THE CHEMISTRY OF SULPHEN INTERMEDIATES

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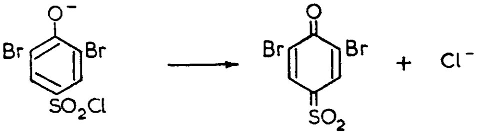
1. Introduction

THE preparation and reaction of keten and its derivatives have been studied in detail in the last fifty years. Similar studies on the sulphonyl analogues of keten, the sulphens ($RR'C{=}SO_2$), have been limited and, until recently, inconclusive. It now appears that sulphens can be conveniently generated by ionic and photochemical methods. In the presence of a suitable acceptor both saturated and unsaturated cyclic sulphones are produced. To date, this area has not been formally reviewed. In the present manuscript an attempt has been made to summarise all synthetic and mechanistic work in this area of sulphur chemistry.

2. Production of Sulphens from Sulphonyl Halides in the Presence of Base

As indicated above, studies in this area have been limited. The earliest reference to the intermediacy of a sulphen is found in the work of Zincke and Brune[1] who studied the decomposition of 2,5-dibromo-4-hydroxybenzenesulphonyl chloride in the presence of sodium acetate. Initially, a yellow colour developed, followed by the formation of a polymer. A semiquinone sulphen was proposed as the intermediate. Such a species could arise by intramolecular displacement of a halide ion from the phenolate ion. Based on our present knowledge of the reactions of quinones and semiquinones such a scheme seems reasonable. Subsequently, it was found that the treatment of toluene-α-sulphonyl chloride with triethylamine produced stilbene and triethylamine hydrochloride.[2] The proposed mechanism for this reaction involved initial abstraction of a proton to produce a benzylic carbanion, chloride-ion elimination to produce the sulphen, loss of SO_2 to form phenylcarbene, and dimerisation of the carbene to produce stilbene.



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[1] T. Zincke and R. Brune, *Ber.*, 1907, **41**, 902.
[2] E. Wedekind and D. Schenk, *Ber.*, 1911, **44**, 198.

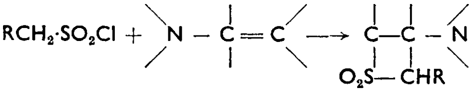
$$\mathrm{Ph{\cdot}CH{-}SO_2{-}Cl \longrightarrow Ph{\cdot}CH{=}SO_2 + Cl^-}$$

$$\mathrm{PhCH{=}SO_2 \longrightarrow Ph\ddot{C}H + SO_2}$$

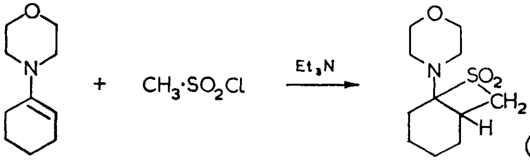
$$\mathrm{2\,Ph\ddot{C}H \longrightarrow PhCH{=}CHPh}$$

Further work with related compounds yielded sulphur-containing derivatives which could have been readily derived from sulphen intermediates.[3,4] Recently, it has been found that if this reaction is carried out in cyclohexane $C_6H_5{\cdot}C(Cl){:}SO$ is formed.[5] It should be emphasized that alternative reaction paths for the formation of stilbene are available, *e.g.*, dimerisation of the sulphen intermediate followed by the loss of two molecules of sulphur dioxide.

Further studies on the generation of sulphens from sulphonyl halides in the presence of base remained dormant until recent studies on the interaction of sulphonyl chlorides with enamines. Stork and co-workers[6] found that aromatic sulphonyl chlorides react with enamines to give, after hydrolysis, β-oxosulphones. This finding was extended to aliphatic sulphonyl chlorides[7,8] and, in the presence of triethylamine, cyclic sulphones were produced. For example, in dioxan solution at room temperature,



reaction of the morpholine enamine of cyclohexanone with one equivalent of methanesulphonyl chloride and one equivalent of triethylamine gave an excellent yield of the cyclic sulphone (I). A similar product is obtained



(I)

from the reaction of methanesulphonyl chloride with the morpholine enamine of cyclopentanone. An alternative mechanism for these reactions is initial formation of an acyclic immonium salt which, after proton abstraction, rearranges to an unstable cyclic immonium salt. Subsequent rearrangement as shown in Scheme 1 would yield the cyclic sulphone.

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[3] E. Wedekind, D. Schenk, and R. Stüsser, *Ber.*, 1923, **56**, 633.

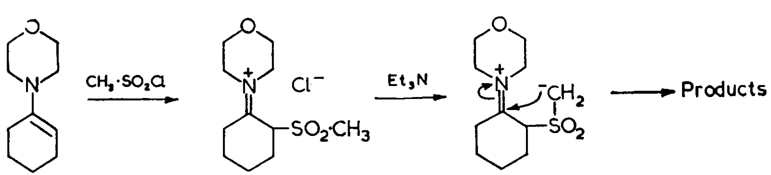
[4] E. Wedekind and R. Stüsser, *Ber.*, 1923, **56**, 1557.

[5] J. F. King and T. Durst, *Tetrahedron Letters*, 1963, 585.

[6] G. Stork, Abstracts, 16th National Organic Chemistry Symposium, Seattle, Washington, June, 1959, p. 52.

[7] G. Stork and I. J. Borowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 313.

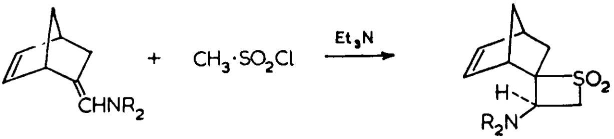
[8] G. Opitz and H. Adolph, *Angew. Chem.*, 1962, **74**, 77.



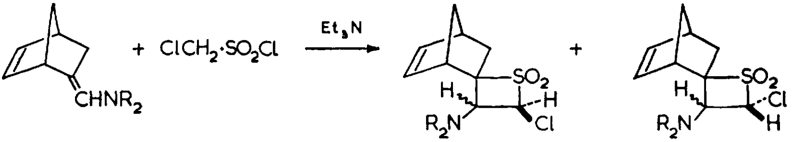
SCHEME 1

This possibility seems unlikely since, in the absence of triethylamine, reaction of an excess of enamine with methanesulphonyl chloride produces only trace amounts of the corresponding methylsulphonyl ketone.[9] Another important aspect of these reactions is that the enamine must be present when the sulphonyl chloride and amine are brought into reaction. In the absence of the enamine, the sulphonyl chloride and the amine react rapidly to produce the amine hydrochloride and presumably, a polymeric form of sulphen $[CH_2{\cdot}SO_2]_n$. Subsequent addition of the enamine produces only low yields (~5 %) of the cyclic sulphone.[9]

Interesting extensions of the above enamine–sulphonyl chloride reactions have been carried out. The reaction of bicyclic enamines with methanesulphonyl chloride was found to be stereoselective.[10] Similarly,



the generation of chlorosulphen ($ClCH{:}SO_2$) from α-chloromethanesulphonyl chloride in the presence of a bicyclic enamine produced a mixture of stereoisomers.[11] It is also possible to extend the enamine–sulphonyl chloride reaction to the preparation of bicyclic thiet sulphones by the use of conventional techniques. For example, if the cyclic aminosulphone produced from the reaction of methanesulphonyl chloride with



the pyrrollidine enamine of cyclohexanone is converted into its quaternary ammonium salt by methyl iodide, decomposition under Hoffmann degradation conditions removes the amine fragment and produces 7-thiabicyclo-[4,2,0]oct-1(8)-ene 7,7-dioxide (II).[12]

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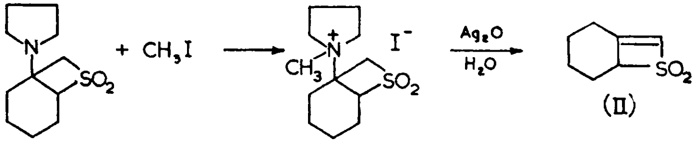
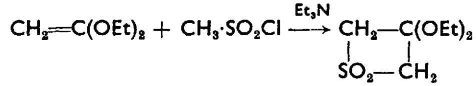
[9] I. J. Borwitz, *J. Amer. Chem. Soc.*, 1964, **86**, 1146.
[10] L. A. Paquette, *J. Org. Chem.*, 1964, **29**, 2851.
[11] L. A. Paquette, *J. Org. Chem.*, 1964, **29**, 2854.
[12] D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, 1964, **29**, 3131.



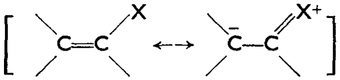
(II)

Closely related to the enamine–sulphonyl chloride reactions is the interaction of keten diethyl acetal and sulphonyl chlorides.[13,14] These reactions are carried out by adding a solution of methanesulphonyl chloride in ether dropwise to a solution of the acetal and triethylamine in ether.

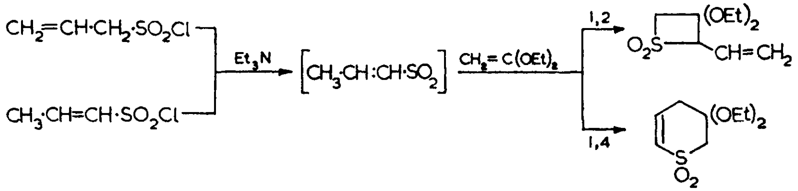


$$CH_2{=}C(OEt)_2 + CH_3{\cdot}SO_2Cl \xrightarrow{Et_3N} \begin{array}{l} CH_2{-}C(OEt)_2 \\ | \quad\;\; | \\ SO_2{-}CH_2 \end{array}$$

This reaction has been employed in the synthesis of a large number of new thietan 1,1-dioxide (cyclic sulphone) derivatives. The cyclisation is apparently quite dependent on the nature of R in $RCH_2{\cdot}SO_2Cl$. Cyclisation occurs when R is an acidifying group but not when it is an alkyl group. Several other unsaturated systems were tested unsuccessfully as sulphen acceptors. Attempts to isolate products from the reaction of methanesulphonyl chloride with the following unsaturated compounds were unsuccessful: ethyl vinyl ether, *p*-tolylmercaptoethane, ethoxyacetylene, diphenylketen, keten diethyl mercaptal, vinylidene chloride, and cyclopentadiene. Based on these results, it would seem that cyclisation occurs most readily when the transition state is highly polar, *i.e.*:



One extremely interesting application of the above reaction is the reaction of allylsulphonyl chloride and prop-1-enesulphonyl chloride with triethylamine and keten diethyl acetal. Both sulphonyl chlorides gave two sulphones in combined yields of 50—60%.[14] Apparently, both reactions proceed by competing 1,2- and 1,4-additions. The structures of both sulphones were elucidated by infrared and nuclear magnetic resonance studies. The reactions of methanesuphonyl chloride with keten diamines



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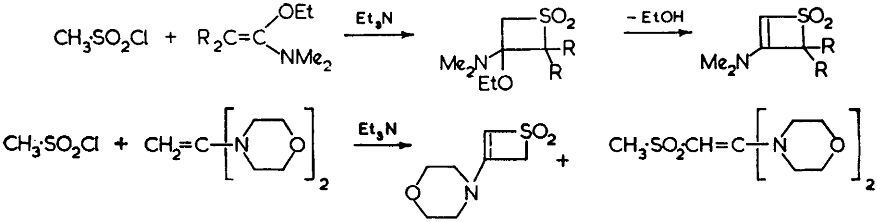
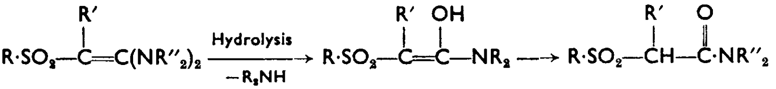
[13] W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Amer. Chem. Soc.*, 1962, **84**, 3030.

[14] W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, 1963, **85**, 3231.

and amino-ethers have also been investigated.[15] The latter readily form cyclic adducts which eliminate ethanol to give the corresponding thiet sulphone. The dimorpholino-acetal gives a cyclic and an acyclic adduct. The diamines predominate in polar solvents; under acidic conditions they can be hydrolysed to amides.[16]





$$R\cdot SO_2-\overset{R'}{C}=C(NR''_2)_2 \xrightarrow[-R_2NH]{\text{Hydrolysis}} R\cdot SO_2-\overset{R'}{C}=\overset{OH}{C}-NR_2 \longrightarrow R\cdot SO_2-\overset{R'}{CH}-\overset{O}{\overset{\|}{C}}\cdot NR''_2$$

Recently, more conclusive evidence for the intermediacy of sulphens has been obtained in the methanolysis of methanesulphonyl chloride in the presence of triethylamine.[17] Treatment of a solution of deuteriomethanol and triethylamine in dry benzene with methanesulphonyl chloride produced methyl methanesulphonate. Mass-spectral and nuclear magnetic resonance data for the ester showed it to be a mixture of the monodeuterated, $DCH_2\cdot SO_3CH_3$, and undeuterated ester. Incorporation of deuterium into the ester can be explained by one of two paths: (i) proton–deuterium exchange *via* the carbanion of the sulphonyl chloride and/or the sulphonate ester:

$$CH_3\cdot SO_2X + B: \rightleftharpoons {}^{-}CH_2\cdot SO_2X + BH^{+} \rightleftharpoons \text{etc.}$$

(ii) an elimination–addition sequence involving an intermediate sulphen:

$$CH_3SO_2X + Et_3N \xrightarrow{-Et_3N,HX} CH_2\cdot SO_2 \xrightarrow{CH_3OD} DCH_2\cdot SO_3CH_3$$

Formation of the monodeuterated ester is consistent with the latter path while the absence of di- and tri-deuterates precludes the former path.

3. Sulphen Production by Photochemical and Related Methods

As previously indicated, reaction of toluene-ω-sulphonyl chloride with triethylamine gives stilbene.[2] An analogous reaction has been reported by Staudinger and Pfenninger[18] who observed that diphenyldiazomethane in

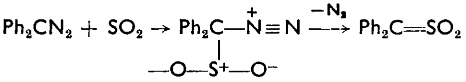
[15] R. H. Hasck, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, 1965, **30**, 1495.

[16] G. Opitz and H. S. Schempp, *Annalen*, 1965, **684**, 103.

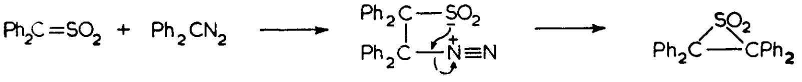
[17] W. E. Truce, R. W. Campbell, and J. R. Norell, *J. Amer. Chem. Soc.*, 1964, **86**, 288.

[18] H. Staudinger and F. Pfenninger, *Ber.*, 1961, **49**, 1941.

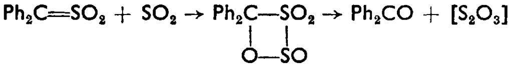
an inert solvent readily reacts with sulphur dioxide to produce tetraphenylethylene sulphone and tetraphenylethylene. Initial reaction of the diazo-compound with sulphur dioxide, followed by loss of nitrogen, could lead to diphenylsulphen. Reaction of the sulphen with another molecule of the diazo-compound leads possibly to a dipolar intermediate which cyclises to the sulphone upon loss of another molecule of nitrogen.



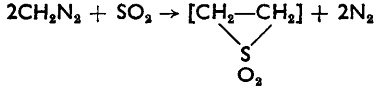
$$\mathrm{Ph_2CN_2 + SO_2 \rightarrow \begin{array}{c}Ph_2C-\overset{+}{N}\equiv N\\ |\qquad\quad\\ -O-S^+-O^-\qquad\end{array} \xrightarrow{-N_2} Ph_2C{=}SO_2}$$



Subsequent expulsion of sulphur dioxide yields tetraphenylethylene. If excess of sulphur dioxide is employed, a competing reaction which leads to the formation of benzophenone occurs. This could involve addition of sulphur dioxide to diphenylsulphen followed by loss of $[S_2O_3]$. If this reaction is carried out in a protic medium products typical of a sulphen intermediate are formed. In water, methanol, and ethanol the sulphonic acid and its corresponding methyl and ethyl esters, respectively, are produced. If the reaction is carried out in the presence of a secondary amine, sulphonamides are formed.[19] Similarly, the reaction of diazomethane with sulphur dioxide has led to the first synthetic route to ethylene sulphone.[20] As expected, the reaction of an arylalkyldiazomethane with sulphur dioxide produces diaryldialkylethylenes.[21]



$$\mathrm{Ph_2C{=}SO_2 + SO_2 \rightarrow \begin{array}{c}Ph_2C-SO_2\\ |\qquad|\\ O-SO\end{array} \rightarrow Ph_2CO + [S_2O_3]}$$



$$\mathrm{2CH_2N_2 + SO_2 \rightarrow \left[\begin{array}{c}CH_2-CH_2\\ \diagdown\ \diagup\\ S\\ O_2\end{array}\right] + 2N_2}$$

An excellent study on the generation of sulphens by the photochemical decomposition of unsaturated sultones has been carried out by King and co-workers.[22] Irradiation of sultone (III) in methanol resulted in the formation of the corresponding methyl ester (IV). The structure of the ester was confirmed by alkaline cleavage to benzoic acid and the known

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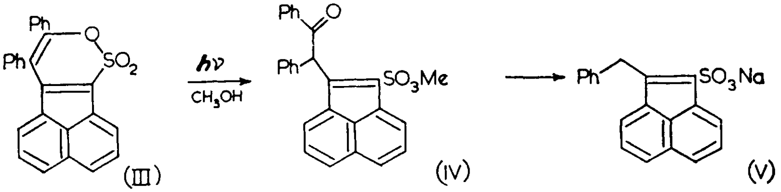
[19] H. Kloosterzeil, M. H. Deinema, and H. J. Bäcker, *Rec. Trav. chim.*, 1952, **71**, 1288, 1235.

[20] G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, 1957, **90**, 2106.

[21] L. V. Vargha and E. Kovacs, *Chem. Ber.*, 1962, **75**, 794.

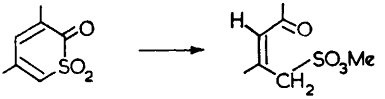
[22] J. F. King, P. DeMayo, E. Morkved, A. B. M. A. Sattar, and A. Stoessl, *Canad. J. Chem.*, 1963, **41**, 100.



(III) (IV) (V)

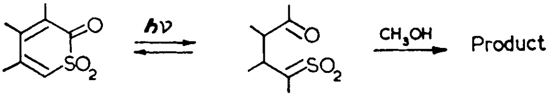
sodium sulphonate (V). Similarly, sultone (VI) yielded the methyl ester (VII) when irradiated in methanol. Irradiation of compound (VI) in ether

(VI)



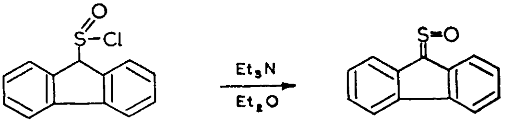
(VII)

in the presence of excess benzylamine gave the corresponding sulphonamide, which was isolated in crystalline form as its 2,4-dinitrophenylhydrazone. Thus, it appears that these photolyses involve initial bond rearrangement to a sulphen.



4. Related species

Recently, several new sulphur-containing intermediates similar to sulphens have been prepared. The first class of compounds to be considered is sulphines (*S*-oxides of thioketones). Sulphines, like the *S*-oxides of thioamides[23] and thioacid chlorides[5] [O=S=C(R)X; X=NR_2 or Cl] are stable enough to be isolated. Like sulphens, sulphines are generated in the presence of an amine in an inert solvent (ether). For example, treatment of 9-fluorenesulphinyl chloride with triethylamine in ether at room temperature resulted in the production of fluorenylidene sulphine[24] in ~75% yield. The sulphine decomposes slowly on standing at room temperature for several days and rapidly at its melting point, evolving sulphur



dioxide. Difluorenylidene (48% yield) was the major product along with a trace of fluorenone. In the presence of the morpholine enamine of cyclo-

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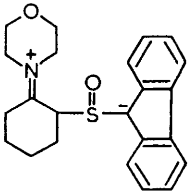
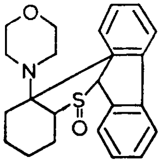
[23] W. Walter and K. D. Bode, *Annalen*, 1962, **660**, 74.

[24] W. A. Sheppard and J. Diekmann, *J. Amer. Chem. Soc.*, 1964, **86**, 1891.

hexanone an acyclic, dipolar sulphoxide (VIII) is produced rather than the cyclic sulphoxide (IX). Failure to obtain a stable cyclic sulphoxide under these conditions could be due partly to the bulkiness of the fluorenyl group. Similarly, the reaction of triethylamine with isopropylsulphinyl chloride in methylene chloride at —20° yielded isopropylidene sulphine (thioacetone *S*-oxide). At room temperature the aliphatic sulphine was unstable and yielded a polymer.

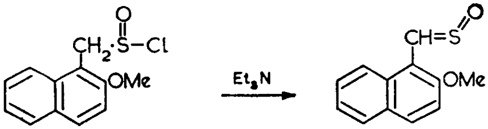


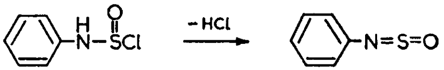
(VIII)



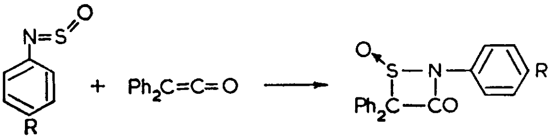
(IX)

To date, only one example of a thioaldehyde *S*-oxide has been reported. Treatment of 2-methoxy-1-naphthylmethylsulphinyl chloride with triethylamine in ether gave the corresponding sulphine.[25]. Similarly, *N*-sulphinylaniline has been prepared from its corresponding *N*-sulphinyl chloride.





In the presence of diphenylketen and bicycloheptene addition across the N=S bond occurs to produce cyclic aminosulphoxides.[26]



As shown above, sulphines are stable enough to be isolated. In contrast, sulphens have only been proposed as unstable intermediates when nitrogen bases react with alkanesulphonyl chlorides. Indeed, the one isolated report of a stable sulphen[27] has recently been proved false.[22] Based on the above reactions, it would also appear that the addition of sulphines to unsaturated compounds requires a less polar transition state than that required for sulphens.

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[25] J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. chim.*, 1964, **83**, 631.
[26] G. R. Collins, *J. Org. Chem.*, 1964, **29**, 1688.
[27] A. Locker and H. E. Fierz, *Helv. Chim. Acta*, 1927, **10**, 642.