# The Nucleophilic Character of *N*-Halogenosulphonamide Ion

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*N*-Chloro-*N*-sodiobenzenesulphonamides react with ethylene oxide in aqueous solution to give the corresponding *N*-chloro-*N*-(2-hydroxyethyl)sulphonamides. The reaction has been shown to involve a nucleophilic attack by *N*-chlorosulphonamide ion on the epoxide; the nucleophilicity of this ion is comparable to that of azide. *N*-Bromobenzenesulphonamide behaves similarly but the instability of the product precludes an accurate assessment of the effect in this case. Two further examples of nucleophilic displacement by *N*-chloro-*N*-sodiosulphonamides are described: the reaction of both aromatic and aliphatic derivatives with propanesultone in water and the reaction of the aliphatic species with ethylene sulphate in acetone.



THE majority of the reactions of *N*-halogeno-*N*-sodioarenesulphonamides described in the literature involve cleavage of the nitrogen–halogen bond.[1] Recent kinetic investigations of the reactions of *N*-chloro-*N*-sodiotoluene-*p*-sulphonamide with *p*-cresol,[2] succinimide,[3] and sulphides [4,5] have shown that, in each case, a nucleophilic displacement of chlorine occurs by way of either the conjugate acid or its disproportionation product, *NN*-dichlorotoluene-*p*-sulphonamide.

A search of the literature did not reveal any previous demonstration of the ability of the *N*-halogenosulphonamide ion to take part in nucleophilic displacements on carbon, although processes of this type on bridged chloronium and bromonium ions have recently been proposed as steps in the addition of *NN*-dichloro- [6] and *NN*-dibromo- [7] benzenesulphonamide to olefins.

A study has now been made of the nucleophilic properties of both aromatic and aliphatic [8] *N*-chloro- and *N*-bromo-*N*-sodiosulphonamides towards saturated carbon; ethylene oxide, propanesultone, and ethylene sulphate have been employed as electrophiles.

## RESULTS AND DISCUSSIONS

The reaction of *N*-chloro-*N*-sodiosulphonamides (1a—d) with ethylene oxide (in excess) proceeds in high yield when the pH of aqueous mixtures at 40° is maintained at about 8 by an automatic titrator on pH-stat operation. The identities of the crystalline products (2)

$$\underset{(1)}{RSO_2{\cdot}NClNa} + \overset{\longrightarrow}{CH_2{\cdot}CH_2{\cdot}O} \xrightarrow{HX} \underset{(2)}{RSO_2{\cdot}NCl{\cdot}[CH_2]_2{\cdot}OH} + NaX$$

a; R = Ph
b; R = *p*-$MeC_6H_4$
c; R = *p*-$ClC_6H_4$
d; R = *m*-$O_2N{\cdot}C_6H_4$

(Table 1) were confirmed by comparison with authentic specimens prepared by the route in Scheme 1. The

$$RSO_2Cl + NH_2{\cdot}[CH_2]_2{\cdot}OH \longrightarrow \underset{(3)}{RSO_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}OH} \xrightarrow{HOCl} (2)$$

SCHEME 1

only observable by-products (t.l.c.) of the epoxide cleavage reaction were trace amounts of the *N*-(2-hydroxyethyl)sulphonamides (3), presumably formed by subsequent hydrolysis of the *N*-chloro-derivatives (2). In the solid state, these materials can be stored for long periods at 0° under anhydrous conditions, but decomposition becomes noticeable at room temperature. *N*-Bromo-*N*-sodiobenzenesulphonamide reacts similarly with ethylene oxide but the product, $PhSO_2{\cdot}NBr{\cdot}[CH_2]_2{\cdot}OH$ (4), is much less stable.

A kinetic investigation of the interaction of the *N*-chloro-species (1) with ethylene oxide was carried out by use of the pH-stat function of an automatic titrator

TABLE 1

Analytical and physical data for the *N*-halogeno-*N*-(2-hydroxyethyl)benzenesulphonamides

| | | Theoretical (%) | | | | Found (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | M.p. (°C) | C | H | N | Available halogen | C | H | N | Available halogen |
| (2a) | 71—72 (72) [a] | 40·75 | 4·3 | 5·95 | 30·1 | 40·75 | 4·25 | 6·05 | 29·7 |
| (2b) | 59—60 (59—61) [a] | 43·25 | 4·85 | 5·6 | 28·4 | 43·3 | 4·8 | 5·5 | 28·4 |
| (2c) | 81—83 | 35·55 | 3·35 | 5·2 | 26·2 | 35·55 | 3·25 | 5·45 | 26·4 |
| (2d) | 97—98 | 34·25 | 3·25 | 10·0 | 25·25 | 34·15 | 3·35 | 10·0 | 24·75 |
| (4) | 99—100 | 34·2 | 3·6 | 5·0 | 57·05 | 34·45 | 3·65 | 5·15 | 56·8 |

[a] M.p. of material prepared by chlorination (HOCl) of the corresponding *N*-(2-hydroxyethyl)sulphonamide.

[1] C. M. Suter, 'Organic Chemistry of Sulphur,' Wiley, New York, 1948, p. 602.
[2] T. Higuchi and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 549.
[3] T. Higuchi, K. Ikeda, and A. Hussain, *J. Chem. Soc.* (*B*), 1968, 1031.
[4] K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Japan*, 1969, **42**, 2631.
[5] F. Ruff and A. Kucsman, *Acta Chim. Acad. Sci. Hung.*, 1969, **62**, 438.
[6] F. A. Daniher, M. T. Melchior, and P. E. Butler, *Chem. Comm.*, 1968, 931.
[7] T. A. Foglia, E. T. Haeberer, and G. Maerker, *J. Amer. Oil Chemists' Soc.*, 1970, **47**, 27.
[8] F. E. Hardy, *J. Chem. Soc.* (*C*), 1970, 2087.

to monitor rate of formation of alkali. Experiments were limited to the pH range 7·5—9·0; at lower pH values, the conjugate acids of the *N*-chloro-*N*-sodiosulphonamides [that of the toluene derivative (1b) has p$K_a$ 4·55] [9] and their disproportionation products [10] must be taken into account, while at higher pH values hydrolysis of *N*-chloro-*N*-alkylsulphonamides becomes significant.[11] A number of other factors, *e.g.* competing hydrolysis of the epoxide and the insolubility of the products (2), as well as their tendency to take part in acid-forming oxidative interactions, meant that kinetic studies were only feasible during the initial phase of reaction; in preliminary experiments (35°) reactions were followed to 6% conversion whilst in the major part of this work (25°) studies were limited to the first 2% of the reaction.

The following results: (i) there is a first-order dependence of rate on both *N*-chloro-compound and epoxide concentrations, (ii) reaction is facilitated by electron-donating substituents in the *N*-chloro-compound and hindered by electron-withdrawing groups [a Hammett plot of kinetic data at 25° shown in Table 2 has a slope (ρ) of −0·44], and (iii) the rate is independent of pH in the range 7·5—9·0 (see, *e.g.*, Table 3); are consistent with a mechanism in which nucleophilic attack by *N*-chlorosulphonamide ion on a carbon atom of the epoxide is rate-determining (Scheme 2).

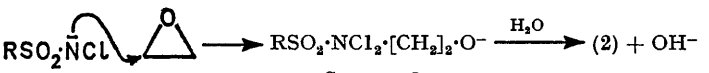
*NN*-dichlorobenzenesulphonamide to but-2-ene at −10° (no solvent). It was proposed that one of the steps in this reaction involves the cleavage of a bridged chloronium ion by *N*-chlorobenzenesulphonamide ion. A noteworthy feature of this work was the isolation of imino-sulphonates as well as the expected sulphonamide addition products, suggesting that both the oxygen and nitrogen atoms of the anion were displaying nucleophilic character. In the present work, nitrogen must clearly be the dominant nucleophilic centre since only sulphonamide derivatives were observed. The high nucleophilic activity of the nitrogen atom in *N*-chlorosulphonamide ion is not surprising. It is frequently found that compounds which contain an electronegative atom (in this case, chlorine) with a free electron pair adjacent to the nucleophilic centre display an unusually high nucleophilicity (the α-effect [16] or supernucleophilicity [17]). There has been much speculation concerning the reason for this enhancement of reactivity and the effect has been discussed in terms of the theory of charge- and frontier-controlled reactions,[17] the effective electron density at the nucleophilic centre,[18] and a repulsive interaction of electron pairs on the adjacent atoms in the nucleophile.[19]

TABLE 2

Kinetic data for the interaction of nucleophiles with ethylene oxide

| Nucleophile | Temp. | No. of determinations | $10^5 k_N$/l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| $PhSO_2 \cdot NCl^-$ | 25° | 6 | 7·63 ± 0·33 [a] |
| $PhSO_2 \cdot NCl^-$ | 35 | 5 | 18·3 ± 1·1 |
| $p\text{-}MeC_6H_4 \cdot SO_2 \cdot NCl^-$ | 25 | 5 | 9·57 ± 0·50 |
| $p\text{-}ClC_6H_4 \cdot SO_2 \cdot NCl^-$ | 25 | 3 | 6·25 ± 0·52 |
| $m\text{-}O_2N \cdot C_6H_4 \cdot SO_2 \cdot NCl^-$ | 25 | 7 | 3·93 ± 0·20 |
| $N_3^-$ | 25 | 4 | 9·00 ± 0·42 |
| $N_3^-$ | 35 | 5 | 22·5 ± 0·7 |
| $I^-$ | 35 | 3 | 78·3 ± 5·8 |
| $Br^-$ | 35 | 3 | 7·0 ± 0·3 |
| $PhSO_2 \cdot NBr^-$ | 25 | 1(7·51) [b] | 8·3 |
| $PhSO_2 \cdot NBr^-$ | 25 | 1(8·03) [b] | 7·2 |
| $PhSO_2 \cdot NBr^-$ | 25 | 1(8·96) [b] | 6·5 |

[a] 95% Confidence limits. [b] pH of determination.




SCHEME 2

Epoxide cleavage is recognised as providing a useful measure of nucleophilicity towards saturated carbon and, indeed kinetic data from such reactions have been correlated with those from other nucleophilic displacements, *e.g.* on methyl bromide and ethyl toluene-*p*-sulphonate, by means of the Swain–Scott equation: [12-14] $\log (k/k_0) = sn$, where $k$ and $k_0$ are the rate constants for reaction of nucleophile and water with a particular substrate, $n$ is the nucleophilic constant of the nucleophile, and $s$ is the substrate reactivity constant. In the present work, the nucleophilicity of *N*-chlorobenzenesulphonamide ion towards ethylene oxide has been compared with those of bromide, azide, and iodide ions, which have nucleophilic constants of 3·89,[12] 4·5,[15] and 5·04,[12] respectively. A plot of log $k$ at 35° (Table 2) against $n$ indicates that the nucleophilic constant of the *N*-chloro-anion is *ca.* 4·4.

Previous reference to the nucleophilicity of *N*-chlorosulphonamide ion towards saturated carbon is limited to a recent communication [6] describing the addition of

It is not possible to make an accurate assessment of the nucleophilicity of *N*-bromobenzenesulphonamide ion. The reaction with ethylene oxide is apparently affected by pH in the range 7·5—9·0 (Table 2), proceed-

[9] J. C. Morris, J. A. Saltar, and M. Wineman, *J. Amer. Chem. Soc.*, 1948, **70**, 2036.
[10] T. Higuchi, K. Ikeda, and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 546.
[11] F. E. Hardy and J. P. Johnston, in preparation.
[12] C. G. Swain and G. B. Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141.
[13] E. A. S. Cavell, R. E. Parker, and A. W. Scaplehorn, *J. Chem. Soc.*, 1965, 4780.
[14] W. L. Petty and P. L. Nichols, *J. Amer. Chem. Soc.*, 1954, **76**, 4385.
[15] A. B. Ash, P. Blumbergs, C. L. Stevens, H. O. Michel, B. E. Hackley, and J. Epstein, *J. Org. Chem.*, 1969, **34**, 4070.
[16] W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, p. 107.
[17] G. Klopman, K. Tsuda, J. B. Louis, and R. E. Davis, *Tetrahedron*, 1970, **26**, 4549.
[18] J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16.
[19] J. D. Aubort and R. F. Hudson, *Chem. Comm.*, 1970, 937.

ing more slowly at higher pH. This almost certainly does not reflect a change in mechanism compared to the *N*-chloro-species but is mainly the result of a much more rapid and extensive hydrolysis of the product,[11] which consumes some of the alkali produced in the epoxide cleavage. It seems reasonable to assume that the rate constant at pH 7·5 will be close to the true value. If this is so, then the data in Table 2 indicate that replacement of chlorine by bromine has little effect on the nucleophilic activity of *N*-halogenosulphonamide ion.

A search for further examples of the nucleophilicity of *N*-chlorosulphonamide ion revealed that both aromatic and aliphatic [8] derivatives react rapidly and cleanly with propanesultone when concentrated aqueous mixtures are warmed to 60—70°. The crystalline products (6; X = Cl) show high stability in the solid state with no significant loss of available chlorine even on prolonged storage at room temperature.

$$\underset{(5)}{RSO_2{\cdot}NXNa} + \overbrace{CH_2{\cdot}[CH_2]_2{\cdot}OSO_2} \longrightarrow \underset{(6)}{RSO_2{\cdot}NX[CH_2]_3{\cdot}SO_3Na}$$

(R = Ph, *p*-$MeC_6H_4$, *p*-$ClC_6H_4$, *o*-$MeC_6H_4$, Me, Et, or $C_{12}H_{25}$)

The identity of the aromatic products was confirmed by comparison with authentic specimens prepared by the route in Scheme 3.

Reaction of the corresponding *N*-bromo-*N*-sodiosulphonamides (5; X = Br) occurred under the same conditions but the much lower stability of the products (6; X = Br) precluded the preparation of pure material by this route. Pure samples, can, however, be obtained by treating the corresponding *N*-chloro-species, in aqueous solution, with an equimolar amount of sodium bromide; conversion is rapid and essentially quantitative.[11]

$$RSO_2{\cdot}Cl + NH_2{\cdot}[CH_2]_3{\cdot}SO_3Na \longrightarrow RSO_2{\cdot}NH{\cdot}[CH_2]_3{\cdot}SO_3Na \xrightarrow{HOCl} (6;\ X = Cl)$$

SCHEME 3

A kinetic analysis of the reaction of *N*-chloro-*N*-sodiosulphonamides with propanesultone was not undertaken because of difficulties in monitoring the reaction and the ease of hydrolysis of the sultone.

*N*-Chlorosulphonamide ion also acts as a nucleophile towards ethylene sulphate. Because of the hydrolytic

$$RSO_2{\cdot}NClNa + \overbrace{CH_2O{\cdot}SO_2{\cdot}OCH_2} \longrightarrow RSO_2{\cdot}NCl{\cdot}[CH_2]_3{\cdot}OSO_3Na$$

instability of the heterocycle, the reaction is best performed under essentially anhydrous conditions. This requirement is more easily satisfied with the aliphatic derivatives (5; X = Cl), particularly the higher homologues, since these can be dehydrated under mild conditions and are readily soluble in acetone.[8]

## EXPERIMENTAL

*N*-Chloro-*N*-sodio-benzenesulphonamide and -toluene-*p*-sulphonamide were obtained from Fluka and B.D.H., respectively; the corresponding *p*-chloro- and *m*-nitro-derivatives were prepared by a published method,[20] as was *N*-bromo-*N*-sodiobenzenesulphonamide.[21] These materials were purified by recrystallisation from water and assayed iodimetrically. Their aliphatic counterparts were prepared as described in an earlier communication.[8] Research grade ethylene oxide and propanesultone (B.D.H.) were employed without further purification; ethylene sulphate was prepared by a published method [22] and redistilled before use.

*Reaction with Ethylene Oxide.*—The Radiometer titration assembly and reaction vessel, used in both preparative and kinetic work, have been described previously.[23]

(a) *Preparative experiments.* These were performed at 40° in a closed system. In general, ethylene oxide (0·2 mol) was added to a solution of the *N*-halogeno-*N*-sodiosulphonamide (0·13 mol) in water (150 ml); pH was maintained in the region 7·5—8·5 by the addition of 4N-sulphuric acid from the SBU 1 syringe burette (5 ml). Reactions were allowed to proceed to 50—70% completion and N-*halogeno*-N-(2-*hydroxyethyl*)*sulphonamides* were isolated by filtration or chloroform extraction in high yield (80—90% based on consumption of *N*-halogeno-*N*-sodiosulphonamide). M.p.s and analytical data for recrystallised specimens are shown in Table 1.

(b) *Kinetic experiments.* Preliminary experiments were carried out at 35 ± 0·05° but the major part of this study was performed at 25 ± 0·05°. In all cases an aqueous system (200 ml, doubly distilled water) was used. Ethylene oxide concentrations were measured just prior to addition of the *N*-halogenosulphonamide by means of the hydrochloric acid–magnesium chloride titration method.[24] In general, the syringe burette (0·5 or 1·0 ml) contained N-sulphuric acid, reagent concentrations were in the range 0·025—0·05M, and reactions, performed in the presence of 0·1M-sodium sulphate, were monitored by recording volume of acid required for pH maintenance against time.

Only the initial period of reaction (<2% conversion at 25°, 6% at 35°) was studied, to minimise the effects of epoxide hydrolysis [25] and the instability and insolubility of the *N*-halogeno-product (2). Control experiments showed that loss of ethylene oxide by evaporation from the closed system used in this work was negligible. It was established that the reaction is first order in each reactant by examining the effect of two-fold variations in initial concentration on the initial rates. Rate constants $k_N$ were determined by solving the second-order rate equation; a computer was used to obtain these data by means of a least mean squares programme. Within the pH range 7·5—9·0, except for *N*-bromo-*N*-sodiobenzenesulphonamide, rate constants were independent of hydroxide ion concentration

[20] J. Petromek and M. Vecera, *Chem. listy.*, 1958, **52**, 1279.
[21] E. Roberts, *J. Chem. Soc.*, 1923, 707.
[22] J. Brunken and G. Glockner, E.Ger. Pat. 15,024 (*Chem. Abs.*, 1960, **54**, 3201).
[23] F. E. Hardy and P. Robson, *J. Chem. Soc.* (*B*), 1967, 1151.
[24] S. Siggia, 'Quantitative Organic Analysis *via* Functional Groups,' Wiley, New York, 1963, p. 238.
[25] J. N. Bronsted, M. Kilpatrick, and M. Kilpatrick, *J. Amer. Chem. Soc.*, 1929, **51**, 428.

(a typical set of data is presented in Table 3). Mean results are summarised in Table 2 together with the corresponding data for the reactions of sodium azide, bromide, and iodide with ethylene oxide.

*Reactions with Propanesultone and Ethylene Sulphate.*—The procedures employed are typified by the following examples.

*Sodium N-chloro-N-p-tolylsulphonyl-3-aminopropane-1-sulphonate.* *N*-Chloro-*N*-sodiotoluene-*p*-sulphonamide (100 g) was dissolved in the minimum volume of warm (60°) water, and propanesultone (47·8 g) was added during 15 min. The mixture was maintained at 60—70° for a further 15 min and then cooled. The crystalline mass was filtered, washed with acetone, and dried. Recrystallisation of this product (105 g, 80%) from water gave the pure N-*alkyl*-N-*chlorosulphonamide* (Found: C, 32·5; H, 4·2; available Cl, 19·3. $C_{10}H_{13}ClNNaO_5S_2,H_2O$ requires C, 32·65; H, 4·1; available Cl, 19·25%).

TABLE 3

Reaction of *N*-chloro-*N*-sodiobenzenesulphonamide with ethylene oxide at 25°

(*a*) Effect of pH

| pH | 7·60 | 7·93 | 8·00 | 8·54 | 8·85 | 9·04 |
|---|---|---|---|---|---|---|
| $10^5k_N$/l mol$^{-1}$ s$^{-1}$ | 7·88 | 7·47 | 7·62 | 7·35 | 8·03 | 7·40 |

(*b*) Details of experiment at pH 8·85

| $t$/min | N-Alkali added (ml × 10²) | *N*-Cl-Compd. $(a-x)$ (M × 10²) | Epoxide $(b-x)$ (M × 10²) | $\ln\frac{(a-x)}{(b-x)}$ |
|---|---|---|---|---|
| 0 | | 5·2700 | 4·6200 | 0·131636 |
| 10 | 2·25 | 5·2588 | 4·6088 | 0·131937 |
| 20 | 4·58 | 5·2471 | 4·5971 | 0·132249 |
| 30 | 6·90 | 5·2356 | 4·5856 | 0·132563 |
| 40 | 9·25 | 5·2238 | 4·5738 | 0·132882 |
| 50 | 11·55 | 5·2125 | 4·5625 | 0·133196 |
| 60 | 13·83 | 5·2010 | 4·5510 | 0·133507 |
| 70 | 16·10 | 5·1900 | 4·5400 | 0·133820 |
| 80 | 18·38 | 5·1790 | 4·5290 | 0·134135 |

$k_N = 8·03 \times 10^{-5}$; correlation coefficient = 0·994.

*Sodium N-chloro-N-methylsulphonyl-3-aminopropane-1-sulphonate.* *NN*-Dichloromethanesulphonamide [26] (51·1 g) was suspended in a solution of methanesulphonamide (29·2 g) in water (150 ml). A solution of sodium hydroxide (24·4 g) in water (50 ml) was added dropwise with stirring and cooling. When all solid material had dissolved, the solution was warmed to 60° and propanesultone (72·5 g) in water (30 ml) was added during 20 min; the temperature was maintained at 60° for a further 20 min. Concentration of the solution *in vacuo* followed by cooling in ice–water gave the crystalline N-*alkyl*-N-*chlorosulphonamide* (92 g, 51%) which was filtered off, washed with acetone, and dried (Found: C, 16·55; H, 4·0; available Cl, 24·2. $C_4H_9ClNNaO_5S_2,H_2O$ requires C, 16·45; H, 3·8; available Cl, 24·3%).

*Sodium N-chloro-N-dodecylsulphonyl-2-aminoethyl sulphate.* A solution of *N*-chloro-*N*-sodiododecanesulphonamide [8] (3·03 g) in warm acetone (50 ml) was added to a solution of ethylene sulphate (1·24 g) in acetone (20 ml). The white precipitate which soon formed was filtered off. Crystallisation from water gave the pure N-*alkyl*-N-*chlorosulphonamide* (3·8 g, 88%) (Found: C, 39·0; H, 6·9; N, 3·2; S, 14·8; available Cl, 16·4. $C_{14}H_{29}ClNNaO_6S_2$ requires C, 39·1; H, 6·8; N, 3·25; S, 14·9; available Cl, 16·5%).

*Preparation of Authentic Specimens.*—The following examples are typical.

N-*Chloro*-N-(2-*hydroxyethyl*)*toluene*-p-*sulphonamide.* *N*-(2-Hydroxyethyl)toluene-*p*-sulphonamide [27] (7·5 g) was dissolved in the minimum volume of water, and hypochlorous acid (0·42M; 108 ml) was added; an emulsion rapidly formed. The required *N*-chlorosulphonamide (7 g) was induced to crystallise by cooling and trituration, filtered off, washed with ice–water, and dried. Recrystallised material [from ether–light petroleum (b.p. 40—60°)] (Found: C, 43·35; H, 4·9; N, 5·85%) had m.p. 59—61°, undepressed on admixture with the product of reaction of *N*-chloro-*N*-sodiotoluene-*p*-sulphonamide and ethylene oxide.

*Sodium N-chloro-N-p-tolylsulphonyl-3-aminopropane-1-sulphonate.* Propanesultone (10 g) was added dropwise to aqueous ammonium hydroxide (*d* 0·88; 200 ml). The solution was stirred at room temperature for 30 min, heated on a steam-bath for 1 h, and evaporated to dryness. The crystalline residue (11·1 g) was dissolved in aqueous sodium hydroxide (6·25 g in 100 ml) and liberated ammonia was removed by evaporation. Toluene-*p*-sulphonyl chloride (12·6 g) was added and the mixture was stirred at 65—75° until it became homogeneous (2 h). This solution was neutralised and evaporated to dryness; the residue was extracted with boiling ethanol–water (9 : 1). Evaporation of the extract gave an amorphous material (20·5 g) which was dissolved in aqueous hypochlorous acid (0·21M; 380 ml). After 30 min, concentration and cooling of this solution gave the required *N*-chlorosulphonamide as a crystalline mass (19 g) which was filtered off and dried (Found: C, 32·55; H, 4·25; available Cl, 19·2%); this material was identical with the product of reaction of *N*-chloro-*N*-sodiotoluene-*p*-sulphonamide and propanesultone (i.r. spectra).

[1/298 *Received, March 16th,* 1971]

[26] A. G. Newcombe, *Canad. J. Chem.*, 1955, **33**, 1250.
[27] A. Bourcherle, G. Carriaz, Y. Virot, and J. Dodu, *Bull. Soc. chim. France*, 1960, 1047.