Evidence for the Nucleophilicity of the Oxygen Atoms of *NN*-Dihalogenosulphonamides in the Addition of *NN*-Dichlorobenzenesulphonamide to *cis*- and *trans*-But-2-ene

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THE addition of *NN*-dihalogeno-amide derivatives,[1-4] particularly *NN*-dichlorocarbamates,[1,2] to olefins is of considerable interest. We now report that the addition of *NN*-dichlorobenzenesulphonamide (Dichloramine B) to the isomeric but-2-enes produces a novel β-chloro-iminosulphonate derivative in addition to the expected β-chlorosulphonamide adduct.

The reaction of Dichloroamine B with *trans*-but-2-ene at −10° gives an oily mixture of mono-adducts. Reduction of the *N*-chloro-group of this mixture with aqueous sodium sulphite affords a 61% yield of *erythro*-sulphonamide† (I-*e*) and a 30% yield of a mixture of diastereomers which have been assigned the β-chloro-iminosulphonate structure (II-*e*).

The structural assignment for compound (I-*e*) has been made on the basis of its elemental analysis, n.m.r.,[5] and i.r. spectra and by its ready conversion into the *trans*-aziridine[5,6] (III-*trans*) in 93% yield.

The β-chloro-iminosulphonate, (II-*e*), gives the correct elemental analysis for $C_{10}H_{14}ClNO_2S$, and a molecular weight of 276. The i.r. spectrum contains a band at 3300 cm.$^{-1}$ (⟩C=NH).[7] The introduction of another asymmetric centre in the form of the pyramidal sulphur affords equal amounts of diastereomers,[8] which display slightly different n.m.r. spectra. The sulphonamide proton of (I-*e*) is readily exchanged by treatment with deuterium oxide. This exchange removed the n.m.r. peak assigned to the NH and simplifies the multiplet assigned to the adjacent proton by elimination of the 9·0 Hz coupling with NH. A similar treatment of (II) removes the NH signal but has no further effect on the spectrum.

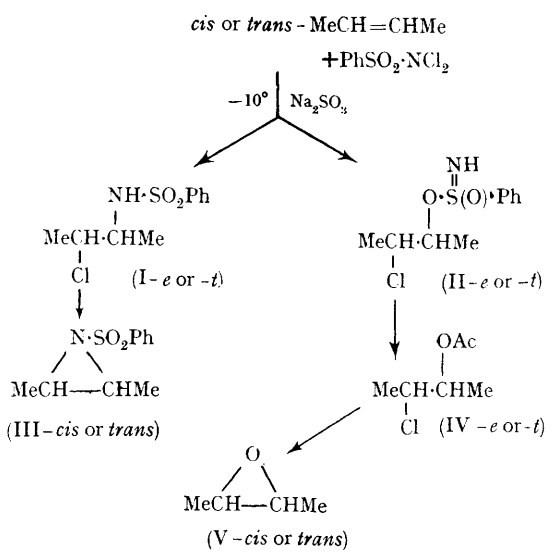
When compound (II-*e*) is heated with glacial acetic acid on a steam bath for 0·5 hr., cleavage occurs to give a 72% yield of benzenesulphonamide and a 62% yield of 2-acetoxy-3-chlorobutane. The reaction of the chlorobutyl acetate with hot aqueous potassium hydroxide gives a 95 : 5 mixture of *trans*- and *cis*-2,3-epoxybutane[9] (V-*trans* and -*cis*), indicating that the chlorobutyl acetate is predominantly in the *erythro*-configuration.

Similarly, sodium sulphite reduction of the *cis*-but-2-ene–Dichloramine B adducts gives a 52% yield of *threo*-sulphonamide[5] (I-*t*) and 21% of the *threo*-β-chloro-iminosulphonate (II-*t*).

The *threo*-sulphonamide is converted in 82% yield to the *cis*-aziridine† by reaction with methanolic potassium hydroxide. The *threo*-β-chloro-iminosulphonate gives benzenesulphonamide and chlorobutyl acetate (75 and 56%) on treatment with acetic acid. This latter acetate is largely in the *threo*-configuration, since conversion to the oxide[10] (V) gives a 92 : 8 mixture of *cis*- and *trans*-isomers respectively.

The addition reaction is insensitive to free-radical inhibitors, proceeding equally well in the dark under an oxygen atmosphere, or under the normal reaction conditions of a nitrogen atmosphere and normal indoor lighting. The highly stereospecific *trans*-addition across the double bond is further evidence for an ionic mechanism.‡

Presumably, the reaction proceeds *via* a bridged chloronium ion[11] which is then opened by either the



† The n.m.r. spectra are in complete agreement with the postulated structures and will be discussed in detail in the full paper.

‡ Examination of the n.m.r. spectra of the aziridines formed from the crude reduction products failed to show greater than 5% of any product arising from *cis*-addition.

N.m.r. data for NN-*dichlorobenzenesulphonamide–but-2-ene adducts*

Compound	R	Chemical shifts[a]				Coupling constants (Hz)			
		δ_{NH}[b]	δ_1	δ_2	δ_3	δ_4	$J_{1,2}$	$J_{1,3}$	$J_{3,4}$	$J_{NH,1}$[b]
(I-*e*)	PhSNH– (O, O)	5·58	3·47	1·03	4·03	1·37	6·6	3·9	6·8	9·0
(II-*e*)[c]	PhS–O– (NH, O)	3·56	4·55 4·57	1·22 1·24	3·95 4·02	1·35 1·37	6·2	4·7	6·6	—
(I-*t*)	PhS–NH– (O, O)	5·14	3·50	1·05	3·98	1·40	6·7	2·8	6·7	9·0
(II-*t*)[c]	PhS–O– (NH, O)	3·50	4·53 4·58	1·16 1·15	3·90 3·94	1·36 1·33	6·5	4·1	6·8	—

R—CH(CH$_3$)—CH(CH$_3$)Cl (positions 1, 2, 3, 4)

[a] N.m.r. spectra were obtained on a standard Varian HA-100 spectrometer. All spectra were obtained for dilute $CDCl_3$ solutions with either Me_4Si or $CHCl_3$ as an internal reference peak for proton-stabilized operation. Chemical shifts are reported as p.p.m. downfield from Me_4Si. All spectral assignments have been confirmed by double and triple irradiation experiments. [b] Only the data from the NH protons in R are given; no attempt to analyse the complex patterns obtained for the aromatic protons was made. [c] Data for two diastereomers (see text) are given. The relative chemical shifts of the two isomers are quite concentration dependent.

nitrogen or the oxygen of the *N*-chlorobenzenesulphonamide anion. The nucleophilicity displayed by the oxygen atoms in this case is quite unusual, since data obtained from spectral studies of simple sulphonamides in strong acid[12] indicate that the oxygen atoms of the sulphonamide group possess little nucleophilic character. The same conclusion has also been reached from a study of the solvolysis of *p*-nitrophenyl-*O*-methanesulphonamidobenzoate.[13]

The solvolyses of the β-chloro-iminosulphonates appear to proceed with participation by the chlorine atom,[14] since retention of configuration about the butane skeleton is observed.

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