 9.4 mmol, 90%) which after 3 days at 0° crystallised; after recrystallisation from ether the mp and mixed mp with toluene-p-sulphonyl chloride were 68-69°.

(c) Reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with pyridine

A solution of pyridine (0.79 g, 0.01 mol) in benzene (50 ml) was slowly added to a solution of N,N-bis-(p-tolylsulphonyl)-hydroxylamine (3.4 g, 0.01 mol) in benzene (250 ml), and was stirred during 4 days. The residue (1.25 g, 0.005 mol, 50% w.r.t. pyridine) was filtered, recrystallised from water and dried. Found: C, 57.6; H, 5.4; N, 5.6%. $C_7H_7SO_3C_5H_5NH$ or $C_{12}H_{13}NO_3S$ requires: C, 57.4; H, 5.2; N 5.6%. Evaporation of the filtrate yielded a mixture of N,N-bis-(p-tolylsulphonyl)imide and pyridine-N-oxide. (mass spectrum). Extraction with ethanol afforded pure N,N-bis-(p-tolylsulphonyl)imide (2.0 g, 0.0062 mol, 62% w.r.t. hydroxylamine). Found: C, 51.6; H, 4.5; N, 4.2%. $C_{14}H_{15}NO_4S_2$ requires: C, 51.7; H, 4.7; N, 4.3%. The remaining residue was dissolved in water and hydrogen chloride gas passed through the solution, which upon evaporation of the solvent, and recrystallisation from iso-propyl alcohol yielded pyridine-N-oxide hydrochloride (0.464 g, 0.004 mol, 40% w.r.t. pyridine) mp 178-179°, lit. 179.5-181 [10].

(d) Other pyridine reactions

(i) Preparation of pyridinium toluene-p-sulphinate

Toluene-p-sulphinic acid (2 g, 0.013 mol) was dissolved in benzene (100 ml) and pyridine (1 g, 0.013 mol) was added

dropwise during 10 minutes. After stirring during 24 h. evaporation of the solvent yielded a white solid (2.51 g, 0.012 mol, 81%). Found: C, 60.9; H, 5.3; N, 5.6%. $C_{12}H_{13}NO_2S$ requires: C, 61.3; H, 5.6; N, 6.0%.

(ii) Reaction of pyridinium toluene-p-sulphinate with pyridine-N-oxide

A solution of pyridinium toluene-p-sulphinate (0.5 g, 0.002 mol) in benzene (50 ml) was slowly added to a solution of pyridine-N-oxide[11] in the same solvent. After stirring during 24 h. evaporation of the solvent yielded a mixture of unchanged starting materials.

(iii) Reaction of pyridinium toluene-p-sulphinate with nitrogen (II) oxide

A solution of pyridinium toluene-p-sulphinate (1.2 g, 0.005 mol) in benzene (100 ml) was stirred during 5 h. while nitrogen (II) oxide was bubbled in. Evaporation of the volatiles afforded a white solid (1.05 g, 0.0042 mol, 83%). Found: C, 56.6; H, 5.1; N, 5.8%. $C_{12}H_{13}NO_3S$ requires: C, 57.3; H, 5.2; N, 5.6%.

(iv) Reaction of toluene-p-sulphinic acid with nitrogen (IV) oxide

Toluene-p-sulphinic acid (0.6 g, 0.0038 mol) was placed in a flask and excess liquid nitrogen (IV) oxide was added. After evaporation of the gas benzene (100 ml) was added and the solid product filtered and weighed. A solution of the product was converted to a sodium salt by addition of an aqueous solution of sodium hydroxide. Found: C, 42.9; H, 3.8%. $C_7H_7NaO_3S$ requires: C, 43.3; H, 3.6%.

(e) The reaction of N,N-bis-(p-tolylsulphonyl)hydroxylamine with lead (IV) oxide in the presence of cyclopentadiene monomer

Cyclopentadiene (0.6 g, 0.01 mol) was slowly added to a solution of the hydroxylamine (1.7 g, 0.005 mol) in benzene (200 ml) and then stirred during 24 h. with excess lead (IV) oxide. The mixture was then centrifuged and evaporation of the solvent yielded crude N,N,O-tris-(p-tolylsulphonyl)hydroxylamine. The product, N,N,O-tris-(p-tolylsulphonyl)hydroxylamine, was recrystallised from toluene (0.8 g, 0.0016 mol, 48.5%, mp 182-183°) and had an identical microanalysis with previous samples. Cyclopentadiene was recovered unchanged when stirred during 24 h. in the presence of excess lead (IV) oxide.

5.5 RESULTS AND DISCUSSION

Sodium toluene-p-sulphinate is converted almost quantitatively to toluene-p-sulphonyl chloride by excess nitrosyl chloride. Equation (1). A plausible intermediate in this reaction

$$p\text{-}CH_3C_6H_4SO_2Na + 2NOCl \longrightarrow NaCl + p\text{-}CH_3C_6H_4SO_2Cl + 2NO \quad (1)$$

is nitrosyl toluene-p-sulphinate, but with a 1:1 molar ratio of the reactants the toluene-p-sulphonyl chloride was again formed (46%) leaving unchanged sodium toluene-p-sulphinate which was characterised by conversion to N,N-bis-(p-tolylsulphonyl)-hydroxylamine[4]. The reaction of the sodium salt with the sulphonyl chloride to yield di-p-tolyldisulphone[12] is slow under these conditions. If nitrosyl toluene-p-sulphinate is an

intermediate, it reacts further with nitrosyl chloride at a rate greater than that of its formation. That no N,N-bis-(p-tolylsulphonyl)hydroxylamine is formed confirms that the corresponding reaction[4] with sodium nitrite and hydrochloric acid mixtures involves nitrous acid rather than nitrosyl chloride. Toluene-p-sulphinic acid likewise gave the toluene-p-sulphonyl chloride with excess nitrosyl chloride, but sodium toluene-p-sulphonate was unaffected.

Toluene-p-sulphonamide is converted almost quantitatively to the sulphonyl chloride[13] by an excess of nitrosyl chloride and to the sulphonic acid by nitrosonium tetrafluoroborate[14] although unaffected by aqueous nitrous acid; but N,N-bis-(p-tolylsulphonyl)-imide was unaffected by nitrosyl chloride, no N-nitroso compound was formed. The low reactivity of sulphonamides in comparison with the corresponding carboxylic acid amides[4] may be a reflection of their low basicity. H_o values for half-protonation in sulphuric acid/water mixtures are for benzamide - 2.16[15] and for benzenesulphonamide - 6.64[16]. However, this difference of ca 4.5 units represents only an upper limit to the basicity difference at nitrogen, since sulphonamides are protonated at nitrogen[17,18], while carboxamides are protonated at oxygen[19] which is thus more basic than the carboxamide nitrogen; furthermore, differences in basicity towards protons may not accurately reflect differences in nucleophilicity towards nitrosating and diazotising agents.

N-Phenylsulphonylhydroxylamine reacts with nitrosyl chloride in a reaction of 1:1 stoichiometry to yield benzenesulphonyl chloride quantitatively; this contrasts with the reaction of N-cyclohexylhydroxylamine with nitrosyl chloride in which N-nitrosation occurs[20] yielding hydrogen chloride and N-nitroso-N-cyclohexylhydroxylamine.

N,N-Bis-(arylsulphonyl)hydroxylamines react with nitrosyl chloride to yield the arenesulphonyl chlorides, but N,N,O-tris-(arylsulphonyl)hydroxylamines did not react: no p-nitrosation[21,22] occurs during the reactions of the phenylsulphonylhydroxylamines. In none of its reactions did nitrosyl chloride act as an oxidising agent to yield bis- or tris-(arylsulphonyl)hydroxylamines from simpler substrates (cf HNO_2 and HNO_3[4]). The nitrogen-containing species attacked by nitrosyl chloride contain either an >NOH or an $-NH_2$ fragment suggesting reaction via $>N-O^{\bullet}$ in the former case and via diazotisation in the latter. The products of the reactions of nitrosyl chloride with a number of related sulphonyl amides and hydroxylamines are summarised in Table 5.1.

Since nitrosyl chloride is slightly dissociated into dichlorine and nitrogen (II) oxide, and since nitrogen (II) oxide may be a primary product in some of its reactions with arylsulphonyl compounds, the corresponding reactions of nitrogen (II) oxide and dichlorine were investigated. The reactions with dichlorine are considered in Chapter 6. The products of the nitrogen (II) oxide reactions are summarised in Table 5.1. The principle products from the arylsulphonylhydroxylamines was the corresponding arenesulphonic acid; toluene-p-sulphinic acid and its sodium salt

were largely unchanged with no conversion to hydroxylamine derivatives as claimed by Konigs[23], but a small quantity of the disulphone $(\underline{p}\text{-}CH_3C_6H_4SO_2)_2$ was isolated from the reaction of the sulphinic acid; the imide $(\underline{p}\text{-}CH_3C_6H_4SO_2)_2NH$ was unaffected by both nitrogen (II) oxide and nitrogen (IV) oxide as by nitrosyl chloride. A number of reagents[2-8] convert N-aryl hydroxylamines, RNHOH, to C-nitrosoarenes RNO, but none of these reagents converts N-phenylsulphonylhydroxylamine RSO_2NHOH ($R=C_6H_5$) to nitrosyl benzenesulphinate RSO_2NO. The reaction of N-phenylsulphonylhydroxylamine with dichlorine in carbon tetrachloride or diethyl ether afforded benzenesulphonyl chloride, while the reaction in either benzene or cyclohexane as solvent fascilitates free-radical chlorination of the hydrocarbon solvent (See Chapter 6). With nitrosyl chloride the sole product is benzenesulphonyl chloride and with nitrogen (II) oxide the products are benzenesulphonic acid and a trace of diphenyldisulphone. The aqueous oxidants, nitrous acid[3], nitric acid, acid sodium dichromate[5], periodic acid[6] and sodium hypochlorite[7] all yield benzenesulphonic acid, although hydrolysis of the phenylsulphonylhydroxylamine alone is slow. Lead (IV) oxide yields N,N,O-tris-(phenylsulphonyl)hydroxylamine, but silver (I,III) oxide, manganese (IV) oxide and mercury (II) oxide do not react. These results contrast markedly with those for the oxidation of N-arylhydroxylamines[2-8] and of N,N-bis-(p-tolylsulphonyl)hydroxylamines[4], which is converted to

N, N, O-tris-(p-tolylsulphonyl)hydroxylamine by silver (I,III) oxide, manganese (IV) oxide, (although not by mercury (II)oxide), and by nitric acid, but which is inert to most other aqueous oxidants.

Peroxomonosulphuric acid[9] did not oxidise toluene-p-sulphonamide to the S-nitroso compound, nor did toluene-p-sulphonyl chloride react with silver nitrite.

The intermediacy of $RSO_2^{\bullet}$ in the route from $(RSO_2)_2NOH$ to $(RSO_2)_2NOSO_2R$, as depicted earlier is supported by the conversion of $(RSO_2)_2NOH$, in its reaction with nitrosyl chloride, to RSO_2Cl rather than $(RSO_2)_2NOSO_2R$. However, no evidence could be found for the intermediacy of RSO_2NO in this route when N, N-bis-(p-tolylsulphonyl)hydroxylamine was oxidised with lead (IV) oxide in the presence of cyclopentadiene. No cyclo adduct[24] was formed; only N, N, O-tris-(p-tolylsulphonyl)-hydroxylamine.

The arylsulphonyl group has been used as a protecting group for C-nitroso compounds[25] producing (N-aryl-N-arylsulphonyl)-hydroxylamines (1). The reaction is carried out in aqueous media

$$Ar^1NO + Ar^2SO_2H \longrightarrow Ar^1N(OH)SO_2Ar^2 \qquad (1)$$

at pH 0-3 and is quantitative at ordinary temperatures. Deprotonation occurs by hydrolysis at ambient temperatures at pH >8 (2).

$$Ar^1N(OH)SO_2Ar^2 + OH^- \longrightarrow Ar^1NO + ArSO_2^- + H_2O \qquad (2)$$

Will a base therefore hydrolyse an N, N-bis-(arylsulphonyl)-hydroxylamine to produce a nitrosylarenesulphinate, $ArSO_2NO$, (3)?

$$Ar^1SO_2\underset{\underset{OH}{|}}{N}SO_2Ar^2 + OH^- \longrightarrow Ar^1SO_2NO + Ar^2SO_2^- + H_2O \qquad (3)$$

In the hope of effecting such a reaction pyridine was added to N,N-bis-(p-tolylsulphonyl)hydroxylamine, and afforded N,N-bis-(p-tolylsulphonyl)imide, pyridinium toluene-p-sulphonate and pyridinium-N-oxide. If the reaction follows a similar pathway to that of (2) the probable products are shown in (4) ie the nitrosylarenesulphinate and pyridinium toluene-p-sulphonate.

$$(ArSO_2)_2NOH + C_5H_5N \xrightarrow[x\%]{A} (ArSO_2)_2NO^- + C_5H_5\overset{+}{N}H$$

$$\downarrow$$

$$ArSO_2NO + ArSO_2^- + C_5H_5\overset{+}{N}H \qquad (4)$$

$$(x\%) \qquad (x\%) \qquad (x\%)$$

Alternatively the base could extract the hydroxyl group and form an N,N-bis-(arylsulphonyl)imide anion, and protonated pyridine-N-oxide. Proton exchange then yields the bis-imide and pyridine-N-oxide. Both routes probably occur simultaneously and the

$$(ArSO_2)_2NOH + C_5H_5N \xrightarrow[y\%]{B} (ArSO_2)_2N^- + C_5H_5\overset{+}{N}HO \longrightarrow$$

$$\longrightarrow (ArSO_2)_2\overset{\bullet}{N}H + C_5H_5NO \qquad (5)$$

$$(y\%) \qquad (y\%)$$

pyridine-N-oxide formed (5) could react with the nitrosylarene-sulphinate to produce nitrogen (IV) oxide and a pyridinium arylsulphonate molecule (6). The nitrogen (IV) oxide can then

$$ArSO_2NO + C_5H_5NO + \tfrac{1}{2}H_2O \longrightarrow C_5H_5\overset{+}{N}H\bar{S}O_3Ar + \tfrac{1}{2}NO + \tfrac{1}{2}NO_2 \qquad (6)$$

$$(x\%) \qquad (x\%) \qquad (x\%) \qquad (x/2\%)$$

$$\downarrow O_2$$

$$\tfrac{1}{2}NO_2$$

$$(x/2\%)\ NO_2 \quad \text{Total} = x\%$$

oxidise the pyridinium arylsulphinate (4) to pyridinium arylsulphonate (7). This oxidation does occur. If the scheme is

$$\underset{(x\%)}{ArSO_2^-} + \underset{(x\%)}{NO_2} \longrightarrow \underset{(x\%)}{NO} + \underset{(x\%)}{ArSO_3^-} \qquad (7)$$

considered to follow the routes A and B with x and y% respectively, then there are 2x% of $ArSO_3^-C_5H_5\overset{+}{N}H$; y% of the bis-imide and (y-x)% of pyridine-N-oxide formed. Hence x = 12.5 and y = 62 at the minimum. The observed figures are; pyridinium-toluene-p-sulphonate (25%); N,N-bis-(p-tolylsulphonyl)imide (62%) and pyridine-N-oxide (40%). The predicted yield for pyridine-N-oxide is 49.5%.

5.6 REFERENCES

1. T.P. Hildich, J. Chem. Soc., 1908, 93, 1524
2. O. Wichterle, V. Gregor, A. Dubansky and V. Seidl, Coll. Czech. Chem. Comm., 1959, 24, 1158
3. C.S. Marvel and O. Kann, J. Amer. Chem. Soc., 1919, 41, 276
4. J.D. Birchall and C. Glidewell, J. Chem. Soc. (Dalton), 1977, 10
5. G.H. Coleman, C.M. McCloskey and F.A. Stewart, Organic Syntheses, Coll. Vol. 3, 1955, 668
6. T. Emery and J.B. Neilands, J. Org. Chem., 1962, 27, 1075
7. E. Bamberger, Ber., 1894, 27, 1555
8. O. Piloty and I. Ruff, ibid., 1897, 30, 1656

9. C.K. Ingold, J. Chem. Soc., 1924, 125, 87

10. H.S. Mosher, L. Turner and A. Carlsmith, Organic Syntheses, 1953, 33, 79

11. J. Meisenheimer, Ber., 1926, 59, 1848

12. E.P. Kohler and M.B. MacDonald, Amer. Chem. J., 1899, 22, 219

13. W.A. Waters, J. Chem. Soc., 1937, 2007

14. G.A. Olah and J.A. Olah, J. Org. Chem., 1965, 30, 2386

15. J.T. Edwards, H.S. Chang, K. Yates and R.A. Stewart, Canad. J. Chem., 1960, 38, 1518

16. P.O. Virtanen and M. Maikkula, Tetrahedron Lett., 1968, 4855

17. R.G. Laughlin, J. Amer. Chem. Soc., 1967, 89, 4268

18. F.M. Menger and L. Mandell, ibid., 1967, 89, 4424

19. R.J. Gillespie and T. Birchall, Canad. J. Chem., 1963, 41, 148

20. E. Müller and H. Metzger, Ber., 1956, 89, 396

21. O. Fischer and E. Hepp, ibid., 1886, 19, 2993

22. P.W. Neber and H. Rauscher, Annalen, 1942, 550, 182

23. W. Konigs, Ber., 1878, 11, 616

24. G. Kreze and W. Kort, Ber., 1961, 94, 2624

25. A. Darchen and C. Moinet, Chem. Comm., 1976, 20, 820

CHAPTER SIX

THE REACTIONS OF ARYLSULPHONYLHYDROXYLAMINES, ARYLSULPHONAMIDES AND CARBOXYLIC ACID AMIDES WITH HALOGENS

6.1 REACTION OF ARYLSULPHONYLHYDROXYLAMINES WITH HALOGENS

(a) Reactions of N,N-bis-(arylsulphonyl)hydroxylamines with halogens

(i) With dichlorine

N,N-bis-(p-tolylsulphonyl)hydroxylamine, (1.70 g, 0.005 mol), was dissolved in benzene (100 ml) and an excess of dichlorine gas was bubbled in. Subsequent removal of the volatiles yielded a pale yellow solid, (9.36 g, mp 90-95°C), which was washed with petrol (60-80), mp 131-140°, and whose mass spectrum is summarised in Table 6.1(a). The accurate mass of the ion at m/e 288 was 287.8584 a.u.; $^{12}C_6{}^{1}H_6{}^{35}Cl_6$ requires 287.8601 a.u. . Microanalysis found: C, 26.7; H, 2.4%. $C_6H_6Cl_6$ requires: C, 25.0; H, 1.4%.

A similar reaction in cyclohexane gave a solid (mp 132-138°C) whose mass spectrum is summarised in Table 6.1(a).

From the analogous reaction in carbon tetrachloride the starting material was recovered unchanged, mp 123-124°. Identical results were obtained for reactions conducted in the presence or absence of light.

(ii) With dibromine

Dibromine, (48.0 g, 0.3 mol), was added during 20 minutes to a solution of the N,N-bis-(p-tolylsulphonyl)hydroxylamine, (0.34 g, 0.001 mol), in benzene (7.8 g, 0.1 mol). After removal of the volatiles, the product (1.50 g, mp 95-105°) had the mass spectrum recorded in Table 6.1 (b).

Dibromine, (192 g, 1.2 mol) was added slowly to a solution of N,N-bis-(p-tolylsulphonyl)hydroxylamine, (0.34 g, 0.001 mol), in cyclohexane (8.4 g, 0.1 mol) and the mixture was stirred overnight. Removal of the volatiles afforded a product (1.10 g, mp 91-102°) whose mass spectrum is summarised in Table 6.1 (b).

(iii) With diiodine

Reaction with diiodine in benzene gave only unchanged starting material, (68%, mp 125-126°).

(b) Reaction of N,N-O-tris-(p-tolylsulphonyl)hydroxylamine with dichlorine

N,N,O-tris-(p-tolylsulphonyl)hydroxylamine, (1.20 g, 0.0024 mol), was dissolved in benzene (100 ml) and an excess of dichlorine gas was bubbled in. Evaporation of the volatiles gave a product (19.8 g, mp 133-139°) whose mass spectrum was identical to that of the product from the dichlorine/benzene/N,N-bis-(p-tolylsulphonyl)-hydroxylamine reaction.

From analogous reactions in carbon tetrachloride or diethyl ether, the starting material was recovered unchanged.

Table 6.1

Mass Spectra of products from $(p\text{-}CH_3C_6H_4SO_2)_2NOH$/Halogen/Hydrocarbon-solvent reactions

(a) Dichlorine

Solvent; C_6H_6			Solvent; C_6H_{12}		
m/e[a]	RI(%)[a]	Assignment	m/e[a]	RI(%)[a]	Assignment
330	v.w.	$C_6H_6{}^{35}Cl_5C_6H_5^+$	252	0.3	$C_6H_5{}^{35}Cl_5^+$
288	0.4	$C_6H_6{}^{35}Cl_6^+$	217	3.6	$C_6H_5{}^{35}Cl_4^+$
251	6.7	$C_6H_4{}^{35}Cl_5^+$	181	4.6	$C_6H_4{}^{35}Cl_3^+$
216	55	$C_6H_4{}^{35}Cl_4^+$	152	2.0	$C_6H_{10}{}^{35}Cl_2^+$
181	100	$C_6H_4{}^{35}Cl_3^+$	117	5.2	$C_6H_{10}{}^{35}Cl^+$
146	31	$C_6H_4{}^{35}Cl_2^+$	116	11	$C_6H_9{}^{35}Cl^+$
111	58	$C_6H_4{}^{35}Cl^+$	81	100	$C_6H_9^+$
77	28	$C_6H_5^+$	80	68	$C_6H_8^+$

(b) Dibromine

Solvent; C_6H_6			Solvent; C_6H_{12}		
m/e[b]	RI(%)[b]	Assignment	m/e[b]	RI(%)[b]	Assignment
471	1.4	$C_6H_4{}^{79}Br_5^+$	471	0.8	$C_6H_4{}^{79}Br_5^+$
313	12	$C_6H_4{}^{79}Br_3^+$	313	6.2	$C_6H_4{}^{79}Br_3^+$
235	24	$C_6H_5{}^{79}Br_2^+$	235	18	$C_6H_4{}^{79}Br_2^+$
234	100	$C_6H_4{}^{79}Br_2^+$	234	21	$C_7H_7SO_2{}^{79}Br^+$
156	25	$C_6H_5{}^{79}Br^+$	155	27	$C_6H_4{}^{79}Br^+$
155	39	$C_6H_4{}^{79}Br^+$	155	49	$C_7H_7SO_2^+$
91	28	$C_7H_7^+$	139	6.2	$C_7H_7SO^+$
78	23	$C_6H_6^+$	91	100	C_7H_7
77	24	$C_6H_5^+$			

a m/e values quoted only for ^{35}Cl: RI values include both isotopes

b m/e values quoted only for ^{79}Br: RI values include both isotopes

(c) Reaction of N-(phenylsulphonyl)hydroxylamine with dichlorine

A solution of dichlorine, (0.002 mol), in carbon tetrachloride (50 ml) was added to a solution of N-(phenylsulphonyl)hydroxylamine (0.84 g, 0.0048 mol) in the same solvent (50 ml). After 24 h. removal of the solvent yielded benzenesulphonyl chloride, (0.42 g, 0.002 mol, 46%). Found: C, 41.1; H, 2.8%. $C_6H_5ClO_2S$ requires: C, 40.8; H, 2.9%; and unreacted starting material, (0.30 g, 0.0017 mol, 35%, mp 123-124°). Use of excess dichlorine with diethyl ether as solvent gave benzenesulphonyl chloride. (Identical microanalysis with previous sample.) Reaction of the hydroxylamine with dichlorine in either benzene or cyclohexane gave small yields of the same product obtained from the dichlorine/benzene/N,N-bis-(p-tolylsulphonyl)-hydroxylamine reaction.

6.2 REACTIONS OF TOLUENE-p-SULPHONAMIDE WITH DICHLORINE

(a) Reaction of toluene-p-sulphonamide with dichlorine

Toluene-p-sulphonamide (0.01 mol) was dissolved or suspended in the substrate as solvent (1.0 mol) at 0° and dichlorine gas (1.0 mol) was slowly introduced in the absence of light. After removal of the volatiles the products were identified by melting points and mass spectrometry. With either benzene or cyclohexane as the substrate, the product had an identical mass spectrum to that of the product from the dichlorine/benzene/N,N-bis-(p-tolylsulphonyl)hydroxylamine reaction.

With carbon tetrachloride, unchanged sulphonamide was recovered (mp 134-137°; lit. 138°). Identical results were obtained in the presence of light.

(b) Reaction of toluene-p-sulphonamide with dichlorine in the presence of halobenzenes

The halobenzene (0.02 mol) was added to a suspension of toluene-p-sulphonamide (0.01 mol) in carbon tetrachloride (150 ml) at 0° and dichlorine gas (1.0 mol) was slowly introduced in the absence of light. For bromobenzene (1 mol) no solvent was used. After stirring during 24 h. any solid product was filtered and dried. Evaporation of the solvent was followed by distillation of the remaining liquid.

For fluorobenzene, chlorobenzene and bromobenzene, the halobenzene was recovered quantitatively and the sulphonamide in yields of 91.2, 94.0 and 97% respectively. For iodobenzene the sulphonamide was recovered (90%) along with $C_6H_5ICl_2$ (5.3 g, 96%), which was identified by mass spectrometry from the ion $C_6H_5I^{35}Cl_2^+$ at m/e 274. No nuclear halogenation was observed for any of these reactions.

(c) Reaction of toluene-p-sulphonamide with dichlorine in the presence of diphenylsilane

A solution of diphenylsilane (3.68 g, 0.02 mol) in carbon tetrachloride was added to a suspension of toluene-p-sulphonamide in the same solvent at 0°, and dichlorine gas (1 mol) was introduced in the absence of light. Filtration of any product after stirring during

24 h. was followed by evaporation of the solvent; which yielded dichlorodiphenylsilane (3.65 g, 72.5%). Chlorination of the silane was confirmed by comparison of the ^{1}H n.m.r. spectrum of diphenylsilane, (δ 4.85 and 7.2 p.p.m.) and the product, (no absorption at δ 4.85 p.p.m.), and also by mass spectrometry. Similar results were obtained in the absence of the sulphonamide.

(d) Reaction of diethyl ether with toluene-p-sulphonamide and dichlorine

Toluene-p-sulphonamide (1.7 g, 0.01 mol), in diethyl ether (150 ml) yielded ethyl 1,2-dichloroethyl ether (70%). [^{1}H n.m.r.; δ 1.28 (t, 3H); 3.50 (q, 2H); 3.75 (d, 2H) and 5.56 (t, 1H) p.p.m.] Identification by comparison (^{1}H n.m.r., mass spectrum and g.l.c.) with an authentic sample.[1]

6.3 REACTIONS OF CARBOXYLIC ACID AMIDES WITH DICHLORINE

(a) The carboxylic acid amide initiator (0.01 mol) was dissolved or suspended in the substrate as solvent (1.0 mol) at 0°, and dichlorine gas (1.0 mol) was introduced in the absence of light. After evaporation of the solvent the products were identified by mass spectrometry, m.p. and mixed m.p. . All the carboxylic acid amides, with benzene as the substrate, yielded a product whose mass spectrum was identical to that of the product from the dichlorine/benzene/N,N-bis-(p-tolylsulphonyl)hydroxylamine reaction. (e.g. acetamide; Yield = 17%, mp = 132-136°). When the substrate was cyclohexane,

only unchanged carboxylic acid amides were isolated; benzamide however did yield a small amount of the polychlorinated product. The initiator was recovered unchanged for each reaction when carbon tetrachloride was the substrate solvent. The carboxylic acid amides were identified by m.p. and mixed m.p., except for N,N-dimethylacetamide [^{1}H n.m.r., δ 1.95 (s, 3H); 2.81 (s, 3H) and 2.98 (s, 3H) p.p.m.]. Thioacetamide did not react with any substrate and was recovered unchanged. Yields and melting points are recorded in Table 6.2.

(b) Triethylamine in benzene reacted with dichlorine to yield a product whose mass spectrum was identical to that previously observed for $C_6H_6{}^{35}Cl_6$. Triethylamine hydrochloride was recovered when the substrates were either cyclohexane or carbon tetrachloride; and after recrystallisation from ethanol gave; Found: C, 52.4; H, 11.7; N, 10.0%. $C_6H_{16}NCl$ requires: C, 52.4; H, 11.7; N, 10.2%. Tetramethylammonium chloride was recovered unchanged for all reactions. Identical results were obtained in the absence of light.

6.4 SOME RELATED REACTIONS

(a) Reaction of sodium toluene-p-sulphinate with dichlorine

Sodium toluene-p-sulphinate (0.87 g, 0.0049 mol) was stirred during 24 h. with dichlorine (0.00243 mol) in carbon tetrachloride (50 ml). After filtration, the residue was dried and treated with aqueous nitrous acid; N,N-bis-(p-tolylsulphonyl)hydroxylamine

Table 6.2

Results of Chlorination Reactions

Initiator	Product from benzene Yield (%) m.p. (°)	Product from cyclohexane Yield (%) m.p. (°)	Product from carbon tetrachloride Yield (%) m.p. (°)
p-$CH_3C_6H_4SO_2NH_2$	$C_6H_6Cl_6$ [a] (37) 132-141	$C_6H_6Cl_6$ (2.2) 132-139	S [b] (88) 134-137 [c]
$(p\text{-}CH_3C_6H_4SO_2)_2NH$ [d]	$C_6H_6Cl_6$ (33) 132-140	$C_6H_6Cl_6$ (4.2) 131-137	S (81) 168-169
$C_6H_5SO_2NHOH$	$C_6H_6Cl_6$ (4.3) 125-135	$C_6H_6Cl_6$ (1.5) 132-136	S (35) 124-126 $C_6H_5SO_2Cl$ [e] (46)
$(p\text{-}CH_3C_6H_4SO_2)_2NOH$	$C_6H_6Cl_6$ (35) 131-140	$C_6H_6Cl_6$ (5.0) 132-138	S (97) 123-124
$(p\text{-}CH_3C_6H_4SO_2)_2NOSO_2C_6H_4CH_3\text{-}p$	$C_6H_6Cl_6$ (21) 133-139	S (50) 183-184	S (98) 183-184

a $C_6H_6Cl_6$ forms always a mixture of stereoisomers. b S denotes nitrogen compound recovered unchanged. c lit. mp 138°C. d also see Chapter 4. e Microanalysis identical to that previously observed.

Table 6.2 (cont.)

Initiator	Product from benzene Yield (%) m.p. (°)	Product from cyclohexane Yield (%) m.p. (°)	Product from carbon tetrachloride Yield (%) m.p. (°)
$C_6H_5CONH_2$	$C_6H_6Cl_6$ (10) 125-135	S (98) 126-127 $C_6H_6Cl_6$ (trace) 132-137	S (88) 122-128 [f]
CH_3CONH_2	$C_6H_6Cl_6$ (17) 132-136	S (92) 74 - 76	S (92) 75 - 76 [g]
$CH_3CON(CH_3)_2$	$C_6H_6Cl_6$ (4.3) 130-137	S (71)	S (86) [h]
CH_3CSNH_2	S (80) 113-115	S (73) 114-115	S (80) 112-114 [i]
$(C_2H_5)_3N$	$C_6H_6Cl_6$ (3.5) 127-135	$(C_2H_5)_3NHCl$ (93) e	$(C_2H_5)_3NHCl$ (88) e
$(CH_3)_4NCl$	S (86)	S (92)	S (94)

f lit. mp = 126-130°C. g lit. mp = 76-81°C. h See ^1H n.m.r. in 6.3(a). i lit. mp = 115°C.

(0.35 g, 0.00103 mol, 42%, mp identical to previous samples), was isolated. The original filtrate was evaporated to yield toluene-p-sulphonyl chloride (0.45 g, 0.00236 mol, 48%), which on recrystallisation from ether gave a mp = 69-71°C. With excess dichlorine gas an almost quantitative yield of toluene-p-sulphonyl chloride was obtained. (m.p. and mixed m.p. = 70-71°).

(b) Reaction of di-p-tolylsulphone with dichlorine

Di-p-tolylsulphone was prepared by the oxidation[2] of the corresponding sulphinic acid with potassium permanganate in glacial acetic acid. (mp = 208-210 d, lit.[3] 210-212 d). When di-p-tolylsulphone (1.50 g, 0.0048 mol) in benzene was treated with an excess of dichlorine gas, toluene-p-sulphonyl chloride (1.8 g, 0.00945 mol, 97%) was obtained after evaporation of the solvent. (m.p. and mixed m.p. = 70-71°).

(c) Reaction of Triphenylamine with dichlorine

Triphenylamine (0.65 g, 0.001 mol) was added to benzene (100 ml) at 0°, and dichlorine gas (1.0 mol) was introduced. The solution immediately went blue-green in colour on addition of triphenylamine. After stirring during one hour evaporation of the solvent afforded a product whose mass spectrum contained ion clusters up to m/e 589 ($C_{12}H_{11}{}^{35}Cl_{12}N^{+}$). The mass of the ion at m/e 451 was 450.8716 a.u.; $^{12}C_{12}{}^{1}H_{11}{}^{14}N{}^{37}Cl{}^{35}Cl_{7}$ requires 450.8370 a.u.; and at m/e 309 was 308.9997 a.u.; $^{12}C_{12}{}^{1}H_{11}{}^{14}N{}^{35}Cl_{4}$ requires 308.9646 a.u.

A series of ion clusters were also present, which were identical to those observed for the product of the dichlorine/benzene/N,N-bis-(p-tolylsulphonyl)hydroxylamine reaction. An identical reaction in carbon tetrachloride produced no ion series corresponding to $C_6H_6Cl_6^+$.

(d) Reaction of p-chlorobenzoic acid with dibromine and N,N-bis-(p-tolylsulphonyl)hydroxylamine in nitrobenzene

One drop of dibromine was added to a solution of p-chlorobenzoic acid (7.83 g, 0.05 mol) in nitrobenzene (6.16 g, 0.05 mol) in the presence of N,N-bis-(p-tolylsulphonyl)hydroxylamine (0.34 g, 0.001 mol). After stirring during 24 h. p-chlorobenzoic acid was recovered (6.2 g) unchanged.

6.5 IDENTIFICATION OF THE STEREOISOMERS OF HEXACHLOROCYCLOHEXANE

H.p.l.c. revealed eight components in the product from the dichlorine/benzene/N,N-bis-(p-tolylsulphonyl)hydroxylamine reaction. The chromatographic behaviour[4] of the compound was first determined. The h.p.l.c. solvent was 1% dioxan in hexane (both redistilled) at 2 ml/minute and the best ultraviolet wavelength for detecting the components was determined to be 240 nm. (See Fig. 6.1). Fractional crystallisation[5] of the crude material afforded authentic samples of the α,β,γ and δ isomers of $C_6H_6Cl_6$, enabling four components to be identified. (See Fig. 6.2 for h.p.l.c. trace). No toluene-p-sulphonyl chloride was present, though one peak may be either N,N-bis-(p-tolylsulphonyl)hydroxylamine or N,N,O-tris-(p-tolylsulphonyl)hydroxylamine.

Fig. 6.1 Ultra-violet spectra of hexane, dioxan and $C_6H_6Cl_6$ for h.p.l.c. detection wavelength

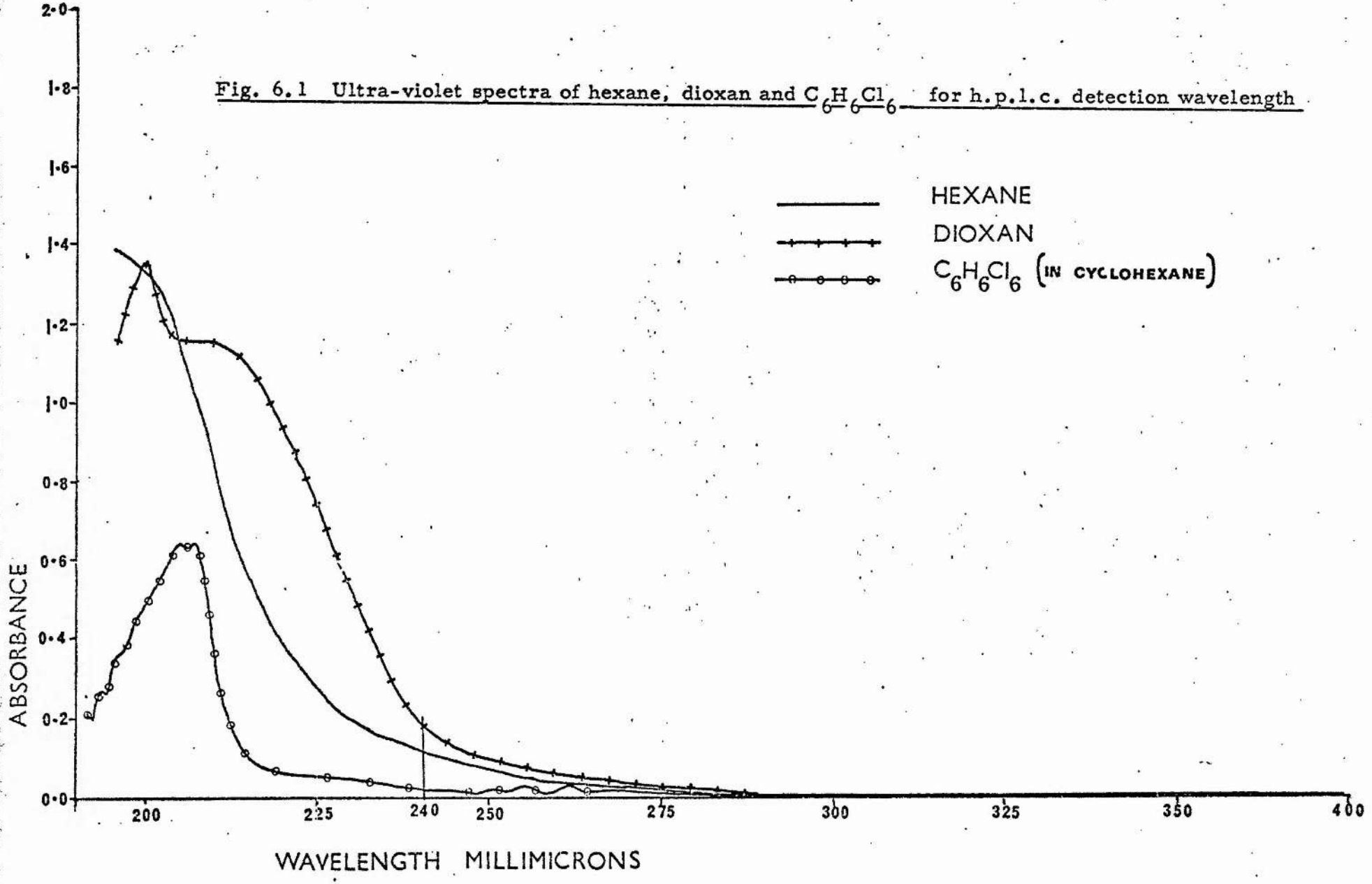
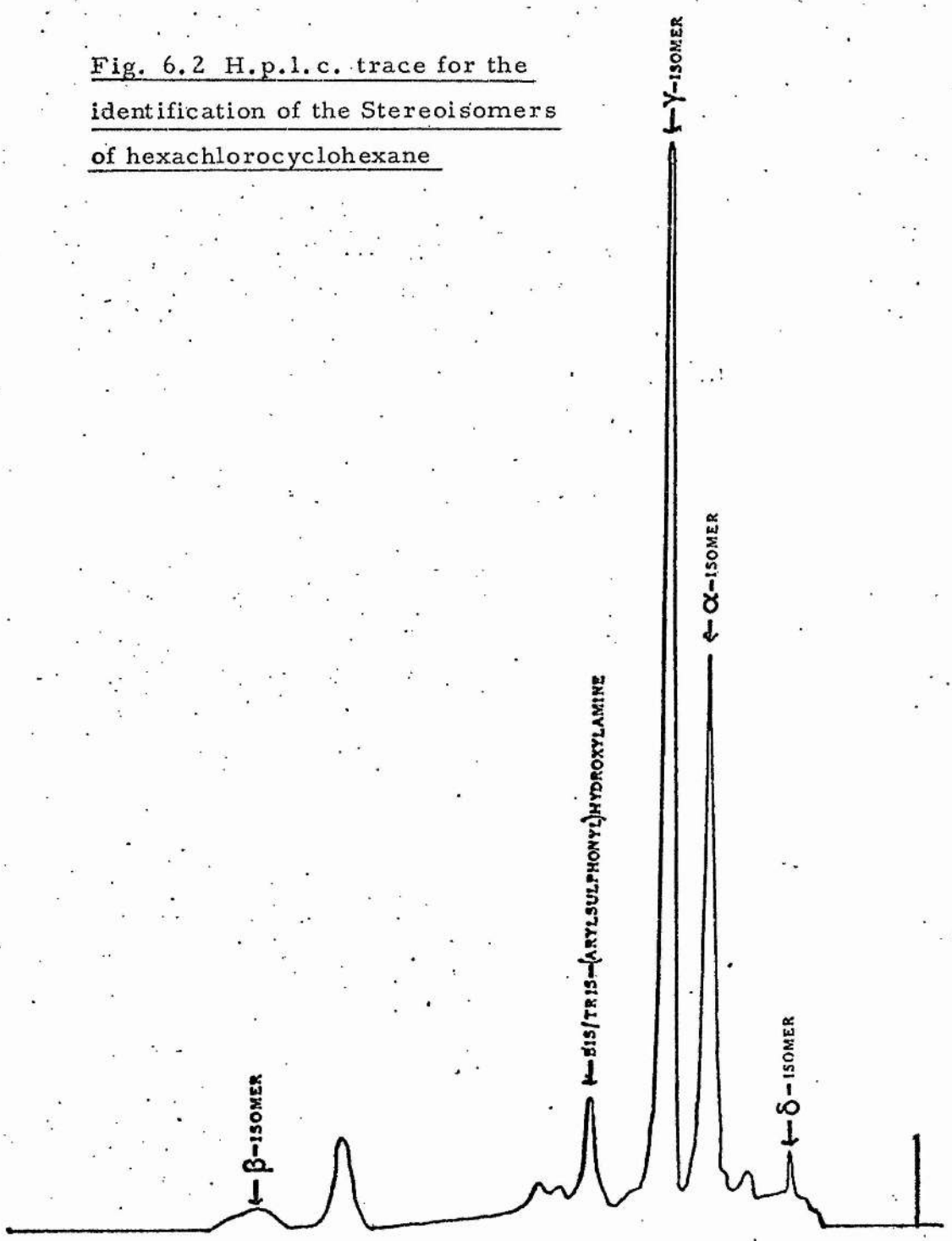


Fig. 6.2 H.p.l.c. trace for the identification of the Stereoisomers of hexachlorocyclohexane



6.6 RESULTS AND DISCUSSION

Dichlorine reacted with sodium toluene-p-sulphinate to yield toluene-p-sulphonyl chloride, when in excess (1) and a mixture of toluene-p-sulphonyl chloride and unchanged sodium salt, but no disulphone when in a 1:2 molar.

$$p\text{-}CH_3C_6H_4SO_2Na + Cl_2 \longrightarrow p\text{-}CH_3C_6H_4SO_2Cl + NaCl \qquad (1)$$

Phenylsulphonylhydroxylamine gave only benzenesulphonyl chloride when treated with an excess of dichlorine in diethyl ether solution; use of a 2.4 fold excess of the hydroxylamine, in carbon tetrachloride yielded no nitrosyl benzenesulphinate, but only benzenesulphonyl chloride and unchanged starting material.

In contrast, N,N-bis-(p-tolylsulphonyl)hydroxylamine did not react with dichlorine in carbon tetrachloride solution, but in benzene or cyclohexane a radical reaction was initiated causing facile halogenation of the solvent. In the mass spectrum of the solid product isolated from benzene solution ions up to $C_6H_6Cl_6^+$ (identified by mass measurement on $C_6H_6{}^{35}Cl_6$) and $C_{12}H_{11}Cl_5^+$ were observed (See Table 6.1). $C_{12}H_{11}Cl_5$ ie. $C_6H_6Cl_5C_6H_5$ could result from the reaction of the $C_6H_6Cl_5$ radical with benzene. Microanalysis suggests that $C_6H_6Cl_6$ is the predominant product and the melting point range, ca. 130-140°, suggests a mixture of isomers as found in the ultra-violet initiated chlorination of benzene[6]. When the reaction is conducted in cyclohexane solution, ions are observed in the mass spectrum of the product up to $C_6H_5Cl_5^+$. This product has a melting range (132-138°C), very similar to that from the benzene chlorination; this and microanalysis, again suggest a mixture of isomers of $C_6H_6Cl_6$ as the predominant

product. Reactions conducted in darkness gave the same products as those conducted in normal daylight, excluding photochemical initiation of the reaction. When dibromine was employed in large excess, either in benzene or cyclohexane the yields of the halogenated hydrocarbon were very much lower than from the chlorination reactions. Ions were observed in the mass spectrum up to $C_6H_4Br_5^+$ in each case and the melting ranges, 95-105°C and 91-102°C, again suggested that a mixture of isomers of $C_6H_6Br_6$ is formed in each case. No reaction whatever was observed when the halogen employed was diiodine, nor was any radical arylation observed when N,N-bis-(p-tolylsulphonyl)-hydroxylamine was treated with dibromine in the presence of a mixture of p-chlorobenzoic acid and nitrobenzene. N,N,O-tris-(p-tolylsulphonyl)-hydroxylamine when treated with excess dichlorine in benzene solution gave the same product as N,N-bis-(p-tolylsulphonyl)hydroxylamine, but from treatment with excess dichlorine in carbon tetrachloride or diethyl ether solution it was recovered unchanged. The efficiency of the chlorination of benzene was generally much higher than that of the chlorination of cyclohexane.

No chlorination of diethyl ether was observed in the presence of N-(phenylsulphonyl)hydroxylamine or N,N,O-tris-(p-tolylsulphonyl)-hydroxylamine, but in the presence of toluene-p-sulphonamide, ethyl 1,2-dichloroethyl ether was formed in ca. 70% yield, although the usual radical-induced chlorination yields a succession of products.[7] Toluene-p-sulphonamide and dichlorine was without action on fluorobenzene, chlorobenzene and bromobenzene, but with iodobenzene gave $PhICl_2$, with no nuclear halogenation.

Simple carboxylic acid amides also initiate free radical chlorination of the hydrocarbon substrate, though the yields are substantially lower compared with those of the hydroxylamine initiated reactions. In contrast to the carboxylic acid amides, thioacetamide initiated no chlorination either of benzene or of cyclohexane.

The $C_6H_6Cl_6$ formed in the chlorination reactions of benzene is a mixture of the stereoisomers of which α- and γ- (the major components) and β- and δ- (minor components) were identified by h.p.l.c. when the initiator was N, N, -bis-(p-tolylsulphonyl)-hydroxylamine; N, N-bis-(p-tolylsulphonyl)hydroxylamine or N, N, O-tris-(p-tolylsulphonyl)hydroxylamine was also identified in the product but toluene-p-sulphonyl chloride was absent.

The free radical chlorination of saturated or aromatic hydrocarbons requires either ultra-violet irradiation or a chemical initiator such as peroxide, but simple amides and hydroxylamides also appear to act as initiators of these chlorinations. The reactions with benzene and cyclohexane indicate formation of halogen atoms, $X^{\bullet}$, in solution which react with benzene by addition and with cyclohexane via the chain process (2) - (4).

$$X^{\bullet} + C_6H_{12} \longrightarrow HX + C_6H_{11}^{\bullet} \qquad (2)$$

$$C_6H_{11}^{\bullet} + X_2 \longrightarrow C_6H_{11}Cl + X^{\bullet} \qquad (3)$$

$$X^{\bullet} + C_6H_{11}Cl \longrightarrow HX + C_6H_{10}Cl^{\bullet} \text{ etc.} \qquad (4)$$

The reaction of N, N, O-tris-(p-tolylsulphonyl)hydroxylamine, N, N-bis-(p-tolylsulphonyl)hydroxylamine or N, N-dimethylacetamide with dichlorine show that an >NH or >NOH fragment is not essential for the initiation of chlorination. Both triethylamine and triphenylamine,

but not the tetramethylammonium cation, initiate the addition halogenation of benzene. The minimum requirement for initiation appears to be an unshared pair of electrons on nitrogen, so that the initiation step may, by analogy with the R_3N/CCl_4 reaction[8] be written (5). This initiation reaction is consistent with the observations

$$R_1R_2R_3N + Cl_2 \rightleftharpoons R_1R_2R_3\overset{+}{N}\cdot + Cl\cdot + Cl^- \qquad (5)$$

above and with the reactivity of the elemental halogens ($Cl_2 > Br_2 > I_2$) towards $R_1R_2R_3N$ in equation (5). When applied to $(ArSO_2)_2NOZ$ (Z = H or $ArSO_2$) it possibly follows equations (6) - (8);

$$(ArSO_2)_2NOZ + X^- \longrightarrow (ArSO_2)_2NO\cdot + ZX \qquad (6)$$

$$(ArSO_2)_2NO\cdot \longrightarrow Y\cdot \qquad (7)$$

$$Y\cdot + X_2 \longrightarrow YX + X\cdot \qquad (8)$$

where Y· is a radical which may be $(ArSO_2)_2NO\cdot$, or more plausibly $ArSO_2\cdot$. Termination of the radical process as in carbon tetrachloride may be by reversal of reaction (5), which could account for recovery of $R_1R_2R_3N$ when no substrate for attack by Cl· is present (as in CCl_4 solution). When $R_1=R_2=R_3=C_2H_5$, further attack by $(C_2H_5)_3N^{+}\cdot$ on $(C_2H_5)_3N$ could yield the observed $(C_2H_5)_3NHCl$. Consistent with this suggested initiation is the reaction of triphenylamine with dichlorine in either benzene or carbon tetrachloride. Dichlorine initially generates the blue-green radical-cation $Ph_3\overset{+}{N}\cdot$, which is subsequently converted to $(C_6H_5Cl_6)_2NH$. Its reaction in benzene, but not carbon tetrachloride also produces $C_6H_6Cl_6$.

6.7 REFERENCES

1. M.F. Shostakovski and F.P. Sidel'kovskaya, Zhur. Obshch. Khim., 1952, 21, 1610
2. T.P. Hildrich, J. Chem. Soc., 1908, 93, 1524
3. C.M. Suter, "Organic Chemistry of Sulphur Tetracovalent Sulphur Compounds, J. Wiley and Sons, Inc., New York, 735.
4. D.C. Abbot, H. Egan and J. Thommson, J. Chromatog., 1964, 16, 481
5. R.E. Slade, J. Soc. Chem. Ind., 1945, 64, 314
6. R. Riemschneider and S. Bäker, Z.Naturforsch, 1954, 98, 751
7. G.E. Hall and F.M. Ubertini, J. Org. Chem., 1960, 15, 715
8. J.R. Lindsay-Smith and Z.A. Malik, J. Chem. Soc. (B), 1970, 920

CHAPTER SEVEN

THE PREPARATION AND OXIDATION OF SOME (N-ARYL-N-ARYLSULPHONYL)HYDROXYLAMINES

7.1 THE PREPARATION OF (N-ARYL-N-ARYLSULPHONYL)-HYDROXYLAMINES

Typically, an ethanolic solution (200 ml) of the N-arylhydroxylamine, p-XC_6H_4NHOH, (0.1 mol), which had been previously prepared[1] by the reduction of the corresponding nitro compound, p-$XC_6H_4NO_2$, was stirred at 0° and the arenesulphonyl chloride (0.05 mol) gradually added over 20 minutes. After stirring during 24 h. and evaporation of the solvent the residue was dissolved in a minimum amount of benzene and petroleum spirit (200 ml) was added; after shaking, the crude product was left suspended in the upper petroleum layer. Following decantation and filtration of this layer, the crude product was recrystallised from a mixture of benzene and petroleum spirit, (1:3 respectively). Any decomposition products of the N-arylhydroxylamine remained dissolved in the original benzene layer and were extracted using suitable solvents after evaporation of the benzene. See Table 7.1 for microanalytical, melting points and yields.

Similar reactions were also carried out using methanesulphonyl chloride and benzoyl chloride (See Table 7.2).

Table 7.1

Microanalyses, melting points and yields of (N-aryl-N-arylsulphonyl)hydroxylamines, $ArSO_2N(OH)Ar'$

Ar	Ar'	Found			Calculated			Mp	Yield
		C	H	N	C	H	N	(°)	(%)
C_6H_5	C_6H_5	57.6	4.2	5.6	57.8	4.5	5.6	123-125[2]	60.0
C_6H_5	p-ClC_6H_4	51.0	3.7	5.2	50.8	3.6	4.9	101-103	54.8
p-$MeOC_6H_4$	p-ClC_6H_4	50.2	3.9	4.2	49.8	3.9	4.5	97- 99	51.7
p-$MeOC_6H_4$	C_6H_5	56.3	4.7	5.2	55.9	4.7	5.0	105-107[2]	35.8
p-MeC_6H_4	C_6H_5	59.6	5.1	5.1	59.3	5.0	5.3	121-124	74.8
p-MeC_6H_4	p-MeC_6H_4	59.9	5.4	5.2	60.6	5.5	5.1	126-128	62.8

Table 7.2

Microanalyses, melting points and yields of products from other N-phenylhydroxylamine reactions

Product	Found			Calculated			Mp	Yield
	C	H	N	C	H	N	(°)	(%)
$CH_3SO_2N(OH)C_6H_5$	45.3	5.1	7.3	44.9	4.9	7.5	91-93	51.0
$C_6H_5CON(OH)C_6H_5$[3]	73.8	5.1	6.4	73.2	5.2	6.6	119-120[3]	90.0

7.2 OXIDATION OF (N-ARYL-N-ARYLSULPHONYL)-HYDROXYLAMINES

(a) Oxidation of (N-phenyl-N-phenylsulphonyl)hydroxylamine with lead (IV) oxide

The hydroxylamine (2.49 g, 0.01 mol) was stirred during 24 h. with excess lead (IV) oxide in benzene (100 ml). The mixture was then centrifuged. Evaporation of the solvent yielded a dark oil which was treated with benzene and petroleum spirit as described earlier. Filtration of the upper solvent layer yielded the crude product which was recrystallised from benzene (0.8 g, 0.002 mol, 41%, mp 110-112°). Found: C, 55.9; H, 4.2; N, 3.6%. $C_{18}H_{15}NO_5S_2$ requires: C, 55.5; H, 3.9; N, 3.6%. Extraction of the residual oil with hot ethanol afforded azoxybenzene (0.1 g, 0.52 mmol, mp 33-34°, lit.[4] 36°). Nitrobenzene was detected mass spectroscopically.

Lead (IV) acetate in methylene chloride produced the same product (identical microanalysis, melting point and mixed melting point). The following reagents failed to oxidise the hydroxylamine, and it was recovered unchanged; (i) silver (I,III) oxide in benzene; (ii) manganese (IV) oxide in benzene and (iii) concentrated nitric acid in glacial acetic acid. Fuming nitric acid did not react with the hydroxylamine in benzene but nitrated the solvent to nitrobenzene, which was identified mass spectroscopically.

(b) Oxidation of (N-p-chlorophenyl-N-phenylsulphonyl)hydroxylamine with lead (IV) oxide

The hydroxylamine (0.53 g, 0.00187 mol) was stirred during

24 h. with excess lead (IV) oxide in benzene (100 ml). Work up of the oily product as described earlier yielded a pale pink solid which was recrystallised from a benzene-petroleum spirit mixture (1:5 respectively). (0.2 g, 0.48 mmol, mp 98-99°). Found: C, 50.4; H, 4.4; N, 2.9%. $C_{18}H_{14}NClO_5S_2$ requires: C, 51.1; H, 3.1; N, 3.3%. Extraction of the remaining oil with carbon disulphide (100 ml) afforded 1-chloro-4-nitrobenzene (0.1 g, 0.64 mmol, 68%, mp and mixed mp 81-82°). Further extraction with hot ethanol (100 ml) yielded 4,4'-dichloroazoxybenzene (0.05 g, 0.2 mmol, mp 156-157°, lit.[5] 158°). Both products were initially identified mass spectroscopically.

(c) Oxidation of [N-p-chlorophenyl-N-(p-methoxybenzene-sulphonyl)]hydroxylamine with lead (IV) oxide

The reaction products from the oxidation of the hydroxylamine (1.5 g, 0.005 mol), were isolated using the same procedures described earlier. The dark red solid product (0.8 g, mp 95-97° Found: C, 48.5; H, 3.5; N, 5.3%), contained ion peaks in its mass spectrum as shown in Table 7.3 and only showed a very broad absorption in its ^1H n.m.r. spectrum. The remaining oily product contained both 4,4'-dichloroazoxybenzene (0.2 g, 0.75 mmol) and 1-chloro-4-nitrobenzene (0.15 g, 0.001 mol). Both were identified mass spectroscopically and by melting point and mixed melting point with earlier samples (Identical mp). A sample of the product (170 mg) in methylene chloride was passed through a silica column (30 g, M-60; 27 x 2 cm) using 30% T.H.F. in

Table 7.3

Mass Spectrum of the product from the oxidation of [N-p-chlorophenyl-N-(p-methoxybenzene-sulphonyl)]hydroxylamine

m/e	I(%)	Assignment
77	100	$C_6H_5^+$
92	58	$OC_6H_4^+$
107	64	$CH_3OC_6H_4^+$
111	12	$^{35}ClC_6H_4$
126	23.2	$^{35}ClC_6H_4NH^+$
139	2.4	$CH_3OC_6H_4S^+$
155	8.2	$CH_3OC_6H_4SO^+$
171	76	$CH_3OC_6H_4SO_2^+$

m/e	I(%)	Assignment
187	6.0	$CH_3OC_6H_4SO_3^+$
201	1.2	$CH_3OC_6H_4SO_3N^+$
297	44.0	$CH_3OC_6H_4SO_2NC_6H_4{}^{35}Cl^+$
313	0.5	$CH_3OC_6H_4SO_3NC_6H_4{}^{35}Cl^+$
376	0.6	$CH_3OC_6H_4SO_3N(SO_2)C_6H_4{}^{35}Cl^+$
468	v.w.	$CH_3OC_6H_4SO_3N(SO_2C_6H_4O^+)\text{-}C_6H_4{}^{35}Cl$
483	v.w.	$CH_3OC_6H_4SO_3NC_6H_4{}^{35}Cl$ ($SO_2C_6H_4OCH_3^+$)

hexane as the solvent. Each sample of the eluant (25 ml) was evaporated and the product analysed mass spectroscopically.

The first two samples were combined and after evaporation yielded a dark red oil (20 mg) whose mass spectrum was identical to that shown in Table 7.3. Found: C, 47.9; H, 6.2; N, 3.5%. $C_{20}H_{18}NClO_7S_2$ requires: C, 49.6; H, 3.8; N, 2.9%. The third and fourth samples (25 mg) also gave an identical mass spectrum to that shown in Table 7.3 and an identical analysis. The next ten samples (50 mg) had spectra which contained the same peaks as in Table 7.3 but each sample contained new peaks at m/e 251 and 252. The mass of the ion at m/e 251 was 250.990781 a.u.; $^{12}C_{12}{}^{1}H_{7}{}^{14}N{}^{35}Cl{}^{16}O$ requires 250.990467 a.u. . Therefore the ion at m/e 252 is $(^{35}ClC_6H_4)_2NO$. A pale yellow band remaining on the column was extracted by passing methanol down the column. Evaporation of the solvent afforded a viscous oil (30 mg) whose mass spectrum contained a molecular ion peak at m/e 188 (1%) corresponding to $CH_3OC_6H_4SO_3H^+$.

If dioxane was used instead of methylene chloride for the sample solvent a progressive sequence of m/e 14 and m/e 60, from m/e 73 up to m/e 429 was observed in the mass spectrum of the products after evaporation of the solvent. Accurate masses on m/e 221, 207 and 147 gave, 221.084378, 207.075312 and 147.064279 a.u. respectively. The difference between m/e 221 and m/e 207 was 14.009066 a.u., and between m/e 207 and 147 was 60.011033 a.u. . $^{12}C^{1}H_2$ requires 14.0156492 a.u., and $(^{16}O^{12}C^{1}H)_2$ requires 60.0211266 a.u. .

(d) Reaction of (N-phenyl-N-phenylsulphonyl)hydroxylamine with nitrous acid

The hydroxylamine, (1.25 g, 0.005 mol) was stirred in an aqueous solution of sodium nitrite (0.69 g, 0.01 mol) and concentrated hydrochloric acid (3 ml) was added during 10 minutes. After stirring during 48 h. the mixture was filtered and afforded a product (0.8g, 0.003 mol, 60%) which was recrystallised from benzene. Found: C, 52.0; H, 3.5; N, 10.1%. $C_{12}H_{10}N_2O_4S$ requires: C, 51.8; H, 3.6; N, 10.1%. mp 85-86°. The mass spectrum of the compound contained a molecular ion peak at m/e 278. The mass of this ion was 278.036229 a.u. $^{12}C_{12}{}^{1}H_{10}{}^{14}N_2{}^{16}O_4{}^{32}S$ requires 278.036124 a.u. . The ^1H n.m.r. contained resonances at δ 6.30 (d, 2H); 6.80 (s, 5H); 7.65 (d, 2H) and 9.85 (br. s., 1H) p.p.m. .

Using an identical procedure with [N-p-tolyl-N-(p-tolylsulphonyl)]hydroxylamine afforded unchanged starting material. (Identical microanalysis and melting point to previous samples.)

7.3 OXIDATIONS OF N-ARYLHYDROXYLAMINES

(a) N-phenylhydroxylamine

An aqueous solution of sodium nitrite (1.4 g, 0.02 mol) containing N-phenylhydroxylamine (2.2 g, 0.02 mol) was stirred continually as concentrated hydrochloric acid (6 ml) was slowly added. When the addition was complete the mixture was stirred for a further 30 minutes before being extracted with benzene

(3 x 150 ml). After drying over anhydrous sodium sulphate for 24 h. evaporation of the solvent afforded an oil whose mass spectrum was identical to that of the oily residue from the oxidation of (N-phenyl-N-phenylsulphonyl)hydroxylamine with lead (IV) oxide. Extraction of the oil with hot ethanol yielded azoxybenzene (0.7 g, 0.0035 mol, mp 33-35°). Careful distillation of the remaining residue yielded a fraction (bp. 206-210°) whose mass spectrum was identical to that of an authentic sample of nitrobenzene. Identical results were obtained when N-phenylhydroxylamine was oxidised with excess lead (IV) oxide in benzene.

(b) N-p-chlorophenylhydroxylamine

N-p-Chlorophenylhydroxylamine (2.8 g, 0.02 mol) was stirred during 48 h. with excess lead (IV) oxide in benzene (150 ml). After centrifuging the mixture, evaporation of the volatiles afforded a dark viscous oil which when extracted with (a) carbon disulphide (100 ml) yielded 1-chloro-4-nitrobenzene (1.0 g, 0.006 mol, mp 80.5-82°; lit. 83°)[6]; and (b) hot ethanol yielded 4,4'-dichloro-azoxybenzene (0.5 g, 0.002 mol, mp 156-157°).

7.4 SOME OTHER REACTIONS

(a) The oxidation of (N-phenyl-N-methylsulphonyl)hydroxylamine with lead (IV) oxide

When adopting an identical procedure to that of the previous oxidations (N-phenyl-N-methylsulphonyl)hydroxylamine (1.8 g,

0.0096 mol), afforded a dark red solid (0.4 g, mp 93-94°). Found: C, 39.9; H, 4.5; N, 5.7%. $C_8H_{11}NO_5S_2$ requires: C, 36.2; H, 4.2; N, 5.3%. The ^1H n.m.r. spectrum of the product contained absorptions at δ 3.05 (s, 3H); 3.32 (s, 3H) and 6.9-7.2 (br., 5H) p.p.m.. The remaining residue from the reaction yielded both azoxybenzene and nitrobenzene, which were isolated and identified as in 7.3 (d). The mass spectrum of the product contained ion peaks up to m/e 186 (48.8%) which was assigned to $C_6H_5N(O)SO_2CH_3^+$.

(b) The oxidation of (N-phenyl-N-benzoyl)hydroxylamine with lead (IV) oxide

The hydroxylamine (2.13 g, 0.01 mol) was stirred during 24 h. with excess lead (IV) oxide in benzene (150 ml). Using the same procedure as before afforded a product (0.9 g, Found: C, 72.7; H, 4.6; N, 6.0%), whose mass spectrum is shown in Table 7.4.

A sample of the product (250 mg) was passed down an identical column to that used in the oxidation of (N-p-chlorophenyl-N-(p-methoxybenzenesulphonyl)hydroxylamine with lead (IV) oxide. The same sampling procedure was adopted. The first four samples (50 mg) had an identical mass spectrum to that shown in Table 7.4. Found: C, 74.9; H, 4.9; N, 4.8%. $C_{20}H_{15}NO_3$ requires: C, 75.7; H, 4.8; N, 4.4%. The mass spectra of the remaining samples (0.12 g) showed a mass peak at m/e 197 corresponding to $C_6H_5CONHC_6H_5^+$. (mp 161-162°, lit. 160-161°[7]) Found: C, 79.3; H, 5.3; N, 7.1%. $C_{13}H_{11}NO$ requires: C, 79.2; H, 5.6; N, 7.1%. The residual oil from the oxidation yielded

Table 7.4

Mass spectrum of the product from the oxidation of (N-phenyl-N-benzoyl)hydroxylamine

m/e	I(%)	Assignment
77	73.6	$C_6H_5^+$
91	20.1	$C_6H_5N^+$
105	100	$C_6H_5CO^+$
122	16.8	$C_6H_5CO_2H^+$
197	38.9	$C_6H_5CONHC_6H_5^+$
317	v.w.	$C_6H_5CON(C_6H_5)OCOC_6H_5^+$

Table 7.5

Diagnostic Infra-red frequencies for (N-aryl-N-arylsulphonyl)-hydroxylamines, $ArSO_2N(OH)Ar'$, and their oxidation products

Ar	Ar'	(O-H) cm^{-1}	(S-O) cm^{-1} oxidation product
C_6H_5	C_6H_5	3380	820
p-$MeOC_6H_4$	C_6H_5	3390	-
p-Me C_6H_4	C_6H_5	3340	-
C_6H_5	p-ClC_6H_4	3375	830
p-$MeOC_6H_4$	p-ClC_6H_4	3320	825

azoxybenzene and nitrobenzene.

7.5 SPECTRAL DATA

(a) Infra-red Spectra

The i.r. spectra of the (N-aryl-N-arylsulphonyl)-hydroxylamines all contain a strong band at ca. 1080 cm^{-1} corresponding to ∂(N-O) and at ca. 3370 cm^{-1} corresponding to ∂(O-H). (N-phenyl-N-benzoyl)hydroxylamine contains a band at 1615 cm^{-1} in its spectrum which can be assigned to ∂(C=O). The main differences between the hydroxylamines and their oxidation products is the presence of only ∂(O-H) in the hydroxylamines and only ∂(S-O) in the oxidation products. (See Table 7.5.) (N-phenyl-N-methylsulphonyl)hydroxylamine contains a band at 3310 cm^{-1} for ∂(O-H), and its oxidation product contains a band at 850 cm^{-1} for ∂(S-O).

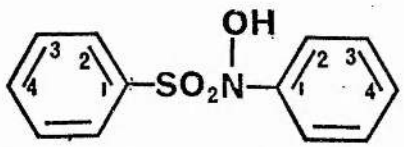
(b) N.M.R. Spectra

The proton spectra (C_6D_6) of the hydroxylamines are as expected. When Ar=p-$MeOC_6H_4$ and Ar^1 is either p-ClC_6H_4 or C_6H_5 the methyl resonances are observed at δ 3.0 and 2.97 p.p.m. respectively. When Ar=p-$CH_3C_6H_4$ and Ar^1=C_6H_5 the methyl resonance is observed at δ 1.80 p.p.m. . (N-phenyl-N-methylsulphonyl)hydroxylamine has a methyl resonance at δ 2.03 p.p.m., while the oxidised hydroxylamine has methyl resonances at δ 3.05 and 3.32 p.p.m. .

Table 7.6

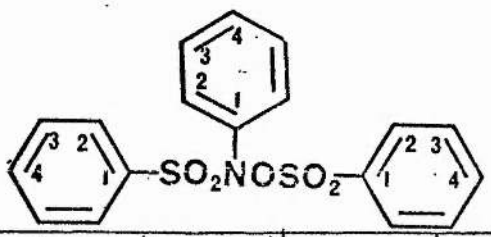
^{13}C n.m.r. spectra of (N-phenyl-N-phenylsulphonyl)hydroxylamine and [N-phenyl-N, O-bis-(phenylsulphonyl)]hydroxylamine

(a)



Carbon Atoms (p.p.m.)	C_4	C_3	C_2	C_1	Others
Compound					
C_6H_5NHOH	119.76	128.73	113.41	152.18	-
$C_6H_5SO_2N(OH)C_6H_5$					
phenyl ring	126.91	-	122.56	142.59	128.58
phenylsulphonyl ring	133.89	-	-	132.61	129.06
					128.14

(b)

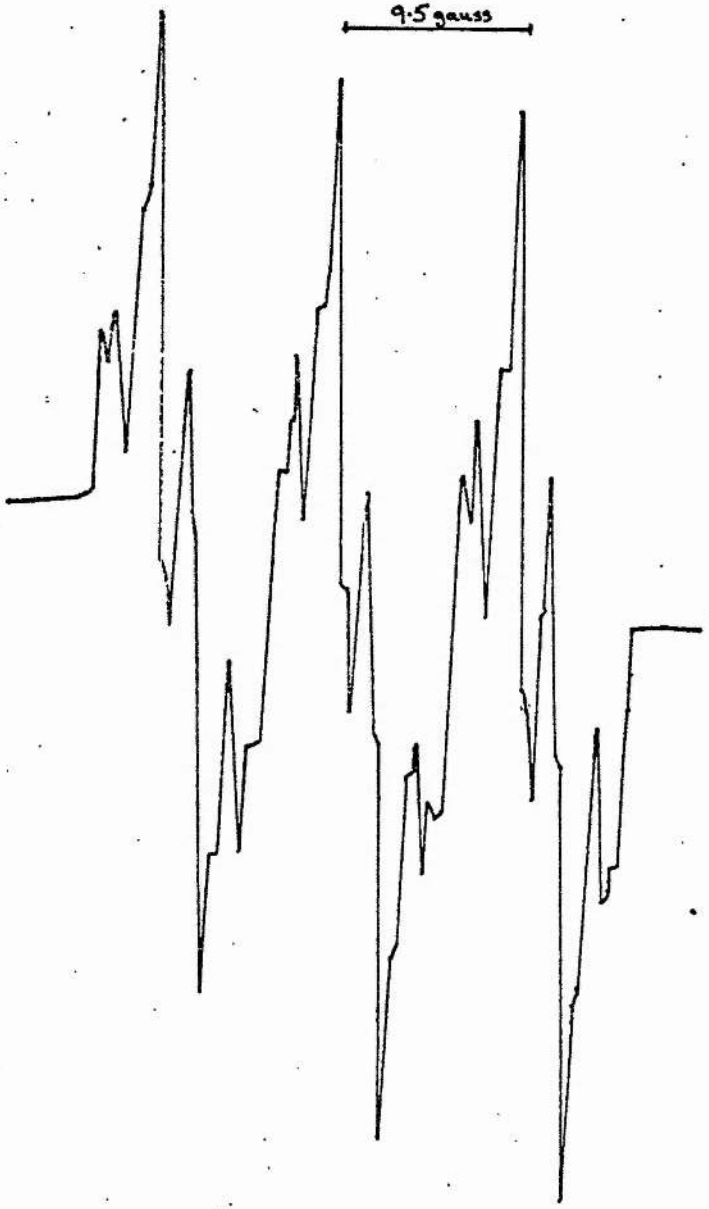


Carbon atoms (p.p.m.)	C_4	C_3	C_2	C_1	Others
phenyl ring	127.31	-	121.99	142.10	129.55
phenylsulphonyl ring	134.88	-	-	132.79	129.08
new ring	140.15	126.63	126.04	124.47	128.11

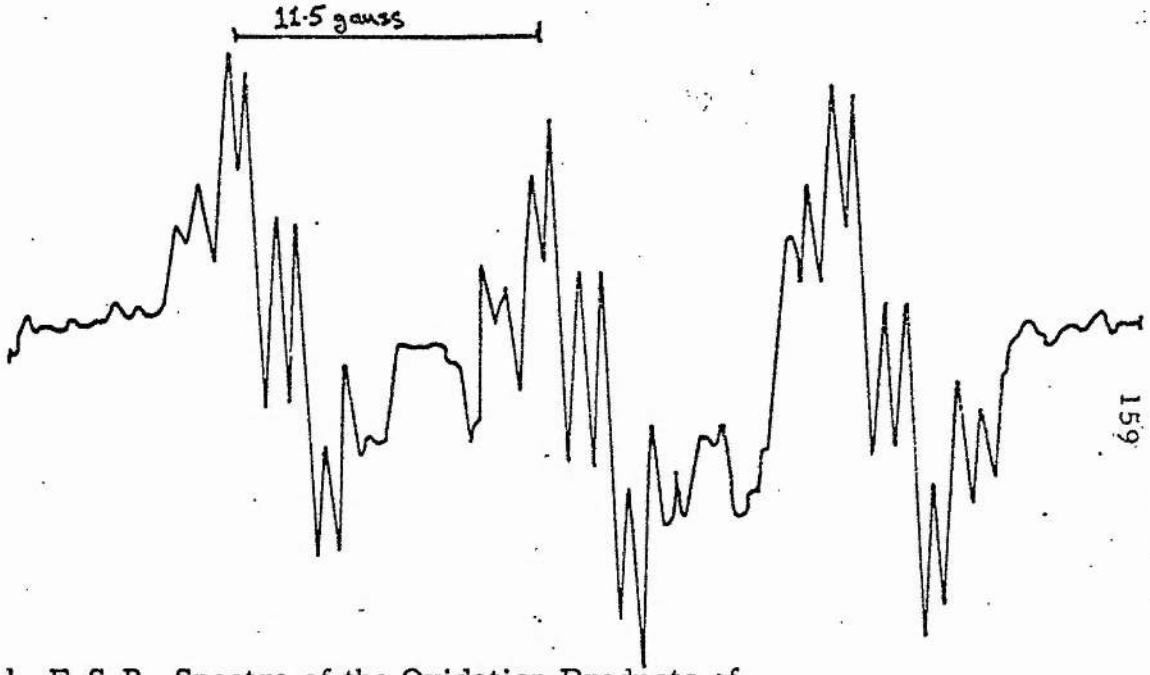
The ^{13}C n.m.r. spectrum (D.M.S.O.) of (N-phenyl-N-phenylsulphonyl)hydroxylamine contains eight absorptions, three of which can be assigned to the N-phenyl ring by comparison with phenylhydroxylamine. Decoupling of the spectrum allows the two C_1 carbon atoms to be assigned. Comparison with the ^{13}C spectrum of N,N-bis-(phenylsulphonyl)hydroxylamine permits the C_4 atom of the phenylsulphonyl ring to be assigned. The remaining absorptions can not be specifically assigned to any of the remaining carbon atoms. [See Table 7.6(a)]. The spectrum of the oxidation product contains twelve absorptions. Comparisons as before allows the assignment of the phenyl and phenylsulphonyl ring; the four remaining resonances can then be assigned to the new ring, though no distinction can be made between the C_2 and C_3 atoms. [See Table 7.6(b)]. This product therefore has three distinct rings, and is therefore an N,N,O-trisubstituted hydroxylamine rather than an amine-oxide.

(c) E.S.R. Spectra

Solutions, in benzene, (0.001 M) of the oxidation products were placed in suitable tubes and carefully degassed. An apparently analytically pure sample of $C_6H_5(C_6H_5SO_2)NOSO_2C_6H_5$, despite giving sharp ^1H and ^{13}C n.m.r. spectra, exhibited an e.s.r. spectrum with coupling to the nitrogen atom, (a_N=11.5 gauss) along with some fine structure. [See Fig. 7.1(b)]. The oxidation product of (N-p-chlorophenyl-N-(p-methoxybenzenesulphonyl)-hydroxylamine showed a well resolved spectrum due to the



(a)

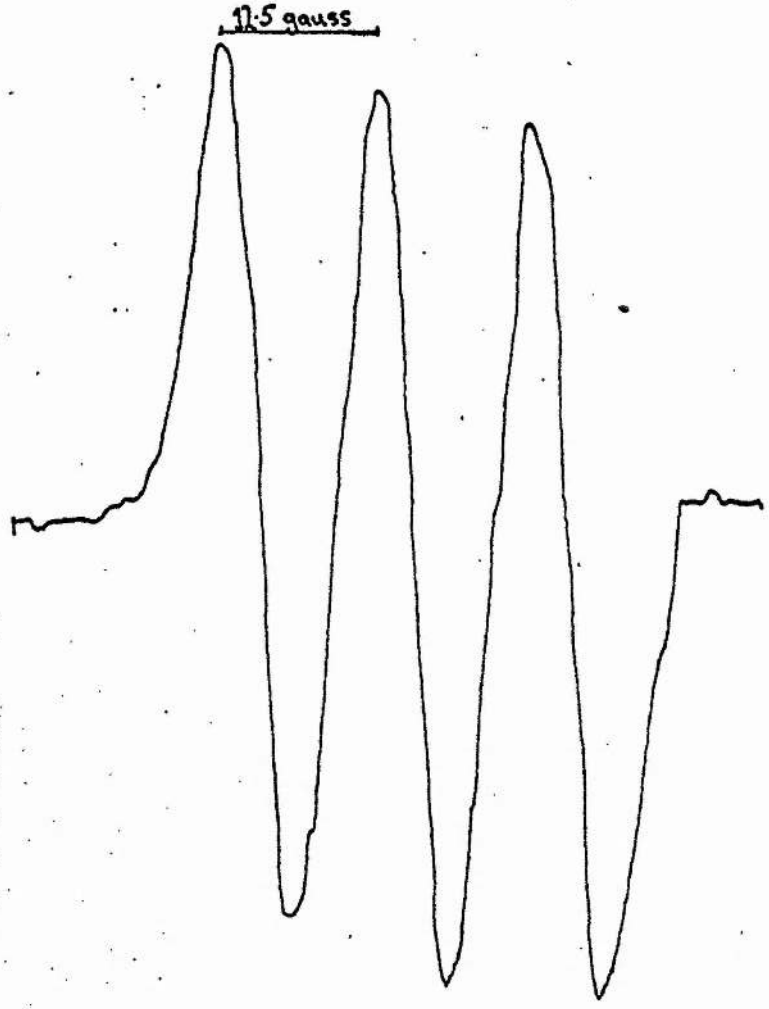


(b)

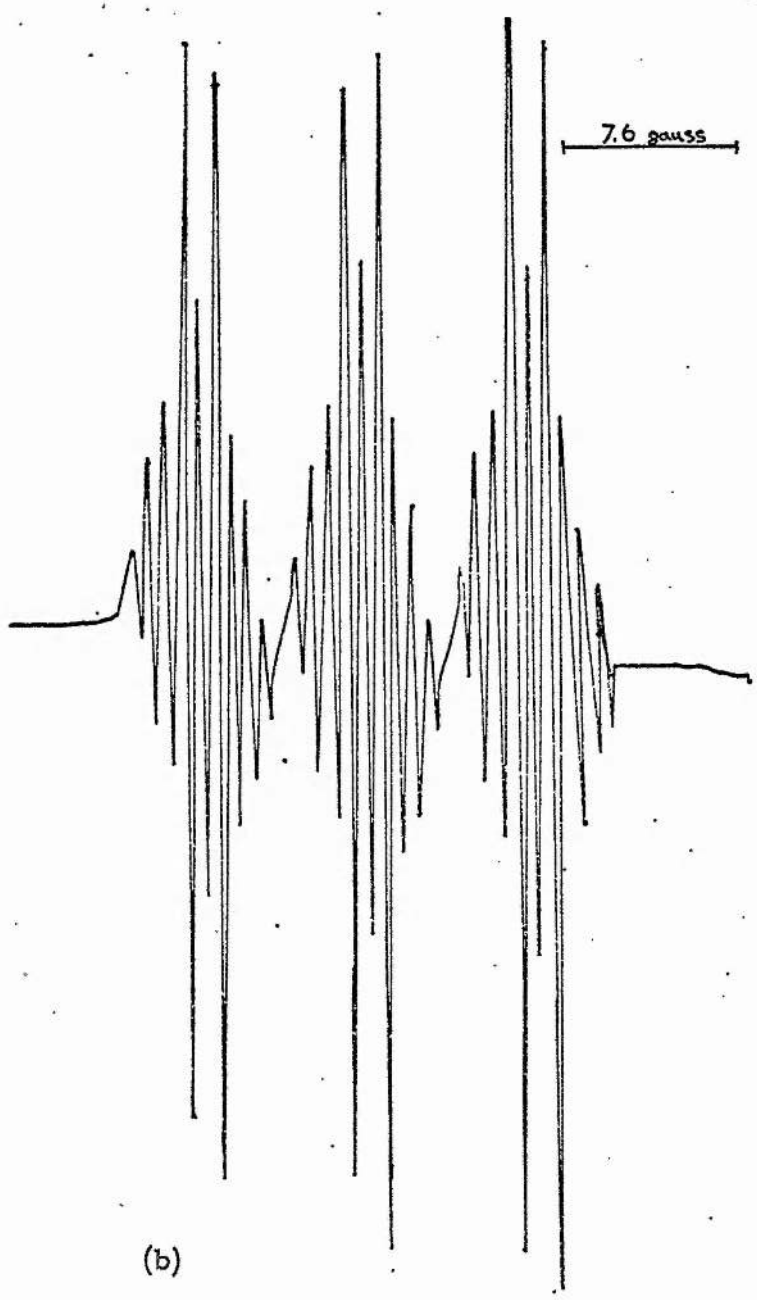
Fig. 7.1 E.S.R. Spectra of the Oxidation Products of

(a) N-p-chlorophenyl-N-(p-methoxybenzenesulphonyl)hydroxylamine

(b) N-phenyl-N-(phenylsulphonyl)hydroxylamine



(a)



(b)

Fig. 7.2 E.S.R. Spectra of the Oxidation Products of

(a) N-phenyl-N-(methylsulphonyl)hydroxylamine

(b) (N-phenyl-N-benzoyl)hydroxylamine

N,N-bis-(p-chlorophenyl)nitroxide radical[8]. [See Fig. 7.1(a)]. a_N=9.5 gauss. This can not contain $PhSO_2$ groups since these would cause a_N to exceed 11.5 gauss[2]. None of the pure radical could be isolated. The oxidation product from (N-phenyl-N-methylsulphonyl)hydroxylamine gave a broad triplet (a_N=12.5 gauss) with no fine structure, [See Fig. 7.2(a)], while the products from the oxidation of (N-phenyl-N-benzoyl)hydroxylamine gave an identical spectrum to that observed previously[9] for (N-phenyl-N-benzoyl)nitroxide. (a_N = 7.6 gauss; $a_{\sigma,pH}$=1.5 gauss $a_{m,H}$=0.6 gauss; [See Fig. 7.2(b)].

7.6 RESULTS AND DISCUSSION

(N-Aryl-N-arylsulphonyl)hydroxylamines, $ArSO_2N(OH)Ar'$, have been previously produced by the reaction[2] of an arenesulphonyl chloride with a suitable N-arylhydroxylamine (1), or by the reaction of nitrosobenzenes[10] with arenesulphinic acids (2). The

$$ArSO_2Cl + Ar'NHOH \longrightarrow ArSO_2N(OH)Ar' + HCl \quad (1)$$

Ar' = C_6H_5; Ar = C_6H_5; p-$CH_3OC_6H_4$; p-$NO_2C_6H_4$:

$$ArSO_2H + Ar'NO \longrightarrow ArSO_2N(OH)Ar' \quad (2)$$

former method was adopted in these investigations. Microanalyses, melting points and yields are given in Table 7.1 . The decomposition product from any excess N-arylhydroxylamine was predominantly azoxybenzene. Similar reactions of N-phenylhydroxylamine with methanesulphonyl chloride and benzoyl chloride yielded

(N-phenyl-N-methanesulphonyl)hydroxylamine and (N-phenyl-N-benzoyl)hydroxylamine[3] respectively. Microanalyses, melting points and yields are given in Table 7.2 . All the hydroxylamines contain bands in their infra-red spectra corresponding to ν(O-H), and the ^{13}C n.m.r. spectrum of (N-phenyl-N-phenylsulphonyl)hydroxylamine indicates the presence of two ring systems, which is consistent with the proposed structure.

(N-Aryl-N-arylsulphonyl)nitroxides, $ArSO_2N(O^{\cdot})Ar'$, have been observed in static[2,11] systems by e.s.r. spectrometry, when either lead (IV) oxide or lead (IV) acetate, (in dioxan, methylene chloride or benzene), is used to oxidise the corresponding hydroxylamine (3). But no attempt has been reported of isolating either the radical or the reaction products

$$ArSO_2NAr' \longrightarrow ArSO_2NAr' \qquad (3)$$
$$\quad\;\; | \qquad\qquad\quad\;\; |$$
$$\quad OH \qquad\qquad\quad O.$$

from such oxidations. A number of oxidising agents were therefore tested in the hope of oxidising the (N-aryl-N-arylsulphonyl)-hydroxylamines to the corresponding nitroxide. Lead (IV) oxide in benzene and lead (IV) acetate in methylene chloride both oxidise (N-phenyl-N-phenylsulphonyl)hydroxylamine to [N-phenyl-N,O-bis-(phenylsulphonyl)]hydroxylamine, and to a dark oil which contains azoxybenzene and nitrobenzene. Identical products to those found in the oil were obtained when phenylhydroxylamine was oxidised with either an excess of

lead (IV) oxide or nitrous acid. The following reagents failed to oxidise the hydroxylamines; (i) silver (I,III) oxide in benzene; (ii) manganese (IV) oxide in benzene and (iii) nitric acid in glacial acetic acid. This contrasts markedly with the oxidation of N,N-bis-(arylsulphonyl)hydroxylamines, which are oxidised by all these reagents to N,N,O-tris-(arylsulphonyl)hydroxylamines. (See Table 3.12) Nitrous acid fails to oxidise both N,N-bis-(arylsulphonyl)hydroxylamines and (N-aryl-N-arylsulphonyl)hydroxylamines to the corresponding tris-compound. But if the 4-position of the aryl ring is unsubstituted, as in (N-phenyl-N-phenylsulphonyl)-hydroxylamine, nitrosation occurs forming [N-(4-nitrosophenyl)-N-phenylsulphonyl]hydroxylamine. No such reaction occurs with [N-p-tolyl-N-(p-tolylsulphonyl)]hydroxylamine.

A benzene solution of [N-phenyl-N,O-bis-(phenylsulphonyl)]-hydroxylamine showed a triplet in its e.s.r. spectrum due to coupling with a nitrogen atom (a_N=11.5 g), which is suggestive of the (N-phenyl-N-phenylsulphonyl)nitroxide radical, $C_6H_5SO_2N(O^{\bullet})C_6H_5$, observed by other workers[2,11]. The fine detail of the spectrum observed suggested that this product was not simply the (N-phenyl-N-phenylsulphonyl)nitroxide radical, even though the a_N value is correct, but possibly a mixture of radicals. This however is unlikely as each radical would have to have the same a_N and g values, and a more likely explanation is the possibility of the radical adopting two conformations due to the phenyl ring. When (N-phenyl-N-phenylsulphonyl)hydroxylamine

is oxidised "in situ" the nitroxide radical signal has been reported[9] to change over a period of 10 minutes to that of N-nitroso-N-phenylnitroxide, $C_6H_5N(NO)O^{\cdot}$, (a_N=10.34 gauss), due to the decomposition of the first nitroxide radical. The mechanism shown in equations (4)-(8) was proposed to explain this decomposition. On prolonged standing the new signal was reported to change again to that of diphenylnitroxide[12], (a_N=10.9 gauss) (8). No signal was reported for the phenylsulphonyl radical[13],($a_{H_{2,6}}$ =1.2 g) and no diphenylsulphone was isolated. No such changes in signal were observed during these investigations.

$$PhSO_2\underset{\underset{OH}{|}}{N}-Ph \xrightarrow{\text{oxidation}} PhSO_2\underset{\underset{O^{\cdot}}{|}}{N}Ph \longrightarrow PhSO_2^{\cdot} + PhNO \qquad (4)$$

$$PhSO_2^{\cdot} + PhNO \longrightarrow PhSO_2Ph + NO \qquad (5)$$

$$PhSO_2^{\cdot} \longrightarrow Ph^{\cdot} + SO_2 \qquad (6)$$

$$PhNO + NO \rightleftharpoons PhN(\underset{\underset{N=O}{|}}{O^{\cdot}}) \rightleftharpoons Ph^{\cdot} + 2NO \qquad (7)$$

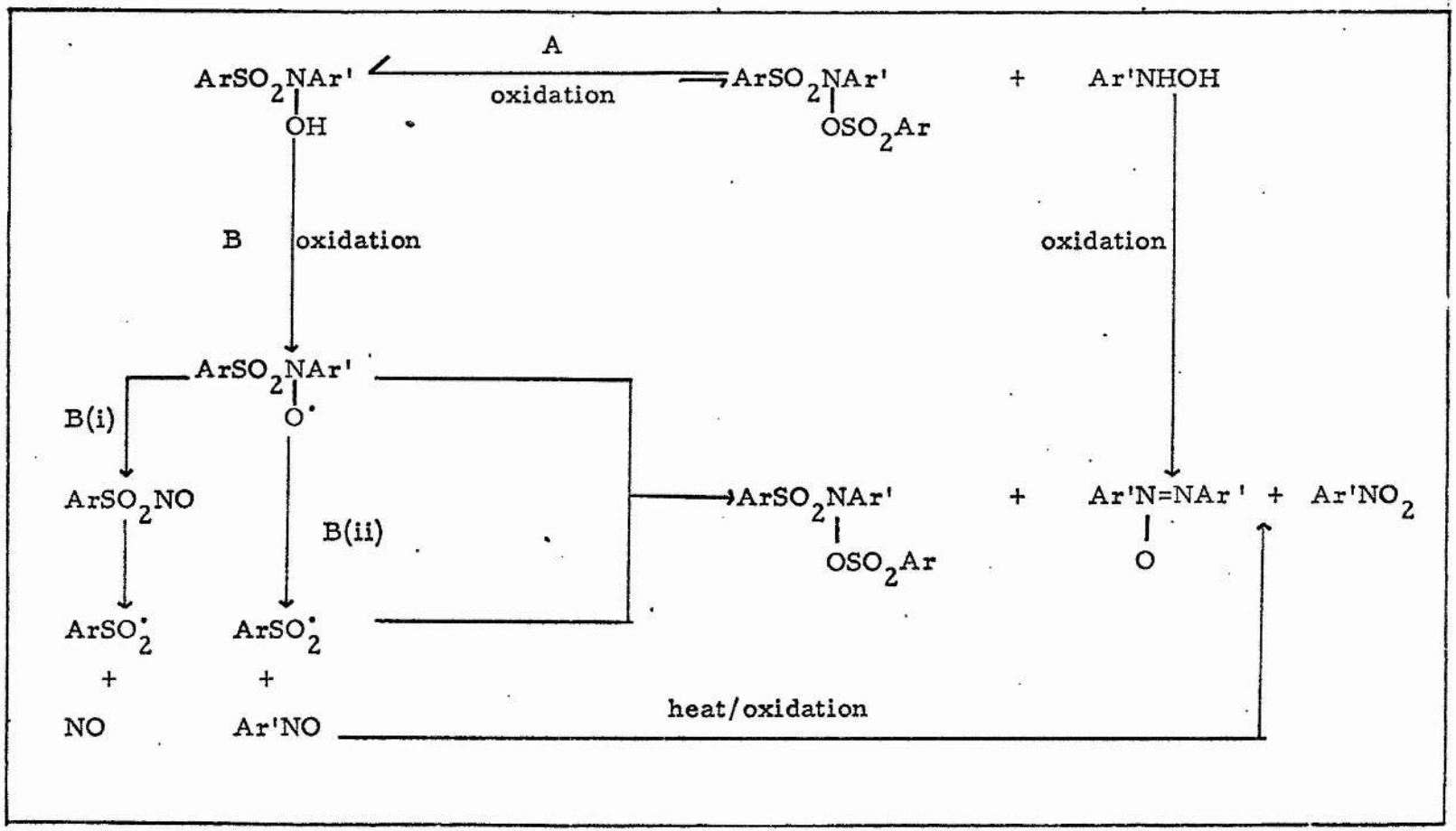
$$PhNO + Ph^{\cdot} \longrightarrow Ph_2NO^{\cdot} \qquad (8)$$

The identification of azoxybenzene and nitrobenzene in the reaction would possibly suggest that phenylhydroxylamine is formed during the oxidation, and any excess oxidising agent would form these two products. The analogous oxidation reaction with (N-p-chlorophenyl-N-phenylsulphonyl)hydroxylamine also appears to produce the azoxy compound, 4,4'-dichloro-azoxybenzene , and 1-chloro-4-nitrobenzene, along with

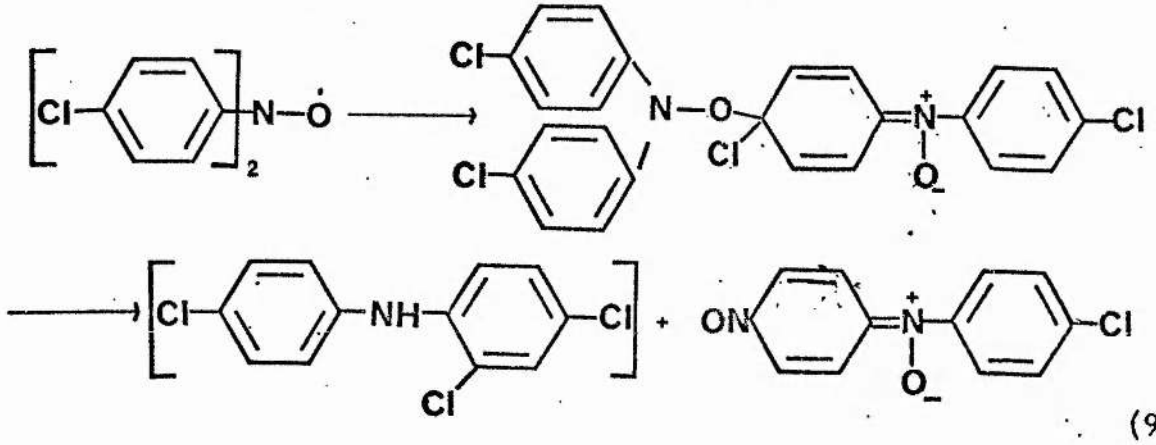
[N-p-chlorophenyl-N,O-bis-(phenylsulphonyl)]hydroxylamine, again suggesting that the N-arylhydroxylamine may be an intermediate. These observations allow two plausible routes to the oxidation products obtained, which are analogous to those proposed during the oxidation of N,N-bis-(arylsulphonyl)-hydroxylamines. [See Scheme 7.1]. Route A, however, can be ruled out since nitrous acid does not convert $ArSO_2N(OH)Ar'$ to $ArSO_2N(OSO_2Ar)Ar'$ but does form azoxybenzene and nitrobenzene when added to phenylhydroxylamine. The alternative route B, which is supported by e.s.r. observations, involves the formation of the nitroxide radical $ArSO_2N(O^{\bullet})Ar'$, which could (i) form an intermediate nitrosoarenesulphinate, and hence an arenesulphonyl radical and nitric oxide; or (ii) form an arenesulphonyl radical directly and a nitrosoarene. Route B(i) can be ruled out as this would provide no means of isolating an azoxy-compound. Route B(ii) however would produce $ArSO_2N(OSO_2Ar)Ar'$ by cross-combination of the two radicals, and a nitrosoarene. The nitrosoarene could then decompose[14] due to heating or the presence of excess oxidising agent and form an azoxy and nitro compound. A combination of both routes [B(i) and B(ii)] can also be eliminated since nitric oxide [B(ii)] would react with the nitrosoarene [B(ii)] to form an N-nitroso-N-aryl-nitroxide, and hence produce a new e.s.r. signal, and this was not observed. No e.s.r. signal was detected for an arene-sulphonyl radical during these investigations.

Scheme 7.1

Possible Routes to the Formation of (N-aryl-N-arylsulphonyl)hydroxylamines



The oxidation of (N-p-chlorophenyl-N-p-methoxybenzenesulphonyl)hydroxylamine with lead (IV) oxide did not appear to produce a pure sample of the tris species; [N-p-chlorophenyl-N,O-bis-(p-methoxybenzenesulphonyl)]hydroxylamine, though the mass spectrum did contain the molecular ion peak m/e 483. 1-Chloro-4-nitrobenzene and 4,4'-dichloroazoxybenzene were again isolated from the oxidation suggesting that a similar reaction had occurred to the previous oxidations. Column chromatography produced an initial fraction whose mass spectrum was identical to the crude product, but an improved analysis suggested that it was a combination of the expected tris-species and the corresponding nitroxide radical. The other chromatographic samples had a similar mass spectrum but each consecutive sample had an increased intensity value for the ion peaks m/e 251 and 252. m/e 251 had a mass of 250.990781 a.u. which corresponds to $^{12}C_{12}{}^{1}H_{7}{}^{14}N{}^{35}Cl_{2}{}^{16}O$ which would suggest that the m/e 252 ion peak is due to N,N-bis-(p-chlorophenyl)nitroxide[8]: this is also supported by the observed e.s.r. signal [Fig. 7.1(a)], even though this radical is known[15] to rapidly decompose to N-(p-chlorophenyl)-p-benzoquinonimine-N-oxide and trichlorophenylamine (9). The presence of a free radical is also suggested



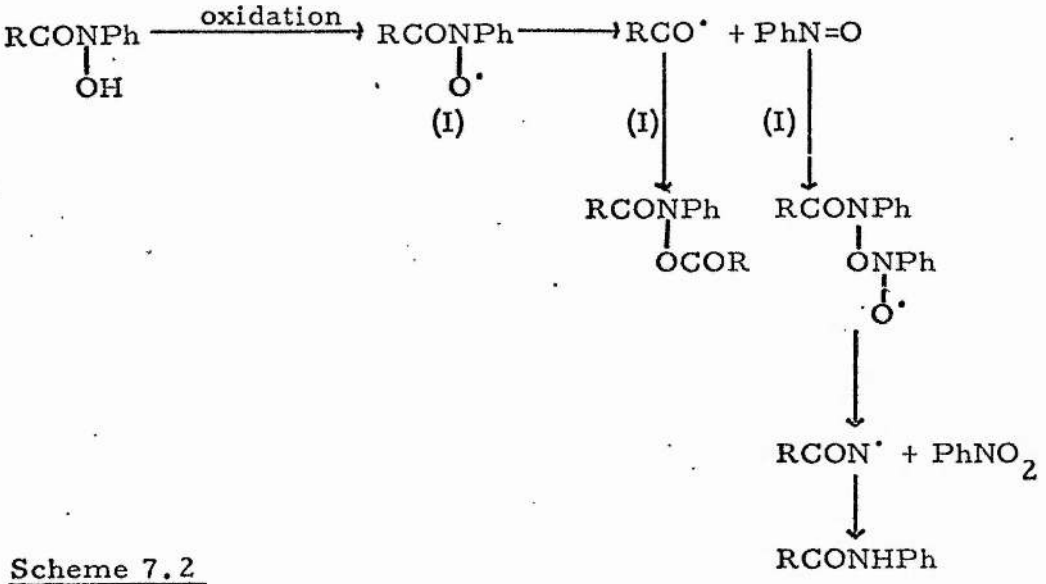
(9)

from the observation that dioxan is polymerised in the presence of the product.

The oxidation product of (N-phenyl-N-methylsulphonyl)-hydroxylamine also appears to be a mixture of the tris-hydroxylamine, $CH_3SO_2N(OSO_2CH_3)C_6H_5$, and a radical (microanalysis). The light red solid does however possess an n.m.r. spectrum which contains two different methyl groups, and in its i.r. spectrum also contains a band for ν(S-O), which is consistent with the proposed structure of the product. A broad triplet is observed in its e.s.r. spectrum (a_N = 12.5 gauss) indicating the presence of a nitroxide radical. Both azoxybenzene and nitrobenzene were isolated from this oxidation which would suggest that the oxidation proceeds *via* the radical route proposed earlier.

The products from the oxidation of (N-phenyl-N-benzoyl)-hydroxylamine appear to be benzanilide, [N-phenyl-N,O-bis-(benzoyl)]hydroxylamine, azoxybenzene and nitrobenzene. The product mixture in benzene had an e.s.r. spectrum identical[9] to that observed for (N-phenyl-N-benzoyl)nitroxide, $C_6H_5CON(O^{\cdot})C_6H_5$, a_N=7.6 g, a_{qpH} 1.59, $a_{m\text{-}H}$ 0.64 but none of the radical could be isolated. This is in agreement with the observations made by Forrester[16] who proposed the scheme below to explain the results. He was however uncertain about the mechanism to benzanilide formation.

[See Scheme 7.2]



Scheme 7.2

All the oxidation products considered contain ϑ (S-O) but no ϑ (O-H) in their i.r. spectra and exhibit an e.s.r. signal in solution, therefore suggesting that they are most likely to be mixtures of the [N-aryl-N,O-bis-(arylsulphonyl)]hydroxylamine and the corresponding nitroxide radical, (N-aryl-N-arylsulphonyl)-nitroxide.

7.7 REFERENCES

1. A.I. Vogel, 'A Textbook of Practical Organic Chemistry', Longmans, Green and Co., 602

2. Th.A.J.W. Wajer, H.W. Geluk, J.B.F.N. Engberts and Th.J. de Boer, Rec. Trav. Chim. Pays. Bas, 1970, 89, 696

3. E. Bamberger, K. Blaskopf and A. Laundau, Ber., 1919, 52, 1116

4. M.O. Forster, J. Chem. Soc., 1898, 73, 786

5. L. Zechmeister and P. Rom, Ann., 1929, 468, 117

6. J.D. Cauwood and W.E.S. Turner, J. Chem. Soc., 1915, 107 276

7. R. Meyer and W. Sundmacher, Ber., 1899, 32, 2112

8. E.T. Strom, A.L. Bluhm and J. Weinstein, J. Org. Chem., 1967, 32, 3853

9. H.G. Aurich and F. Baer, Tetrahedron Lett., 1965, 3879

10. A. Darchen and C. Moinet, Chem. Comm., 1976, 20, 820

11. A.T. Balaban and N. Negoita, Rev. Roumainie Chim., 1972, 17, 1227

12. J.R. Thomas, J. Amer. Chem. Soc., 1960, 82, 5955

13. M. McMillan and W.A. Waters, J. Chem. Soc. B, 1966, 422

14. E. Bamberger, Ber., 1900, 35, 1939

15. K. Tokumaru, H. Sakuragi, and O.Simomura, Tetrahedron Lett., 1964, 3945

16. A.R. Forrester, J.M. Hay and R.H. Thomson, "Organic Chemistry of Stable Free Radicals", London-New York, Academic Press, 1968, 217

CONCLUSION

The aims of the research work for this thesis are set out in the first chapter and the experimental details in the relevant chapters thereafter.

A series of N,N-bis-(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOH$, (X=H, CH_3, Cl, MeO and F), were produced by the reaction of arenesulphinic acids with nitrous acid and were identified by elemental analysis and mass spectrometry. Their proposed structure was confirmed from infra-red spectra. The reaction of (N-arylsulphonyl)hydroxylamines with arenesulphonyl chlorides, but not iron (III) chloride, also provides a useful route to these compounds. The corresponding N,N-bis-(alkylsulphonyl)-hydroxylamines, $(RSO_2)_2NOH$, (R=CH_3 or $n\text{-}C_4H_9$), could not be isolated although higher alkyl analogues have been prepared.[1] A series of (N-aryl-N-arylsulphonyl)hydroxylamines, $p\text{-}XC_6H_4(p\text{-}X'C_6H_4SO_2)NOH$, were also prepared and identified in a similar manner.

Although it appears that arylsulphonylaminyloxides can not be isolated as such in a pure state, they are apparently present to a small extent in the oxidation products of N,N-bis-(arylsulphonyl)-hydroxylamines and (N-aryl-N-arylsulphonyl)hydroxylamines, since e.s.r. spectra have been observed, from what appear to be analytically pure samples of the tris-hydroxylamines. They all have well resolved n.m.r. spectra (^1H, ^{13}C or ^{19}F). A wide range of oxidising agents were found to oxidise N,N-bis-(aryl-sulphonyl)hydroxylamines to N,N,O-tris-(arylsulphonyl)hydroxylamines

rather than to N,N-bis-(arylsulphonyl)aminyloxides, $(p\text{-}XC_6H_4SO_2)_2NO^{\bullet}$, which is in complete contrast to diarylhydroxylamines[2]. Similarly the (N-aryl-N-arylsulphonyl)hydroxylamines yield on oxidation a mixture of the corresponding tris compound, $p\text{-}XC_6H_4(p\text{-}X'C_6H_4SO_2)NOSO_2C_6H_4X'\text{-}p$- and an aminyloxide, along with an azoxy, $p\text{-}XC_6H_4N(O)NC_6H_4X\text{-}p$, and nitro compound, $p\text{-}XC_6H_4NO_2$.

Two routes are considered to the formation of the tris-compound for both the N,N-bis-(arylsulphonyl)hydroxylamines and the (N-aryl-N-arylsulphonyl)hydroxylamines. The route involving the formation of hydroxylamine is ruled out in both cases since certain oxidants fail to produce the tris-species, but all oxidise the hydroxylamine to the observed products under the conditions which they fail to convert either $(p\text{-}XC_6H_4SO_2)_2NOH$ or $p\text{-}XC_6H_4(p\text{-}X'C_6H_4SO_2)NOH$ to $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$ or $p\text{-}XC_6H_4(p\text{-}X'C_6H_4SO_2)NOSO_2C_6H_4X'\text{-}p$ respectively. The alternative route involves the formation of an aminyloxide radical which then decomposes to form an arylsulphonyl radical. Subsequent cross-combination of the aminyloxide and arylsulphonyl radicals can then yield the tris-species. Any excess oxidising agent will then form the other observed products. Support for this route is given by the e.s.r. spectra obtained for $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$ (X=H, CH_3, Cl and F), which are identical to those observed during the 'in situ' oxidation of the bis-species $(p\text{-}XC_6H_4SO_2)_2NOH$. Each spectrum consists of a well defined triplet characteristic of a sulphonylaminyloxide radical (a_N=10.5-12.0 gauss).

In the case of the mixed hydroxylamines, $p\text{-}XC_6H_4(p\text{-}X'C_6H_4SO_2)NOSO_2C_6H_4X'\text{-}p$ the e.s.r. spectra were

not so unambiguous. When X=X'=H, a spectrum of the tris-compound was observed (a_N = 11.5 gauss), which suggested the presence of a sulphonylaminyloxide, but the spectrum was not found to change as suggested[3] by other workers. When X=Cl and X' = MeO, column chromatography produced what appeared to be an inseparable mixture containing the tris-species, p-ClC_6H_4(p-$MeOC_6H_4SO_2$)$NOSO_2C_6H_4OMe$-p and N,N-bis-(p-chlorophenyl)nitroxide. The radical was identified by its molecular ion peak and by its e.s.r. signal (a_N=9.5 gauss), and clearly can not be a spectrum of a radical containing any arylsulphonyl groups. Likewise, on oxidation other mixed hydroxylamines, e.g. (N-phenyl-N-methylsulphonyl)hydroxylamine, also appear to be a mixture of the tris-hydroxylamine and an aminyloxide radical (a_N=12.5 gauss). The oxidation product of (N-phenyl-N-benzoyl)hydroxylamine similarly forms a mixture of [N-phenyl-N,O-bis-benzoyl]hydroxylamine and (N-phenyl-N-benzoyl)aminyloxide, $C_6H_5(C_6H_5CO)NO^{\cdot}$, ($a_N$=7.6 gauss); but none of the radical could be isolated. Benzanilide, azoxybenzene and nitrobenzene were also isolated. The presence of free-radicals is also supported by the observation that oxidation of (p-$XC_6H_4SO_2)_2NOH$ to (p-$XC_6H_4SO_2)_2NOSO_2C_6H_4X$-p- is suppressed in cyclohexene, and the solvent is oligomerised.

(N-Phenyl-N-phenylsulphonyl)hydroxylamine, N,N-bis-(arylsulphonyl)hydroxylamines and their analogous tris-species were unambiguously identified by elemental analysis and n.m.r. spectroscopy

(^{1}H, ^{13}C and ^{19}F), which together with infra-red data and theoretical considerations suggested that the tris-species are hydroxylamines, R_2NOR, rather than amine oxides, $R_3N(\rightarrow O)$. This deduction apparently agrees with the recently[4] observed structure for potassium hydroxylamine trisulphonate, $(KSO_3)_2NOSO_3K$.

All the N,N-bis-(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOH$, are stable in dry air, and also in moist air when X=CH_3 and Cl. Nitrogen oxides are evolved, and the corresponding tris-hydroxylamine and arylsulphonic acid are formed when X=F and H after exposure to moist air for a prolonged period. When X=MeO a black tar was isolated. The tris-hydroxylamines were found to be stable in moist air when X = H, CH_3 and MeO, but when X = Cl or F the analogous sulphonic acid is formed and oxides of nitrogen are evolved.

N,N-bis-(arylsulphonyl)imides, $(p\text{-}XC_6H_4SO_2)_2NH$ failed to be oxidised to the corresponding aminyloxide by the same reagents that convert secondary amines, R_2NH, to the analogous free-radical, $R_2NO^{\bullet}$. A considerable amount of work was done trying to prepare suitable amines from the reaction of imido-bis-(sulphuryl.chloride), $HN(SO_2Cl)_2$, with either amines or alcohols. Although two amines were characterised, little or no success was to be had from this line of research. However, the formation of $(p\text{-}XC_6H_4SO_2)_2NO^{\bullet}$ as the first step in the oxidation of $(p\text{-}XC_6H_4SO_2)_2NOH$ is supported by the failure of the bis-imides to undergo oxidation by any of the reagents which oxidise $(p\text{-}XC_6H_4SO_2)_2NOH$.

In an attempt to synthesise amines and hydroxylamines from the reaction of hydroxylaminedisulphonates, $HON(SO_3M)_2$ or imidodisulphonates, $HN(SO_3M)_2$, ($M=Ag^+, Pb^{2+}, Hg^{2+}, Hg_2^{2+}, Tl^+$), with alkyl or aryl halides, the reactions of the imidodisulphonate ion, $HN(SO_3)_2^{2-}$, hydroxylaminedisulphonate ion, $HON(SO_3)_2^{2-}$ and the nitrosodisulphonate ion, $ON(SO_3)_2^{2-}$ with M were investigated. The imidodisulphonate ion fails to produce any simple imidodisulphonates with the metal ions employed, though the di- and trisilver imidodisulphonates, $Ag_2KN(SO_3)_2$ and $Ag_3N(SO_3)_2$, were isolated using tripotassium imidodisulphonate. These salts failed to react with any alkyl or aryl halides. Similarly no simple hydroxylaminedisulphonates of these metal ions could be obtained, and potassium hydroxylaminedisulphonate in the presence of Pb^{2+} and Hg^{2+} ions decomposes to the metal sulphate along with sulphate and sulphite ions. Silver ions are reduced to the metal with the production of sulphate ion. No precipitates are formed with Hg_2^{2+} and Tl^+ ions. The normal decomposition of potassium nitrosodisulphonate is enhanced in the presence of Ag^+, Pb^{2+}, Hg^{2+} and Tl^+ ions, and may proceed via the hydroxylamine disulphonate ion, which then decomposes as described above.

Nitrosylarenesulphinates, $p\text{-}XC_6H_4SO_2NO$, were proposed as intermediates during the oxidation of $(p\text{-}XC_6H_4SO_2)_2NOH$ to $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$. In the hope of isolating these species the reactions of arylsulphonylhydroxylamines, arenesulphinic acids and some similar compounds with nitrosyl chloride

and nitrogen (II) oxide were considered. However, no such species was isolated, and N,N-bis-(arylsulphonyl)hydroxylamines, (N-arylsulphonyl)hydroxylamines, arylsulphonamides and arenesulphinates all yield arenesulphonyl chlorides with nitrosyl chloride, while N,N,O-tris-(arylsulphonyl)hydroxylamines and N,N-bis-(arylsulphonyl)imides are unaffected. Arylsulphonylhydroxylamines and arenesulphinates react with nitrogen (II) oxide to yield the corresponding sulphonic acid. The nitrosylarenesulphinate could not be trapped in the presence of cyclopentadiene, even though such adducts are known. This species is also postulated to explain the production of an N,N-bis-(arylsulphonyl)imide, pyridine-N-oxide and pyridinium arylsulphonate during the reaction of an N,N-bis-(arylsulphonyl)hydroxylamines with pyridine. Similarly no species of this type could be isolated when (N-phenylsulphonyl)hydroxylamine was oxidised under the same conditions that convert N-arylhydroxylamines to C-nitrosoarenes.

With dichlorine in carbon tetrachloride, (N-arylsulphonyl)-hydroxylamines, sodium arenesulphinates and diarylsulphones all produce the corresponding arenesulphonyl chloride rather than a nitrosylarenesulphinate. But, N,N-bis-(arylsulphonyl)hydroxylamines, arylsulphonamides and N,N-bis-(arylsulphonyl)imides do not react. However, in benzene or cyclohexane they initiate free radical halogenation of the solvent producing an isomeric mixture of $C_6H_6Cl_6$, which contains the α and γ isomers, (major components) along with the β and δ isomers (minor components). The chlorination of benzene is much more efficient than that of cyclohexane, and arylsulphonamides appear to initiate greater yields of

the isomer mixture. With dibromine, but not diiodine, halogenation also occurs, but to a much lower extent. Simple carboxylic acid amides were also found to initiate free radical chlorination of the solvent hydrocarbon, but the yields are much lower compared to those of the hydroxylamine initiated reactions. Initiation of this reaction is shown to occur when a species containing an unshared pair of electrons on the nitrogen atom is present, by analogy with the radical-cation $Ph_3\dot{N}^+$, which is formed when dichlorine reacts with triphenylamine in carbon tetrachloride; $(C_6H_5Cl_6)_2NH$ is eventually produced. In benzene however $C_6H_6Cl_6$ is also produced. Further work is really necessary to obtain the individual yields of the $C_6H_6Cl_6$ isomers, so as to allow a comparison with other methods of production.

Some useful lines of research, in order to continue this work, would be to; (a) confirm the proposed structure of the N,N-bis-(arylsulphonyl)hydroxylamines, N,N,O-tris-(arylsulphonyl)hydroxylamines and the mixed hydroxylamines by determining their crystal structures. Useful information may also be obtained from ^{15}N n.m.r. spectra of these compounds. (b) The reaction of disulphinic acids with nitrous acid in an attempt to produce cyclic bis-hydroxylamines, which may then be oxidised to aminyloxides. 1,2-Benzene-disulphinic acid may also prove to be of interest in this respect.

It is useful to point out that isolating aminyloxides from their corresponding hydroxylamines appears to become more difficult as sulphonyl groups are introduced into the molecules.

N,N-bis-phenylnitroxide is readily isolated, though unstable; while as this work has shown (N-aryl-N-arylsulphonyl)aminyl-oxides and N,N-bis-(arylsulphonyl)aminyloxides can only be detected by e.s.r. spectrometry, even though their oxidation products do appear to contain the free radical. (See diagram for general reactions of arylsulphonylhydroxylamines.)

Although no stable neutral analogues of Fremy's salt were isolated as such during this work, it has shown that these species not only exist, but along with their related compounds possess a chemistry which is both interesting and challenging, in this somewhat neglected field.

REFERENCES

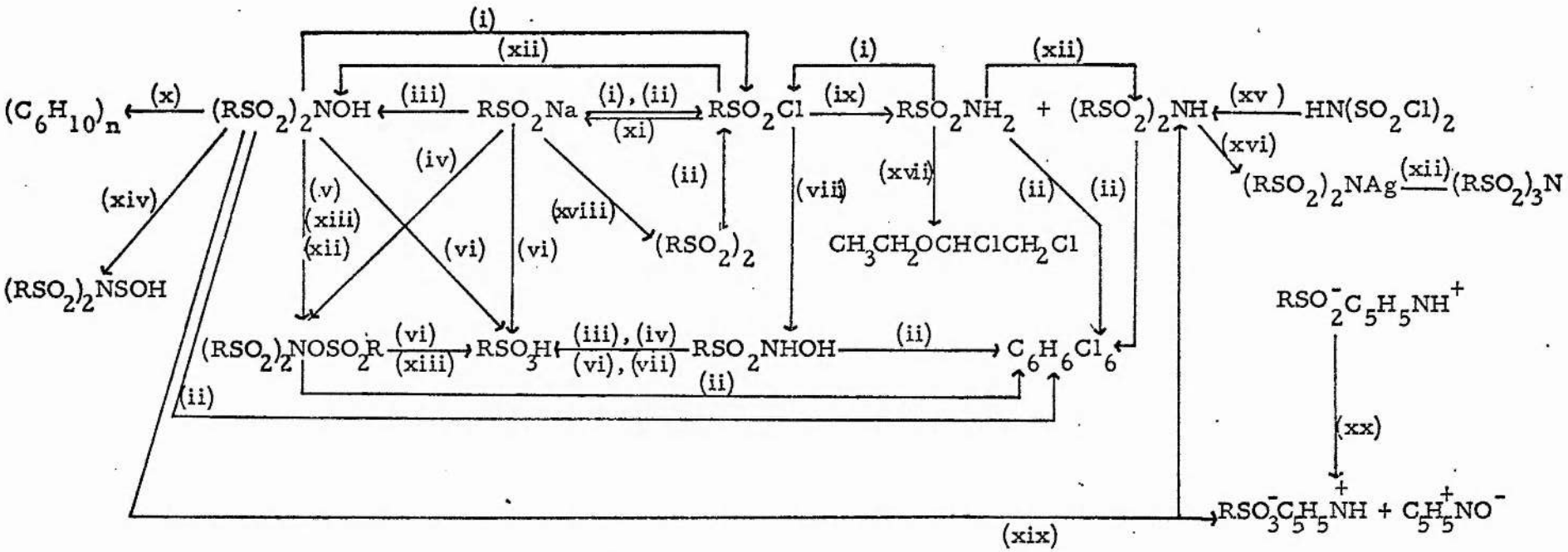
1. C.S. Marvel and R.S. Johnson, J. Org. Chem., 1948, 13, 822

2. A.R. Forrester, J.M. Hay and R.H. Thomson, "Organic Chemistry of Stable Free Radicals', Chapter 5, London-New York; Academic Press, 1968

3. A.T. Balaban and N. Negoita, Rev. Roumainie Chim., 1972, 17, 1227

4. G.M. Brown and O.A.W. Strydom, Acta Crystallogr., 1977, B33, 1591

The General Reactions of Arylsulphonylhydroxylamines and their Related Compounds



(i) $NOCl-Et_2O$ (ii) $Cl_2-C_6H_6$ (iii) aq.HNO_2 (iv) HNO_3 (v) $PbO_2-C_6H_6$ (vi) $NO-Et_2O/C_6H_6$ (vii) aqu. oxidants (viii) NH_2OH (ix) $NH_3(g)$ (x) PbO_2/cyclohexene (xi) Zn/propanal/Na_2CO_3 (xii) RSO_2Cl (xiii) decomposition with evolution of NO_x (xiv) SO_2 (l) (xv) $2C_5H_{10}NH$ (xvi) $AgNO_3$ (xvii) Cl_2-Et_2O (xviii) $KMnO_4/CH_3CO_2H$ (xix) pyridine (xx) NO_2

APPENDIX

A.1 CARBON-13 NUCLEAR MAGNETIC RESONANCE EXAMINATION OF ARENESULPHINATES AND ARYLSULPHONAMIDES

To date very little work[1,2] has been reported concerning the ^{13}C n.m.r. spectra arylsulphonamides, arenesulphinates and arylsulphonylhydroxylamines. The ^{13}C n.m.r. spectra of the N,N-bis-(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOH$, and N,N,O-tris-(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$, are reported in Chapter 3, (Tables 3.8 and 3.9), while the spectra of (N-phenyl-N-phenylsulphonyl)hydroxylamine and [N-phenyl-N,O-bis-(phenylsulphonyl)]hydroxylamine are recorded in Chapter 7, (Table 7.6). Table A.1 records the spectra of the previously reported compounds while Table A.2 considers the spectra of simple arylsulphonamides and arenesulphinates.

Assignments, which are to be regarded as tentative only, were based upon the following considerations:

(i) off resonance decoupling distinguishing the resonances due to quaternary carbon atoms from those due to C-H;

(ii) the resonances of carbon bonded to chlorine were assigned by use of their observed long relaxation times;

(iii) in $p\text{-}FC_6H_4X$ species, the resonances were assigned by means of J(C-F), C_1 and C_2 being distinguished by off-resonance decoupling;

(iv) use of the appropriate additive properties of substituent effects on chemical shifts, as well as internal comparisons, enabling most of the assignments to be made.

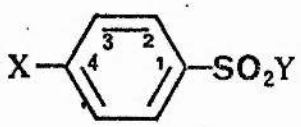


Table A.1

X	Y	Solvent (M)	Carbon Atoms (p.p.m.) C_1	C_2	C_3	C_4
NH_2 2	NH_2	DMSO(M)	131.3	128.4	113.6	152.5
		$NaOD/D_2O$(M)	136.9	127.1	115.6	149.6
NH_2 2	$NHC(NH)NH_2$	DMSO(M)	131.0	127.9	113.0	151.9
NH_2 2	NH– 	DMSO(M)	126.0	129.1	112.8	152.8
		$NaOD/D_2O$(M)	131.9	128.5	115.2	150.4
NH_2 2	NH– 	DMSO(M)	125.0	130.2	112.4	153.2
		$NaOD/D_2O$(M)	131.9	128.4	115.3	150.2
$CH_3C_6H_5$ 3			125.6	128.5	129.3	137.8
$NH_2C_6H_5$			119.2	130.0	116.3	147.9

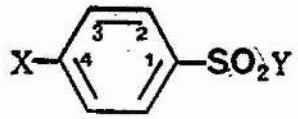


Table A.2

X	Y	Solvent (M)	Carbon Atom (p.p.m.) C_1	C_2	C_3	C_4	Others
CH_3	NH_2	Me_2CO (2M)	143.19	126.71	130.01	141.79	$\delta(CH_3)$ 21.27
H	NH_2	Me_2CO(2.5M)	144.77	126.70	129.58	132.64	
H	OH [1]	H_2O	143.5	126.3	129.8	132.3	
H	Cl [1]	$CDCl_3$	144.1	126.8	129.7	135.3	
CH_3	Na^+	H_2O (1.2M)	153.14	131.84	125.82	143.27	$\delta(CH_3)$ 22.94
H	Na^+	H_2O (2M)	156.03	131.45	125.92	132.86	
Cl	Na^+	H_2O (0.4M)	154.36	131.58	127.78	129.69	
F	Na^+	H_2O (0.4M)	130.62	118.49	128.44	149.42	
		coupling J=9.4Hz		22.2	8.9	240.1	
MeO	Na^+	H_2O (0.4M)	157.83	130.00	116.79	127.93	$\delta(CH_3)$ 56.97
CH_3	p-$CH_3C_6H_4SO_2NH$	DMSO (0.3M)	142.4	127.3	128.7	141.1	$\delta(CH_3)$ 21.1
Cl	p-$ClC_6H_4SO_2NH$	Me_2CO(0.2M)	139.76	130.07	129.58	140.40	
H	C_2H_5	$CHCl_3$	133.59	129.26	128.19	133.66	$\delta(CH_3)$ 18.10 $\delta(CH_2)$ 50.62

A.2 SOME ATTEMPTED REACTIONS WITH HYDROXYLAMINE

(i) In Chapter Four, N,N-bis-(diethylaminosulphonyl)imide, $(Et_2NSO_2)_2NH$, was synthesised from diethylamine and imido-bis-(sulphuryl chloride). The analogous hydroxylamine, $(Et_2NSO_2)_2NOH$, could be approached by the reaction of diethylsulphonyl chloride with hydroxylamine (1).

$$Et_2NSO_2Cl + NH_2OH \longrightarrow Et_2NSO_2NHOH \xrightarrow{Et_2NSO_2Cl} (Et_2NSO_2)_2NOH \quad (1)$$

The reaction of diethylsulphamoyl chloride with hydroxylamine hydrochloride

Diethylsulphamoyl chloride was prepared[4] from diethylamine and sulphuryl chloride. (84%; Found: C, 27.8; H, 5.9; N. 8.0%. $C_4H_{10}NClO_2S$ requires: C, 28.0; H, 5.9; N, 8.2%. The sulphamoyl chloride (8.58 g, 0.05 mol) was gradually added over 15 minutes to a stirred suspension of hydroxylamine hydrochloride, (3.48 g, 0.05 mol), in ethanol (150 ml) containing triethylamine, (10.1 g, 0.1 mol). After stirring during 24 h. any triethylamine hydrochloride was filtered, and the solvent evaporated from the resulting filtrate. No homogenous product could be isolated. Identical results were obtained with benzene.

(ii) In an attempt to synthesise bis-hydroxylamines which contain phosphorus atoms rather than sulphur atoms the reactions of diphenylphosphoryl chloride, diphenyl phosphite and diphenyl-chlorophosphine with hydroxylamine may prove interesting. All of these species have been isolated[5], and could therefore react with a mole of $(\emptyset O)_2P(O)Cl$ or $\emptyset_2PCl$ and form a suitable hydroxylamine to be oxidised to an aminyloxide, eg. (1)

$$(\text{ØO})_2\text{P(O)NHOH} + (\text{ØO})_2\text{P(O)Cl} \longrightarrow [(\text{ØO})_2\text{P(O)}]_2\text{NOH}$$

$$\xrightarrow{\text{oxidation}} [(\text{ØO})_2\text{P(O)}]_2\text{NO}^{\bullet}$$

The attempted reactions are outlined in Table A.3. No homogenous product was isolated for any of the reactions.

Table A.3

Some attempted reactions with hydroxylamine hydrochloride

Substrate	base	solvent	conditions
$(\phi O)_2P(O)Cl$	Et_3N	C_6H_6	stir, 24 h.
	NH_3	EtOH	stir, 24 h.
	-	EtOH	reflux
	Et_3N	petrol	0^o, stir 24 h.
	Et_3N	CCl_4	0^o, stir 24 h.
	Et_3N	ether	0^o, stir 24 h.

Table A.4

Mass Spectrum of the product from the reaction of silver N-(p-tolylsulphonyl)anilide with toluene-p-sulphonyl chloride

m/e	I(%)	Assignment
91	100	$CH_3C_6H_4^+$
139	27.3	$CH_3C_6H_4SO^+$
155	75.8	$CH_3C_6H_4SO_2^+$
167	6.1	$C_6H_5NC_6H_4^+$
172	4.5	$CH_3C_6H_4SO_3H^+$
182	10.6	$C_6H_5NC_6H_4CH_3^+$
215	6.2	$C_6H_5NHSC_6H_4CH_3^+$
247	15.2	$C_6H_5NHSO_2C_6H_4CH_3^+$
369	6.4	$C_6H_5N(SC_6H_4CH_3)SO_2C_6H_4CH_3^+$
401	9.1	$C_6H_5N(SO_2C_6H_4CH_3)_2$

A.3 THE PREPARATION OF N,N-BIS-(p-TOLYL-SULPHONYL)ANILIDE

(i) Reaction of aniline with toluene-p-sulphonyl chloride

Triethylamine (10.1 g, 0.1 mol) was gradually added during 15 minutes to a stirred mixture of aniline (9.3 g, 0.1 mol) and toluene-p-sulphonyl chloride (19 g, 0.1 mol) in benzene (150 ml). After stirring during 3 days filtration of any triethylamine hydrochloride was followed by evaporation of the solvent to afford a clear oil. The oil was dissolved in benzene (100 ml) and thoroughly washed with water (5 x 100 ml) and then stirred overnight. After a further washing the solution was dried over anhydrous sodium sulphate for 24 h.. Removal of the drying agent was followed by evaporation of the solvent, and addition of petroleum spirit (200 ml). The product was filtered and recrystallised from benzene (16.9 g, 0.068 mol, 68%, mp 112-114°, lit. 115-116°). Found: C, 63.1; H, 5.3; N, 5.6%. $C_{13}H_{13}NO_2S$ requires: C, 63.1; H, 5.3; N, 5.7%.

(ii) Reaction of N-(p-tolylsulphonyl)anilide with sodium hydroxide and silver nitrate

Aqueous sodium hydroxide (0.8 g, 0.02 mol) was slowly added to an aqueous suspension of N-(p-tolylsulphonyl)anilide (4.9 g, 0.02 mol). Evaporation of the solvent after stirring during 24 h. afforded a white solid which was dissolved in water and added dropwise to a solution of silver nitrate (3.4 g, 0.02 mol). The product (6.0 g, 0.017 mol, 84.5%) was dried at 40°. Found: C, 42.4; H, 3.1; N, 3.8%. $C_{13}H_{12}NAgO_2S$ requires: C, 44.1; H, 3.4; N, 4.0%.

(iii) Reaction of silver N-(p-tolylsulphonyl)anilide with toluene-p-sulphonyl chloride

The silver salt (7 g, 0.02 mol) and toluene-p-sulphonyl chloride (3.8 g, 0.02 mol) were ground together in a pestle and mortar, and the mixture heated to 170° on an oil bath under oil pump vacuum for 3h.. Extraction of the residue with benzene (200 ml) afforded a dark red-blue oil on removal of the volatiles. The mass spectrum of the product is given in Table A-4. A ^{1}H n.m.r. spectrum of the product (C_6D_6) contained a very broad region over δ 6.80-8.0 (13H) and two singlets at δ 2.34 (3H) and 2.46 (3H) p.p.m.. Found: C, 49.0; H, 4.9; N, 4.2%. Column chromatography (30 g, M-60 silica) with 42% T.H.F. in hexane isolated a dark blue powdery solid. Found: C, 50.2; H, 4.9; N, 2.5%. $C_{20}H_{19}NO_4S_2$ requires: C, 60.0; H, 4.8; N, 3.5%. No pure N-phenyl-N,N-bis-(p-tolylsulphonyl)imide could be isolated.

A.4 REACTION OF N,N-BIS(p-TOLYLSULPHONYL)-HYDROXYLAMINE WITH PYRIDINE IN THE PRESENCE OF CYCLOPENTADIENE MONOMER

In Chapter 5 an attempt to isolate a diene adduct of $ArSO_2NO$, during the oxidation of N,N-bis-(p-tolylsulphonyl)-hydroxylamine with lead (IV) oxide, was reported. The same species was also postulated during the reaction of pyridine with N,N-bis-(p-tolylsulphonyl)hydroxylamine. No adduct was isolated during the oxidation, but the reaction of $(p\text{-}CH_3C_6H_4SO_2)_2NOH$ with pyridine takes a different course when cyclopentadiene is present. N,N-bis-(p-tolylsulphonyl)imide was formed as described for the pyridine reaction but neither $C_5H_5\overset{+}{N}HSO_2C_6H_4CH_3\text{-}p$ or $C_5H_5\overset{+}{N}HSO_3C_6H_4CH_3\text{-}p$, nor an adduct of $ArSO_2NO$ with cyclopentadiene was detected; instead the only product containing cyclopentadiene was $C_5H_5OSO_2C_6H_4CH_3\text{-}p$. (m/e Found: 236.0511 a.u.; $^{12}C_{12}{}^{1}H_{12}{}^{16}O_3{}^{33}S_1$ requires: 236.0507).

REFERENCES

1. J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972

2. C.J. Chang, H.G. Floss and G.E. Peck, J. Medicinal. Chem., 1975, 18, 505

3. L.F. Johnson and W.C. Jankowski, Carbon-13 NMR Spectra, Wiley, New York, 1972.

4. W.W. Binkley and E.F. Degernig, J. Amer. Chem. Soc., 1939, 61, 3250

5. L. Cates, J. Med. Chem., 1968, 11, 382

PUBLICATIONS

1. J.D. Birchall and C. Glidewell, J.Chem.Soc.(Dalton), 1977, 10.
"Sulphur-Nitrogen Compounds: the Preparation, Oxidation and Decomposition of N,N-bis-(arylsulphonyl)-hydroxylamines"

2. J.D. Birchall and C. Glidewell, ibid., 1977, 1976.
"Sulphur-Nitrogen Compounds, Part 2. Reactions of Arylsulphonylhydroxylamines with Nitrosyl Chloride, Nitrogen (II) Oxide, and Chlorine, and Some Related Reactions"

3. J.D. Birchall and C. Glidewell, Inorg.Chim.Acta, submitted for publication.
"Sulphur-Nitrogen Compounds, Part 3. Reaction of Heavy-metal Cations with Nitrosodisulphonate, Hydroxylamine-N,N-disulphonate, and Similar Anions"

4. J.D. Birchall and C. Glidewell, ibid., 1977, 25, L67.
"Sulphur-Nitrogen Compounds, Part 4. Reactions of Bis-(tolylsulphonyl)hydroxylamines with Bases"

5. J.D. Birchall and C. Glidewell, "Chlorination Process", British Patent applied for 46304/77.

6. J.D. Birchall and C. Glidewell, in press JCS (Dalton).
"Sulphur-Nitrogen Compounds, Part 5. Preparation and Oxidation of (N-aryl-N-arylsulphonyl)hydroxylamines