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THE REACTION OF N,N-DICHLOROETHANESULFONAMIDE WITH 1-OLEFIN

T. OHASHI, M. SUGIE, M. OKAHARA and S. KOMORI
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Japan

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Abstract—The competitive ionic and radical reactions of N,N-dichloroethanesulfonamide and 1-olefins yielded two isomers of the 1:1 adduct under the normal indoor lighting, but the predominant formation of the anti-Markownikoff adduct was observed under photoirradiation. By photoirradiation of the products obtained in the reaction under the normal indoor lighting, two corresponding rearranged products were obtained. These 1:1 adducts and rearranged products were converted to N-ethanesulfonylaziridine derivatives by alkali treatment. A mechanism for the participation of N-monochloroethanesulfonamide has been proposed.

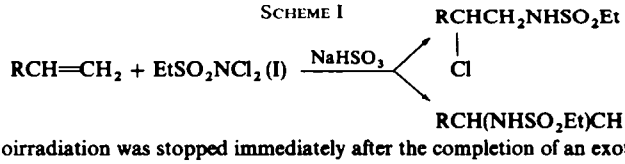
INTRODUCTION

IN ADDITION to earlier papers,[1-3] the addition of N-aryl-N-halosulfonamides to various olefins has been studied.[4-7] Kharasch reported the difference in the mode of addition between N-bromo-N-methyl-arylsulfonamides and N,N-dibrominated arylsulfonamides[2] and Seden[5] and Daniher[7] discussed the mode of addition of N,N-dichlorinated arylsulfonamides to styrene derivatives, propylene, isobutylene, 1,3-butadiene and chloroprene, and reported the predominant anti-Markownikoff orientation. Further Daniher has recently reported the ionic addition,[8] and the authors[9] have reported the radical addition of N,N-dichloroethanesulfonamide to 1-hexene accompanying the free-radical rearrangement. In a further investigation of this reaction, we found that the orientation in the addition reaction was affected by the reaction condition and the yields of addition products varied with the molar ratio of 1-olefin to N,N-dichloroethanesulfonamide. In the present paper, the ionic and radical addition reactions of N,N-dichloroethanesulfonamide to long chain 1-olefins and the photo-induced rearrangement have been studied.

RESULTS AND DISCUSSION

The reaction* of N,N-dichloroethanesulfonamide (I) with 1-hexene under photoirradiation was immediately followed by an exothermic reaction and afforded the anti-Markownikoff 1:1 adduct, but the formation of the Markownikoff adduct accompanying the anti-Markownikoff adduct was observed after the reduction with sodium bisulfite in the reaction under the normal indoor lighting as shown in Scheme I.

SCHEME I



* When photoirradiation was stopped immediately after the completion of an exothermic reaction, the anti-Markownikoff adduct was obtained after the reduction with sodium bisulfite and the rearranged product, which was obtained by photoirradiation for a long time,[9] was not observed.

The anti-Markownikoff adduct was easily isolated in crystalline form from the mixture of two isomers by column chromatography, but the Markownikoff adduct could be isolated only from the reaction of dodecene with I by fractional crystallization. The presence of the Markownikoff adduct was confirmed by NMR analysis and conversion to the identical compound by the alkali treatment of the mixture of two isomers. In the NMR spectrum of this mixture, the methyne proton adjacent to N-ethanesulfonyl group and the methylene protons on the carbon with attached chlorine were observed (τ = 6·3–6·4) together with the ABX pattern of the anti-Markownikoff adduct (τ = 6·5–6·7, τ = 6·0). The mixture of two isomers was easily converted in high yield to 2-butyl-1-ethanesulfonylaziridine by alkali treatment (Scheme II).

SCHEME II

$$RCH(NHSO_2Et)CH_2Cl + RCHClCH_2NHSO_2Et \xrightarrow{NaOH/H_2O} RCH\!\!-\!\!CH_2 \quad (N\text{–}SO_2Et)$$

The formation of two isomers was confirmed also in the reaction of I with 1-butene, 1-octene and 1-dodecene (Table 2), but the predominant formation of the anti-Markownikoff adduct was observed in the reaction of I with styrene. The ratio of formation of each isomer in the reaction of I with 1-hexene under a variety of conditions was determined by GLPC as shown in Table 1. These results suggest that the predominant formation of the anti-Markownikoff adduct occurs under photoirradiation and the ionic reaction accompanies the radical addition reaction under the normal indoor lighting. This is in accordance with the report by Daniher, who has recently suggested the ionic addition in the reaction of dichloramine B with 1-propene,[7] and reported[8] the ionic addition of dichloramine B to but-2-ene accompanying the formation of β-chloro-iminosulfonate under normal indoor lighting. The complete inhibition of the radical reaction under the normal indoor lighting could not be assumed from our results, and the formation of β-chloro-iminosulfonate was not confirmed in our reaction.

Results obtained in the reaction of I with various 1-olefins under a variety of conditions are described in Table 2.

TABLE 1. COMPOSITION[a] OF ISOMERS OF 1 : 1 ADDUCT OBTAINED IN THE REACTION OF I WITH 1-HEXENE

Addition conditions	Markownikoff adduct	Anti-Markownikoff adduct
Under photoirradiation in the nitrogen atmosphere[b]	Trace	100%
Under the normal indoor lighting[b]	60%	40%
Under an atmosphere of oxygen in dark[b]	67%	33%
In the presence of $AlCl_3$[c]	69%	31%
In the presence of *p*-benzoquinone[b]	68%	32%
Under the normal indoor lighting under N_2[b]	55%	45%

[a] Weight % of each isomer.

[b] An equimolar quantity of N,N-dichloroethanesulfonamide was added to the solution of 1-hexene in benzene at 20 ~ 25° and the solution was treated by sodium bisulfite.

[c] An equimolar quantity of 1-hexene was added to the solution of N,N-dichloroethanesulfonamide and $AlCl_3$ in chloroform, and the solution was heated under reflux.

In the reaction by method B in Table 2, two rearranged products were obtained with the corresponding two isomers of 1:1 adduct (Scheme III). One of rearranged products was isolated in crystalline form and its structure was confirmed as N-(2,4-dichlorohexyl)ethanesulfonamide by NMR, but the isolation of the other rearranged product was unsuccessful. Its structure was confirmed by analysis of products was obtained after alkali treatment of two rearranged products.

SCHEME III

$$R'(CH_2)_3CH(NClSO_2Et)CH_2Cl \ (II) \xrightarrow{h\nu} R'CHCl(CH_2)_2CH(NHSO_2Et)CH_2Cl$$

$$R'(CH_2)_3CHClCH_2NClSO_2Et \ (III) \xrightarrow{h\nu} R'CH_2CHClCH_2CHClCH_2NHSO_2Et$$

In a manner similar to the 1:1 adducts, the mixture of two rearranged products was easily converted to the corresponding N-ethanesulfonylaziridine derivatives and the formation of N-ethanesulfonyl pyrrolidine derivatives was not observed (Scheme IV). The structure of another rearranged product obtained in the reaction

SCHEME IV

$$R'CHCl(CH_2)_2CH(NHSO_2Et)CH_2Cl \xrightarrow{NaOH/H_2O} R'CHCl(CH_2)_2CH\!\!<\!\!\begin{matrix}CH_2\\ |\\ NSO_2Et\end{matrix}$$

$$R'CH_2CHClCH_2CHClCH_2NHSO_2Et \xrightarrow{NaOH/H_2O} R'CH_2CHClCH_2CH\!\!<\!\!\begin{matrix}CH_2\\ |\\ NSO_2Et\end{matrix}$$

of 1-hexene proved to be N-(1,5-dichloro-2-hexyl)ethanesulfonamide because the terminal protons are split into a doublet due to the presence of 2-(3-chlorobutyl)-1-ethanesulfonylaziridine and also the triplet signal of 2-(2-chlorobutyl)-1-ethanesulfonylaziridine in the NMR spectrum of the products obtained by the alkali treatment of the two rearranged products. From the integration ratio of terminal Me protons (τ = 8·95 triplet and τ = 8·48 doublet) of two rearranged isomers* or two ethanesulfonylaziridine derivatives obtained from these isomers, the composition of the two rearranged isomers was determined (Table 2).

As described in Table 2, the ratio of N-(1-chloro-2-hexyl)ethanesulfonamide/N-(2-chlorohexyl)ethanesulfonamide decreased and the ratio of N-(1,5-dichloro-2-hexyl)ethanesulfonamide/N-(2,4-dichlorohexyl)ethanesulfonamide was relatively high after the photoirradiation reaction. This result suggests that the intermediate N-chloro-N-(1-chloro-2-hexyl)ethanesulfonamide rearranges more easily to N-(1,5-dichloro-2-hexyl)ethanesulfonamide via the 1,5-hydrogen transfer than the intermediate N-chloro-N-(2-chlorohexyl)ethanesulfonamide. This is reasonable, if the I-Effect of chlorine on the hexyl group and the stability* of radical formed via the 1,5-hydrogen transfer is considered.

Evidently this rearrangement proceeds via the free radical mechanism, because the

* In the NMR spectrum of the mixture of two rearranged products obtained in the reaction of I with 1-hexene, the methyne proton adjacent to N-ethanesulfonyl group and the methylene protons on the carbon with attached chlorine of N-(1,5 dichloro-2-hexyl)ethanesulfonamide were observed (τ = 6·3 ~ 6·4) together with the ABX pattern of N-(2,4-dichlorohexyl)ethanesulfonamide (τ = 6·5 ~ 6·7, τ = 5·8).

* Because of the contribution of the hyperconjugation of Me group, the radical $Me\cdot\dot{C}H(CH_2)_2CH(NHSO_2Et)CH_2Cl$ seems to be more stable than the radical $Et\cdot\dot{C}HCH_2CHClCH_2NHSO_2Et$.

TABLE 2. YIELDS OF 1:1 ADDUCTS AND REARRANGED PRODUCTS

Olefin	Method[a]	Mole ratio of olefin to (I)	Reaction time (min)	Yields (% based on (I))		
				1:1 adduct	(Composition[b] of 1:1 adducts)	Rearranged product[c]
1-hexene	A	equimole	30	56·1	(1·5 ~ 1·6)	—
1-hexene	A	twicemole	30	68·7	(1·5)	—
1-hexene	B	equimole	2210	19·6	(0·8 ~ 0·9)	41·6 (1·8)
1-hexene[d]	B	twicemole	1385	33·5	(0·5)	45·1 (1·7)
1-octene	A	equimole	30	54·4	(1·5)	—
1-octene	B	equimole	3600	22·1	(1·2)	37·9
1-dodecene	A	equimole	30	42·0	(1·5)	—
1-butene	A	excessmole	30	56·0	(1·6)	—
styrene	A	equimole	30	80·1	—	—

[a] The method A is as follows; (I) was added to the benzene solution of 1-olefin in the atmosphere and and after the exothermic reaction benzene solution was washed with aqueous sodium bisulfite. Another method B; After the addition as described above, the solution was irradiated under nitrogen until the active chlorine content was negligible.

[b] The formation ratio of two isomers. Markownikoff adduct/Anti-Markownikoff adduct.

[c] The formation ratio of two rearranged products. N-(1,5-dichloro-2-alkyl)ethanesulfonamide/N-(2,4-chloroalkyl)ethanesulfonamide.

[d] The formation of 1:2 adduct (10·0%) was observed.

reaction is initiated by photoirradiation, but it is interesting that this reaction proceeds in the absence of acid catalyst which is required for the known Hofmann–Löffler type reaction.[10] This result is probably due to the electrophilic sulfonamide radical, which is formed with the aid of chlorine attached to the β-position of the alkyl group.

The 1:2-adduct was obtained in the reaction using 2 moles of 1-hexene to N,N-dichloroethanesulfonamide, but the detailed structure was not further investigated.

In order to study the mechanism, the by-products were analysed by measurement of the concentration change of the active chlorine and the olefin in the reaction of N,N-dichloroethanesulfonamide with 1-hexene (Tables 3 and 4). As shown in Tables 2 and 3, the yields of addition products and by-products (monochlorohexene and 1,2-dichlorohexane) were greater in the reaction using 2 moles of 1-hexene than when equimolar amounts were used. In contrast, the yield of ethanesulfonamide was low in the reaction using 2 moles of 1-hexene. Further, the active chlorine content* was lower in the reaction using 2 moles of 1-hexene than when equimolar amounts were used. A similar result was observed in the reaction of dichloramine B with 1-hexene (Table 4). It is suggested that N-monochloroethanesulfonamide participates to some extent in the presence of excess 1-hexene as shown in Scheme V. The reactivity of N-monochloroethanesulfonamide is under investigation.

SCHEME V

Addition (II) and (III)

Reaction-1

$$R''CH_2CH{=}CH_2 + EtSO_2NCl_2 \longrightarrow R''CHClCH{=}CH_2 + R''CH{=}CHCH_2Cl + EtSO_2NHCl$$

* The active Cl after the reaction using 2 moles of 1-hexene was less than one-half its initial value.

Reaction-2

$$R''CH_2CH{=}CH_2 + EtSO_2NHCl \begin{cases} \nearrow \text{1:1-Adducts} \\ \searrow \text{Chlorination of olefin} + EtSO_2NH_2 \end{cases}$$

TABLE 3. YIELDS[a] OF BY-PRODUCTS OBTAINED IN THE REACTION OF 1-HEXENE WITH I

Method	Mole ratio of 1-hexene to (I)	Monochlorohexene[b]	1,2-Dichlorohexane	Ethanesulfonamide
A	equimole	4·4	5·6	33·3
A	twicemole	11·3	14·1	27·1
B	equimole	2·9	16·1	29·2
B	twicemole	6·3	20·2	15·7

[a] Based on N,N-dichloroethanesulfonamide (%).
[b] Mixture of 1-chloro-2-hexene and 3-chloro-1-hexene.

TABLE 4. CONCENTRATION CHANGE OF THE ACTIVE CHLORINE AND 1-HEXENE IN THE REACTION[b]

$R\text{-}SO_2NCl_2$ (I')	Mole ratio of 1-hexene to (I')	Initial Concentration[a]		Concentration[a] after the mixing of reagents	
		(Active chlorine)	(1-Hexene)	(Active chlorine)	(1-Hexene)
$R = C_2H_5$	equimole	16·4	19·5	8·5	1·0
$R = C_2H_5$	twicemole	13·7	32·6	4·9	10·3
$R = C_6H_5$	equimole	9·3	11·0	5·2	1·6
$R = C_6H_5$	twicemole	8·4	24·7	3·1	8·3

[a] Weight %.
[b] Method A.

As shown in Table 4, reaction 1 proceeds almost completely after the mixing of reagents based on the consumption of active chlorine and olefin. This shows the high reactivity of N,N-dichlorinated sulfonamide, as compared with N-chloro-N-methylethanesulfonamide which does not initiate a spontaneous reaction. Further, N-chloro-N-t-butylethanesulfonamide does not cause addition and acts as an allylic chlorinating agent in analogy with N-chloro-N-cyclohexylbenzenesulfonamide.[11] The difference in the structure and reactivity of N-halogenated sulfonamides will be reported separately.

EXPERIMENTAL

Light petroleum had b.p. 40 ~ 60°. The commercial pure grade of benzene was dried over Na wire and used as the reaction solvent. The olefins used were chromatographically pure. GLPC analyses were conducted using Apieson L grease 10%, Apieson L grease 10% and Carbowax 20M 2%, Tritone X 305 or silicone DC 200 10% on Diasolid L, 60–80 mesh, 4·5 mm × 1 m column. Titrations for positive Cl were conducted by $Na_2S_2O_3$ assay of I_2 liberated from 10% aqueous KI acidified with 0·1N HCl.

N,N-*Dichloroethanesulfonamide*. Chlorination of ethanesulfonamide was according to the procedure of N-chlorination of N-alkylalkanesulfonamides.[12] N,N-Dichloroethanesulfonamide obtained quantita-

tively was purified by distillation under reduced press, b.p. 78° (3 mm) lit.[13] b.p. 108 ~ 110° (10 mm). Iodometric analysis indicated a purity greater than 99·6%; UV absorptions $\lambda_{max}^{benzene}$ (ε); 276 mμ (4·7 × 10^2).

Addition of N,N-*dichloroethanesulfonamide to olefins and rearrangement by photoirradiation*

General method A. N,N-Dichloroethanesulfonamide (0·1 mole) was added dropwise to a benzene soln (18 g benzene) of the olefin (0·1 or 0·2 moles) at a rate to maintain the reaction temp at 20–25°. After the addition was complete, an exothermic reaction occurred in 5 min. After this was complete, the reaction mixture was kept at room temp for 20 min; 20% $NaHSO_3$ aq (100 ml) was added at 25°. The organic layer was extracted with two 50 ml portions of ether and dried over Na_2SO_4. After evaporation of ether, each reaction product was isolated by distillation under reduced press and by column chromatography.

Method B. After the addition of N,N-dichloroethanesulfonamide to the olefin as described above except for the treatment by $NaHSO_3$, the benzene soln was irradiated with a high press Hg lamp (150 W) inside the reaction flask at 20–25° under N_2 until the active Cl_2 content of the soln was negligible. Results obtained by methods A and B are described in Tables 2 and 3.

Isolation and analyses of 1:1 *adducts*

N-(2-*Chlorohexyl*)*ethanesulfonamide.* Prepared from 1-hexene by methods A and B, and isolated from the mixture of N-(2-chlorohexyl)ethanesulfonamide and N-(1-chloro-2-hexyl)ethanesulfonamide by column chromatography on active alumina ($CHCl_3$ fraction), the product was recrystallized from light petroleum and chloroform, m.p. 47·5°. Characteristic IR bands appeared at 3320, 2960, 1315 and 1135 cm^{-1}; NMR, τ in $CDCl_3$; 5·02 (1H) 6·00 (mμ, 1H) 6·65 (mu, 2H) 6·93 (qu, 2H) 8·60 (mu, 9H) 9·10 (tr, 3H). (Found: C, 42·05; H, 7·86; N, 6·11; Cl, 15·6. Calc. for $C_8H_{18}ClNO_2S$: C, 42·19; H, 7·97; N, 6·15; Cl, 15·5%).

N-(2-*Chlorooctyl*)*ethanesulfonamide.* This was prepared from 1-octene by methods A and B, and isolated from the mixture of N-(2-chlorooctyl)ethanesulfonamide and N-(1-chloro-2-octyl)ethanesulfonamide by distillation under reduced press and crystallization from light petroleum and chloroform, m.p. 82°; IR, 3320, 2940, 1320 and 1140 cm^{-1}; NMR, τ in $CDCl_3$; 5·05 (1H) 6·00 (mu, 1H) 6·65 (mu, 2H) 6·95 (qu, 2H) 8·65 (mu, 13H) 9·10 (tr, 3H). (Found: C, 46·69; H, 8·70; N, 5·43; Cl, 13·5. Calc. for $C_{10}H_{22}ClNO_2S$: C, 46·79; H, 8·67; N, 5·48; Cl, 13·8%).

N-(2-*Chlorododecyl*)*ethanesulfonamide.* This was prepared from 1-dodecene by method A, and isolated from the mixture of N-(2-chlorododecyl)ethanesulfonamide and N-(1-chloro-2-dodecyl)ethanesulfonamide by crystallization from cold light petroleum, m.p. 61°; IR, 3280, 2920, 1310 and 1130 cm^{-1}; NMR, τ in $CDCl_3$; 5·00 (1H) 6·05 (mu, 1H) 6·70 (mu, 2H) 6·95 (qu, 2H) 8·70 (mu, 21H) 9·10 (tr, 3H). (Found: C, 53·48; H, 9·81; N, 4·27; Cl, 11·2. Calc. for $C_{14}H_{30}ClNO_2S$: C, 53·91; H, 9·69; N, 4·49; Cl, 11·4%).

N-(1-*Chloro*-2-*dodecyl*)*ethanesulfonamide.* On cooling the filtrate obtained after the isolation of N-(2-chlorododecyl)ethanesulfonamide to −40°, N-(1-chloro-2-dodecyl)ethanesulfonamide was obtained as a white ppt, m.p. 41°; IR, 3300, 2920, 1310 and 1135 cm^{-1}; NMR, τ in $CDCl_3$; 5·30 (1H) 6·35 (mu, 3H) 6·93 (qu, 2H) 8·70 (mu, 21H) 9·10 (tr, 3H). (Found: C, 53·60; H, 9·69; N, 4·24; Cl, 11·3. Calc. for $C_{14}H_{30}ClNO_2S$: C, 53·91; H, 9·69; N, 4·49; Cl, 11·4%).

N-(2-*Chlorophenethyl*)*ethanesulfonamide.* Prepared from styrene by method A, the product was recrystallized from light petroleum and chloroform, m.p. 68°; IR, 3280, 1590, 1310 and 1130 cm^{-1}; NMR, τ in $CDCl_3$; 2·60 (s, 5H) 5·00 (tr, 2H, 1H exchangeable) 6·40 (tr, 2H, collapsed to doublet on D_2O treatment 7·05 (qu, 2H) 8·73 (tr, 3H). (Found: C, 48·54; H, 5·68; Cl, 14·0. Calc. for $C_{10}H_{14}ClNO_2S$: C, 48·48; H, 5·70; Cl, 14·3%).

Isolation of rearranged product

N-(2,4-*Dichlorohexyl*)*ethanesulfonamide.* Prepared from 1-hexene by method B and isolated by distillation under reduced press (b.p. 153–154°/1 mm), the product was crystallized from light petroleum and chloroform, m.p. 94°; IR, 3280, 2920, 1320 and 1140 cm^{-1}; NMR, τ in $CDCl_3$; 5·00 (1H) 5·80 (mu, 2H) 6·60 (mu, 2H) 6·95 (qu, 2H) 8·20 (mu, 4H) 8·65 (tr, 3H) 8·95 (tr, 3H). (Found: C, 36·72; H, 6·73; Cl, 26·9. Calc. for $C_8H_{17}Cl_2NO_2S$: C, 36·65; H, 6·54; Cl, 26·8%).

Preparation of 2-*alkyl*-1-*ethanesulfonylaziridine*

General procedure of alkali treatment. 45 g of 10% NaOH aq was added to the mixture of two isomers of 1:1-adducts (0·1 mole) obtained by method A and the soln was heated to 60° with stirring for 1 hr. The organic layer was extracted with ether and dried over Na_2SO_4. The crude product was then isolated by removal of ether under vacuum and purified by distillation under reduced press.

2-*Butyl*-1-*ethanesylfonylaziridine*. This was prepared from 1:1-adducts of 1-hexene, b.p. 88° (0·5 mm), yield, 80%; IR, 2960, 1330 and 1150 cm^{-1}; NMR, τ in CCl_4; 6·95 (qu, 2H) 7·35 (mu, 2H) 8·03 (do, 1H) 8·60 (mu, 9H) 9·10 (tr, 3H). (Found: C, 50·51; H, 8·79. Calc. for $C_8H_{17}NO_2S$: C, 50·23; H, 8·88%); n_D^{20} 1·4582.

2-*Hexyl*-1-*ethanesulfonylaziridine*. This was prepared from 1:1-adducts of 1-octene, b.p. 104° (1 mm), yield, 83%; IR, 2950, 1330 and 1150 cm^{-1}; NMR, τ in CCl_4; 6·95 (qu, 2H) 7·50 (mu, 2H) 8·03 (do, 1H) 8·60 (mu, 13H) 9·10 (tr, 3H). (Found: C, 54·75; H, 9·57. Calc. for $C_{10}H_{21}NO_2S$: C, 54·76; H, 9·65%); n_D^{20} 1·4587.

2-*Ethyl*-1-*ethanesulfonylaziridine*. This was prepared from 1:1-adducts of 1-butene, b.p. 76° (1 mm), yield, 82%; IR, 2960, 1330 and 1150 cm^{-1}; NMR, τ in CCl_4; 7·00 (qu, 2H) 7·55 (mu, 2H) 8·05 (do, 1H) 8·60 (mu, 5H) 9·00 (tr, 3H). (Found: C, 44·16; H, 8·17. Calc. for $C_6H_{13}NO_2S$: C, 44·15; H, 8·03%); n_D^{20} 1·4570.

2-*Decyl*-1-*ethanesulfonylaziridine*. This was prepared from 1:1-adducts of 1-dodecene, yield; 78%; IR, 2920, 1330 and 1150 cm^{-1}; NMR, τ in CCl_4; 6·98 (qu, 2H) 7·50 (mu, 2H) 8·05 (do, 1H) 8·65 (mu, 21H) 9·10 (tr, 3H). (Found: C, 60·68; H, 10·71. Calc for $C_{14}H_{29}NO_2S$: C, 61·05; H, 10·61%); n_D^{20} 1·4628.

Preparation of 2-(*chloroalkyl*)-1-*ethanesulfonylaziridine from the rearranged products* (Alkali treatment was conducted in the same manner as described above, react temp 60–80°).

2-(2-*Chlorobutyl*)1-*ethanesulfonylaziridine*. This was prepared from N-(2,4-dichlorohexyl)ethanesulfonamide by alkali treatment, b.p. 114° (0·5 mm), yield 82%; IR, 2920, 1330 and 1150 cm^{-1}; NMR, τ in CCl_4; 6·15 (mu, 1H) 6·95 (qu, 2H) 7·45 (mu, 2H) 7·90–8·30 (mu, 1H + 4H) 8·60 (tr, 3H) 8·95 (tr, 3H). (Found: C, 42·46; H, 7·28; Cl, 15·8. Calc. for $C_8H_{16}ClNO_2S$: C, 42·57; H, 7·14; Cl, 15·7%).

2-(3-*Chlorobutyl*)1-*ethanesulfonylaziridine*. This was prepared from the mixture of N-(2,4-dichlorohexyl)-ethanesulfonamide and N-(1,5-dichloro-2-hexyl)ethanesulfonamide. Its formation was confirmed by elemental analysis and NMR of two ethanesulfonylaziridine derivatives,* yield 85%; NMR, τ in CCl_4; 6·05 (mu, 1H) 6·95 (qu, 2H) 7·50 (mu, 2H) 7·90–8·30 (mu, 1H + 4H) 8·48 (do,) 8·60 (tr,) 8·95 (tr). (Found: C, 42·31; H, 7·38; Cl, 15·8. Calc. for $C_8H_{16}ClNO_2S$: C, 42·57; H, 7·14; Cl, 15·7%).

2-(2-*Chlorohexyl*)1-*ethanesulfonylaziridine and* 2-(3-*chlorohexyl*)1-*ethanesulfonylaziridine*. These compounds prepared from the mixture of N-(2,4-dichlorooctyl)ethanesulfonamide and N-(1,5-dichloro-2-octyl)-ethanesulfonamide were also obtained as the mixture of two ethanesulfonylaziridine derivatives, b.p. 129° (0·05 mm), yield 75%; IR, 2940, 1330 and 1150 cm^{-1}; NMR, τ in CCl_4: 6·05 (mu, 1H) 6·95 (qu, 2H) 7·90–8·75 (mu, 12H) 9·05 (tr, 3H). (Found: C, 47·62; H, 8·02; Cl, 14·1. Calc. for $C_{10}H_{20}ClNO_2S$: C, 47·72; H, 7·94; Cl, 14·0%).

1:2-*Adduct obtained from* 1-*hexene*, N,N-*bis*-(*chlorohexyl*)*ethanesulfonamide*. The 1:2-adduct was isolated by column chromatography on active alumina from the reaction products obtained by method B using 2 moles of 1-hexene. Elution with CCl_4 afforded the 1:2-adduct, but the detailed structure was not confirmed; IR, 2960, 1340 and 1150 cm^{-1}; NMR, τ in CCl_4; 5·95 (mu) 6·40–6·70 (mu) 6·95 (qu) 8·65 (mu) 9·10 (tr); M.W. 340 (346). (Found: C, 49·46; H, 8·74; Cl, 20·5. Calc. for $C_{14}H_{29}Cl_2NO_2S$: C, 48·58; H, 8·44; Cl, 20·2%).

Isolation and analyses of by-products

Ethanesulfonamide. This was isolated by water washing of the crude reaction mixture followed by evaporation of the water, m.p. 59° (lit. 58·8°);[14] IR, 3280, 1560, 1320 and 1140 cm^{-1}. (Found: N, 12·6. Calc. for $C_2H_7NO_2S$: N, 12·8%).

Monochlorohexene. This was isolated by distillation of the crude reaction mixture, and was proved to be the mixture of 1-chloro-2-hexene and 3-chloro-1-hexene (7:3), b.p. 62–65° (75 mm); IR, 3080, 3020, 2920, 1665, 1645, 1250, 990, 965 and 920 cm^{-1}; NMR, τ; 4·35 (mu) 4·95 (mu) 6·00 (mu). (Found: Cl, 29·7. Calc. for $C_6H_{11}Cl$: Cl, 29·9%). 1-Chloro-2-hexene was isolated from the mixture described above by fractional distillation, b.p. 65° (75 mm) (lit.[15] 129–130°/760 mm), IR, 3020, 2920, 1665, 1250 and 965 cm^{-1}; NMR, τ; 4·35 (mu, 2H) 6·00 (mu, 2H) 8·00 (mu, 2H) 8·65 (mu, 2H) 8·65 (mu, 2H) 9·10 (tr, 3H). (Found: Cl, 29·9. Calc. for $C_6H_{11}Cl$: Cl, 29·9%).

1,2-*Dichlorohexane*. This was isolated from the crude reaction mixture, b.p. 72° (30 mm); NMR, τ in CCl_4; 6·10 (mu, 1H) 6·35 (mu, 2H) 8·55 (mu, 6H) 9·10 (tr, 3H). (Found: Cl, 45·4. Calc. for $C_6H_{12}Cl_2$: Cl, 45·7%).

* The mixture of 2-(2-chlorobutyl)1-ethanesulfonylaziridine and 2-(3-chlorobutyl)1-ethanesulfonylaziridine.

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