Addition of N,N-Dibromosulfonamides to Internal Olefins: Synthesis of N-Sulfonylaziridines[1]

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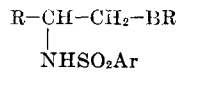
Abstract

The addition of N,N-dibromobenzenesulfonamide (NNDBS) to internal acyclic olefins has been investigated. The major products formed were shown to be β-bromosulfonamides. The reaction has been applied to pairs of *cis-trans* olefins and has been found to proceed in a stereoselective fashion. To account for this observed selectivity an ionic mechanism has been proposed. The β-bromosulfonamides prepared have been cyclized with base to N-sulfonylaziridines. The configurations of the latter have been shown to be the same as those of the starting olefins.

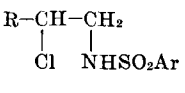
Introduction

Recent reports (1) have demonstrated an interest in the chemistry of N,N-dihaloamides and especially in the reaction of these active halogen compounds with unsaturated materials. The addition of N,N-dihalosulfonamides to olefins has been an area of particularly active investigation. Earlier workers (2–4) have observed that the addition of N,N-dibromoarylsulfonamides to various styrene and norbornylene derivatives apparently proceeds by an ionic pathway and yields after reduction addition products of type A. In contrast, the reaction of the corresponding N,N-dichloroarylsulfonamides with alkenes has been observed (6) to occur by a free radical mechanism to give addition products of type B. Daniher et al. (7,8) have confirmed the free radical nature of some additions of N,N-dichlorosulfonamides to olefins, but have found that in other instances an ionic mechanism prevails.

More recently Ueno et al. (5) have reported that N,N-dibromo- and N,N-dichlorobenzenesulfonamide react with cyclohexene via a radical pathway to yield a mixture of products, the principal components of which were identified as *cis-* and *trans*-N-(2-halocyclohexyl)benzenesulfonamide (C). The adducts formed initially, N-halo-N-(2-halocyclohexyl)benzenesulfonamide (D), were shown to react further with cyclohexene to yield cyclohexadiene, 1,2-dihalocyclohexane and cyclohex-3-enone. This latter reaction sequence was unequivocally shown to proceed by a radical mechanism.



A



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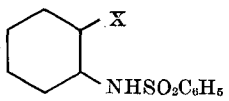

X = Cl or Br

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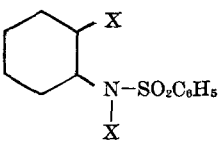


X = Cl or Br

D

In view of this dichotomy of behavior in the addition of N,N-dihaloarylsulfonamides to olefins we have examined the reaction of N,N-dibromobenzenesulfonamide with internal acyclic olefins of known stereochemistry. Also investigated was the ring closure of the addition products to the corresponding N-sulfonylaziridines of known stereochemistry.

Results

The present study concerns the addition of N,N-dibromobenzenesulfonamide to *cis-* and *trans*-3-hexene, *cis*-2-heptene, *cis*-5-decene, *cis-* and *trans*-9-octadecene and methyl oleate. The yields of isolated, analytically pure β-bromosulfonamides are in the range of 40–70% (Table I).

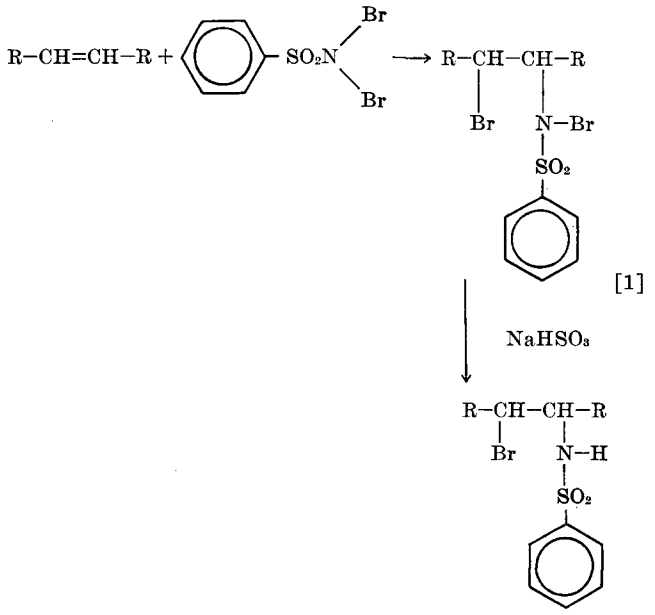
In general, the reactions were performed by the dropwise addition of the olefin to a chilled slurry of N,N-dibromobenzenesulfonamide (NNDBS) in carbon tetrachloride. In all cases the reaction proceeded spontaneously and exothermally. Progress of the reac-

[1] Presented at the AOCS Meeting, San Francisco, April 1969.
[2] ARS, USDA.

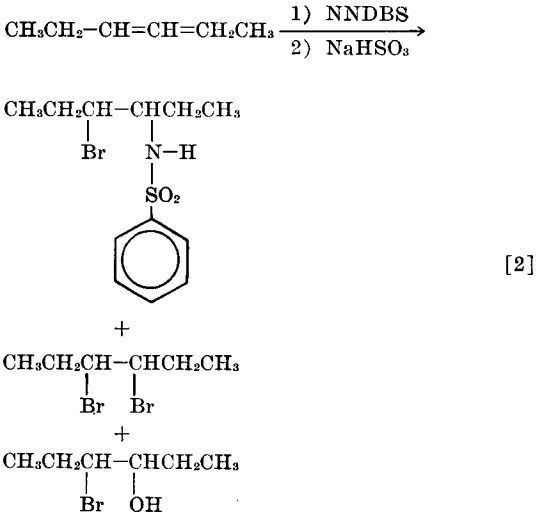
TABLE I
β-Bromosulfonamides by Addition NNDBS to Internal Olefins

β-Bromosulfonamide	Yield, %[a]	C, %		H, %		N, %		Br, %		S, %	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
threo-$CH_3CH_2CH(Br)-CH(NHSO_2C_6H_5)-CH_2CH_3$	65	45.0	45.2	5.67	5.79	4.37	4.38	24.9	24.7	10.0	9.97
erythro-$CH_3CH_2CH(Br)-CH(NHSO_2C_6H_5)-CH_2CH_3$	52	45.0	44.8	5.67	5.86	4.37	4.32	24.9	24.6	10.0	9.96
threo-$CH_3(CH_2)_3CH(Br)-CH(NHSO_2C_6H_5)-CH_3$	65[b]	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
threo-$CH_3(CH_2)_3CH(Br)-CH(NHSO_2C_6H_5)-(CH_2)_3CH_3$	60	51.1	51.0	6.96	7.18	3.72	3.44	21.2	21.4	8.52	8.58
threo-$CH_3(CH_2)_7CH(Br)-CH(NHSO_2C_6H_5)-(CH_2)_7CH_3$	42	59.0	59.6	8.66	8.81	2.87	3.07	16.4	16.1	6.56	6.60
erythro-$CH_3(CH_2)_7CH(Br)-CH(NHSO_2C_6H_5)-(CH_2)_7CH_3$	38	59.0	59.4	8.66	8.20	2.87	3.06	16.4	16.0	6.56	7.00
threo-$CH_3(CH_2)_7CH(Br)-CH(NHSO_2C_6H_5)-(CH_2)_7CO_2CH_3$	60[b]	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

[a] Pure products, yields based on starting olefin.
[b] Acceptable analyses could not be obtained.



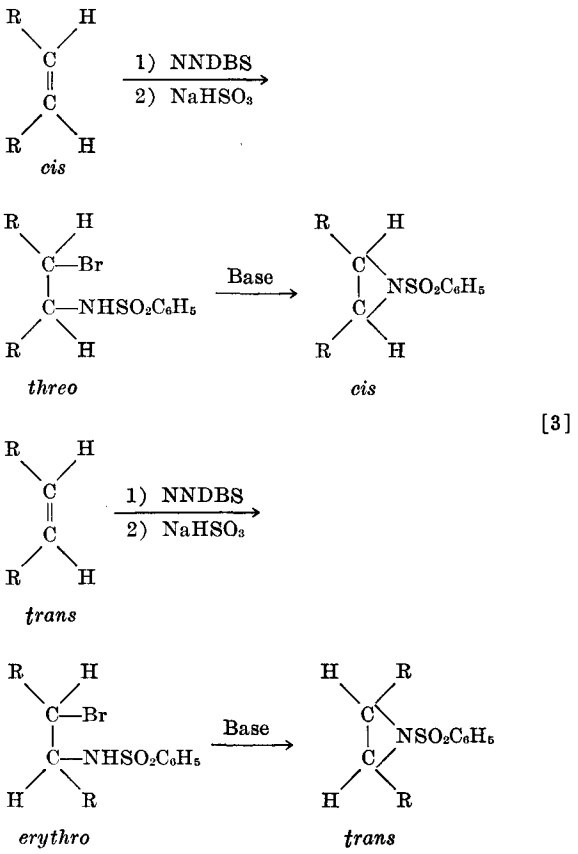
[1]



[2]

tion was monitored by the disappearance of olefin by glpc. Alternatively, the reaction could be judged complete when the reaction medium achieved homogeneity. Generally the reactions were complete 15 min after the last addition of olefin. The initially formed adducts, N-bromo-β-bromosulfonamides, were not isolated, but were reduced to the corresponding β-bromosulfonamides by treatment with aqueous sodium bisulfite [1].

Initial studies were carried out on the model compounds *cis*- and *trans*-3-hexene with the object of obtaining the diastereomeric β-bromosulfonamide addition products. The addition of NNDBS to *cis*-3-hexene gave a white crystalline adduct (mp = 79.5–80.5 C) which was assigned the *threo*- configuration on the basis of physical and chemical evidence. (See



[3]

Discussion for details.) The adduct obtained from *trans*-3-hexene (mp = 92–93 C) was accordingly assigned the *erythro*- configuration on the basis of the same considerations. The crude *threo* and the crude *erythro* adducts were found to be contaminated by small amounts of the other configurational isomer. Also identified as byproducts in these reactions were the corresponding dibromides and bromohydrins of the starting olefins [2]. In both examples over 80% of the starting olefin was accounted for by these products.

Addition of NNDBS to *cis*-5-decene gave a 60% yield of the corresponding *threo*-β-bromosulfonamide adduct as a crystalline solid. As in the case of the hexenes the major side products were found to be the dibromo and bromohydrin derivatives. A minor amount of the *erythro* isomer was presumably present but was not isolated.

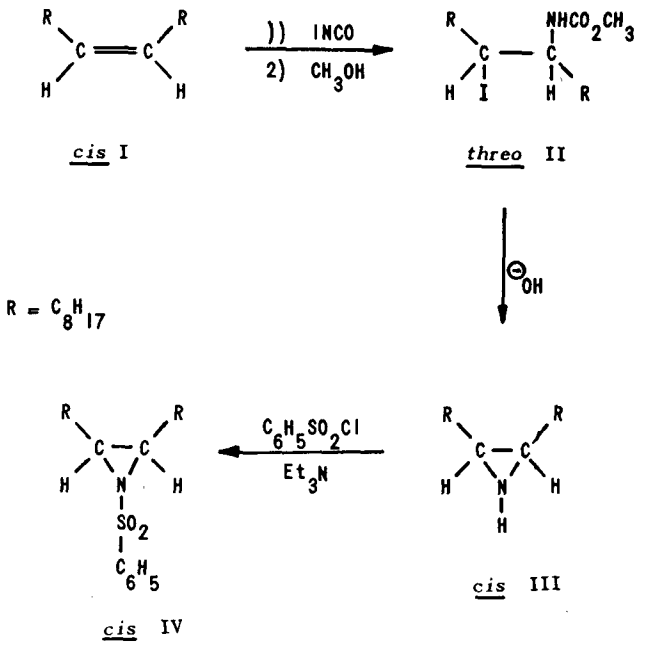
Reaction of *cis*- and *trans*-9-octadecene with NNDBS yielded the diastereomeric *threo*- and *erythro*-9-bromo-10-benzenesulfonamidooctadecane derivatives as viscous oils. These materials were readily purified by column chromatography on Florisil. In addition to the bromosulfonamides, the corresponding diastereomeric dibromides and bromohydrins were isolated in yields of 15% and 10% respectively.

TABLE II
Aziridines from β-Bromosulfonamides and Base

Aziridine	Yield,[a] %	C, %		H, %		N, %		S, %	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
cis-3,4-(N-benzenesulfonylepimino)hexane	75	60.2	59.7	7.16	7.02	5.85	5.98	13.40	13.5
trans-3,4-(N-benzenesulfonylepimino)hexane	80	60.2	60.3	7.16	7.11	5.85	5.70	13.40	13.3
cis-2,3-(N-benzenesulfonylepimino)heptane	75	61.6	61.6	7.56	7.54	5.53	5.50	12.7	12.9
cis-5,6-(N-benzenesulfonylepimino)decane	75	65.1	65.3	8.53	8.61	4.74	4.85	10.9	10.7
cis-9,10-(N-benzenesulfonylepimino)octadecane	80	70.7	70.7	10.1	10.1	3.44	3.40	7.87	7.94
trans-9,10-(N-benzenesulfonylepimino)octadecane	65	70.7	70.5	10.1	10.0	3.44	3.78	7.87	7.94
cis-Methyl-9,10-(N-benzenesulfonylepimino)-octadecanoate	70	66.5	66.3	9.15	9.16	3.10	2.98	7.10	6.97

[a] Pure products, yields based on starting β-bromosulfonamides.

SCHEME I



The *threo*-β-bromosulfonamides obtained from *cis*-2-heptene and from methyl oleate were mixtures of positional isomers. The crude products were chromatographed on Florisil, and the pure adducts were obtained as clear oils. The assignment of configuration as *threo* adducts is based on extension of the results obtained with the symmetrical *cis* olefins.

Table II lists the N-benzenesulfonylaziridines prepared from β-bromosulfonamide precursors by treatment with base. Proof of stereochemical assignment as a *cis*- or *trans*-aziridine is given in the Discussion section. As a consequence of the procedure used, *cis*-aziridines are obtained from *cis*-olefins and *trans*-aziridines from *trans*-olefins [3].

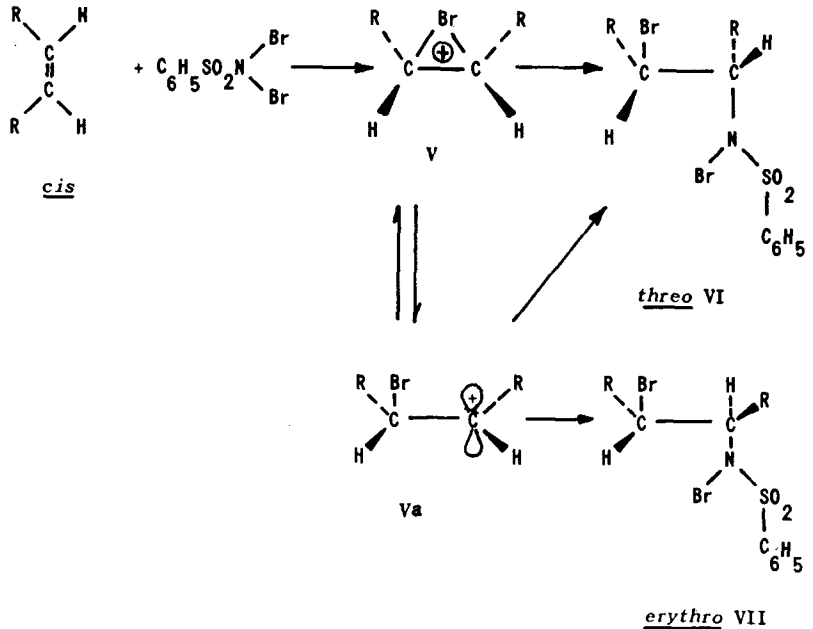
Discussion

It has been postulated (4) that the ionic addition of N,N-dibromoarylsulfonamides to olefins involves the intermediacy of a cyclic bromonium ion. Such a mechanism would predict that addition of NNDBS to a *cis*- or *trans*-alkene should be a stereoselective process. Indeed the major addition products obtained from *cis*- and *trans*-olefins have been found in the present work to be *threo* and *erythro* diastereomers. Establishment of these adducts as diastereomers is based on the following physical and chemical considerations.

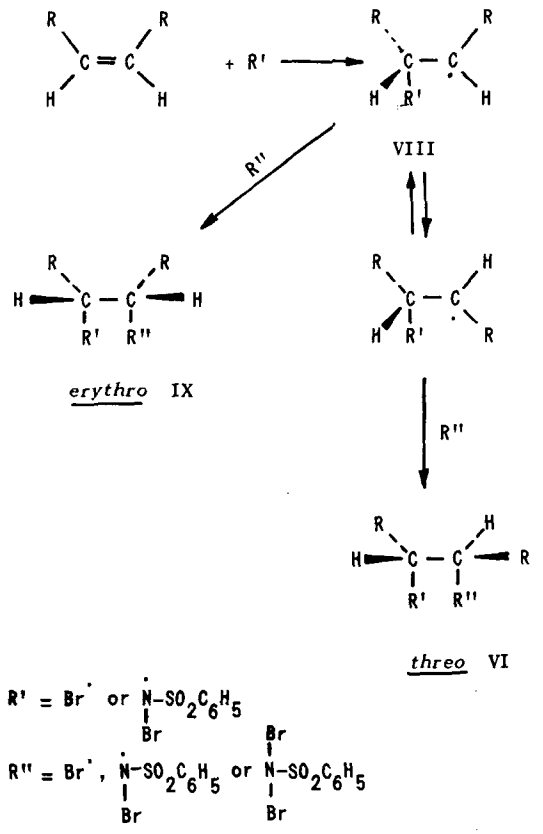
The β-bromosulfonamides obtained from *cis*- and *trans*-3-hexene and *cis*- and *trans*-9-octadecene are clearly separable and distinguishable by TLC. Examination of the crude reaction mixtures by TLC shows a major and minor component. The minor component from the *cis*-olefin corresponds to the major component from the *trans*-olefin and vice versa. Although the infrared spectra of the diastereomers obtained from *cis*- and *trans*-3-hexene are very similar, the *erythro* isomer exhibits adsorption bands at 930, 860 and 775 cm^{-1} which are absent in the *threo* isomer, while the latter has an absorption band at 970 cm^{-1} not present in the *erythro* isomer. Further proof of the assigned structures as *erythro*-*threo* adducts is found in the correlation of the NMR coupling constants of the methine protons as 3 cps for the *erythro* isomer and 2 cps for the *threo* isomer. These data are in agreement with those reported for the *erythro*- and *threo*-β-chlorosulfonamides obtained from *cis*- and *trans*-2-butene and dichloroamine-B (8).

Chemical proof of structure for the β-bromosulfonamide adducts was obtained by their chemical cyclization with base to the corresponding N-sulfonylaziridines in good yields. The base cyclization of β-haloamides is known to proceed with inversion of configuration (9). Accordingly, cyclization with base of the *threo* and *erythro* β-bromobenzenesulfonamides yields the *cis*- and *trans*-N-benzenesulfonylaziridines, respectively. For confirmation of the aziridine struc-

SCHEME II



SCHEME III



tures, *cis*-9,10-(N-benzenesulfonylepimino)octadecane was synthesized by an alternate method from *cis*-9-octadecene as shown in Scheme I (10–12). Reaction of *cis*-9,10-epiminooctadecane (III) with benzenesulfonylchloride in the presence of triethylamine, yielded *cis*-9,10-(N-benzenesulfonylepimino)octadecane (IV), mp 30–30.5 C. This latter reaction does not alter the stereochemistry of the aziridine ring system.

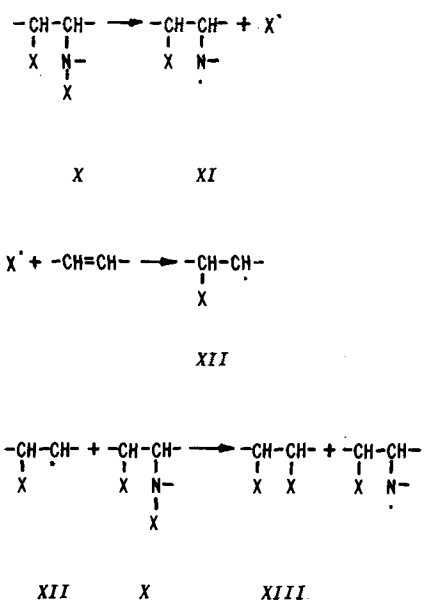
Basic cyclization of the *threo*-β-bromosulfonamide prepared from *cis*-9-octadecene and NNDBS gave an N-sulfonylaziridine, mp = 30–30.5 C, in 80% yield. The compound was identical in every respect with IV (infrared and NMR spectra, TLC and GLC, mixture melting point determination showed no depression). Thus NNDBS adds to internal olefins in a stereoselective fashion producing as the major product the β-bromosulfonamide derived from *trans*-addition to the double bond.

Two mechanisms can be proposed for the formation of β-bromosulfonamides from NNDBS and olefinic compounds. The one pathway involves an ionic mechanism as shown in Scheme II. The initial step involves the formation of the bromonium ion intermediate V. Nucleophilic attack on the bottom side of ion V by the sulfonamido gegen ion produces the intermediate N-bromo-β-bromosulfonamide VI. Reduction of VI with bisulfite gives the corresponding β-bromosulfonamide.

The alternative reaction pathway leading to addition products is via a radical addition mechanism. This latter mechanism is analogous to the reaction of other N-haloamides with olefinic compounds (13) and is shown in Scheme III.

If the reaction were proceeding via the ionic pathway one should obtain a stereoselective or even a

SCHEME IV



stereospecific adduct. Alternatively, if the reaction proceeded via a radical mechanism the product distribution should be random in the absence of other complicating factors. Experimentally the reaction was found to be stereoselective. Ueno et al. (5) also observed this selectivity in their studies of the reaction of NNDBS with cyclohexene and cyclopentene. In view of this observed selectivity of addition of NNDBS to internal olefins it would appear that the ionic mechanism is operative. Formation of an isomer mixture is best rationalized by the assumption that the reactive intermediate exists partially as bromonium ion V and partially as carbonium ion Va and that both of these species are involved in product formation.

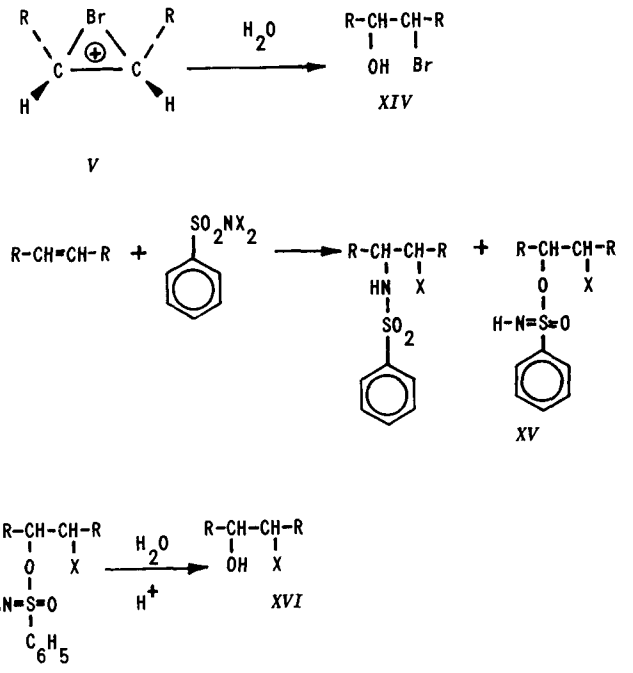
Identification of the major side products of the reaction of NNDBS with olefins as dibromides and bromohydrins was made on the basis of the following considerations. In a number of examples (see Experimental section) these byproducts were isolated by glpc or column chromatography. Structures were assigned on the basis of elemental analyses and comparison of the glpc retention times and infrared spectra with those of authentic samples. Unfortunately no stereochemical assignments could be made for these addition products.

The formation of dibromides in the reaction of NNDBS with olefins has also been observed by Ueno et al. (5), who has shown that these byproducts are the result of a reaction of the N-bromo-β-bromosulfonamide formed initially and a second molecule of olefinic substrate. This secondary reaction proceeds by a radical chain mechanism and is shown in Scheme IV.

The formation of bromohydrins as side products is somewhat more difficult to rationalize. These compounds could arise by attack of water on the bromonium ion V (Scheme V), but this hypothesis is tenuous, since the reactions were carried out under essentially anhydrous conditions. (Disappearance of olefin is complete prior to addition of bisulfite). An alternate explanation can be found in the results obtained by Butler and Daniher (8) in their studies

of the reaction of dichloramine B with *cis*- and *trans*-2-butene. These workers isolated by-products which they characterized as β-chloroiminosulfonates. These latter materials are formed by nucleophilic attack of oxygen rather than nitrogen on the carbonium ion intermediate (Scheme V). The iminosulfonate derivatives (XV) are readily solvolyzed by acetic acid to the corresponding β-chloroacetates. In the present series of reactions, attack by oxygen would lead to the analogous N-bromo-β-bromoiminosulfonates. However, all attempts to isolate such intermediates proved unsuccessful. It is thought that hydrolysis of the bromo derivatives by aqueous acids occurs much more readily than hydrolysis of the β-chloroiminosulfonate analogs and that isolation is thus precluded. This argument, however, is speculative, and until further work is carried out, the formation of bromohydrin derivatives in the reaction of NNDBS with olefins is still subject to doubt.

SCHEME V



Experimental Procedures

Materials

N,N-Dibromobenzenesulfonamide (NNDBS). Prepared by bromination of benzenesulfonamide (14). Purity 98–99% as determined by sodium thiosulfate titration.

Cis-3-hexene (96%), *trans*-3-hexene (99%) and *cis*-5-decene (96%) were purchased from Chemical Samples, Inc. and were used as received. *Cis*-2-heptene (95%) was used as received from Phillips 66. Methyl oleate (98%) was used as received from Applied Science Laboratories.

Cis-9-octadecene and *trans*-9-octadecene were prepared by the lithium aluminum hydride reduction of the tosylates of oleyl and elaidyl alcohols (15). Purity, as determined by glpc and TLC was 98–99%.

Cis-9,10-Epiminooctadecane. This material was prepared by the method of Gebelein et al. from *cis*-9-octadecene (10). Purity by perchloric acid titration (16) was >98%.

Addition of N,N-Dibromobenzenesulfonamide to Olefins. General Procedure

A mixture of NNDBS (5.9 g, 0.016 mole) and carbon tetrachloride (35 ml) was placed in a 100 ml flask and cooled to 15 C. The olefin (0.016 mole) was then added dropwise at a rate to maintain the reaction temperature at 15–20 C. When addition was complete the reaction mixture was allowed to warm to room temperature, and it was stirred until complete disappearance of olefin was noted by glpc. A 20% aqueous solution of sodium bisulfite (25 ml) was added at 15–20 C. The organic layer was then separated, and the aqueous phase was extracted with three 25 ml portions of chloroform. The combined organic layers were washed with two 25 ml portions of water and dried over anhydrous sodium sulfate. The crude reaction product was isolated by removal of the solvents under vacuum. Yields and elemental analyses of products are listed in Table I.

Product Isolation and Purification

Threo-3-Bromo-4-(N-Benzenesulfonamido)hexane. Prepared from *cis*-3-hexene, the product was recrystallized from 50% ether-hexane at −20 C; mp 79.5–80.5 C.

Erythro-3-Bromo-4-(N-Benzenesulfonamido)hexane. Prepared from *trans*-3-hexene, the product was recrystallized from 50% ether-hexane at −20 C; mp 92–93 C.

Threo-2(3)-Bromo-3(2)-(N-Benzenesulfonamido) heptane. Prepared from *cis*-2-heptene, the product, a viscous liquid, was purified by column chromatography on Florisil (1 g/35 g). Elution with 5% ether-benzene gave the adduct as a clear oil. TLC showed this material to be a single component, R_f .55 (10% ether-benzene; silica gel).

Threo-5-Bromo-6-(N-Benzenesulfonamido)decane. Prepared from *cis*-5-decene, the product was recrystallized from petroleum ether (bp 30–60 C) at −20 C; mp 39–40 C.

Threo-9-Bromo-10-(N-Benzenesulfonamido)octadecane. Prepared from *cis*-9-octadecene, the crude product, a mixture of three components, was purified by chromatography on Florisil (1 g/35 g). Elution with hexane (500 ml) afforded 9,10-dibromooctadecane (yield 9%).

Analysis. Calculated for $C_{18}H_{36}Br_2$: C, 52.4; H, 8.80; Br, 38.8. Found: C, 52.4; H, 8.70; Br, 38.6.

Further elution with 10% benzene-hexane (800 ml) gave 9-bromo-10-hydroxyoctadecane (yield 13%).

Analysis. Calculated for $C_{18}H_{37}BrO$: C, 61.9; H, 10.7; Br, 22.9. Found: C, 61.8; H, 10.6; Br, 22.9.

Elution with 50% benzene-hexane (1500 ml) gave the bromosulfonamide as a clear oil. TLC showed this material to be one component, R_f 0.25 (50% benzene-hexane; silica gel).

Erythro-9-Bromo-10-(N-Benzenesulfonamido)octadecane. Prepared from *trans*-9-octadecene, the crude product was chromatographed on Florisil. Elution with hexane gave the corresponding dibromide (11.5%), while 10% benzene-hexane yielded the bromohydrin (12%). Finally, elution with 50% benzene-hexane gave the bromosulfonamide. TLC showed this material to be one component, R_f 0.20 (50% benzene-hexane; silica gel).

Methyl-threo-9(10)-Bromo-10(9)-(N-Benzenesulfonamido)octadecanoate. Prepared from methyl oleate, the crude product, a viscous liquid, was purified by

chromatography on Florisil (1 g/30 g). Elution with 10% ether-benzene gave the adduct as a clear oil. TLC showed this material to be a single component, R_f 0.45 (10% ether-benzene; silica gel).

N-Sulfonylaziridines from β-Bromosulfonamides

Cis-3,4-(N-Benzenesulfonylepimino)hexane. A typical procedure is given in detail. *Threo*-3-bromo-4-(N-benzenesulfonamido)hexane (2.2 g, 7 mmole) in 95% ethanol (10 ml) was added in one portion to a solution of sodium hydroxide (0.32 g, 8 mmole) in 50% ethanol (5 ml). The solution was heated to reflux for 15 min, cooled to room temperature and poured into water (40 ml) and extracted with ether (3 × 30 ml). The combined extracts were washed with water until the washings were neutral, dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The residual oil was crystallized from 5% ether-hexane at −20 C to yield the aziridine as a white solid, mp = 39–40 C. Purity by perchloric acid titration (16) was 98.5%. Elemental analyses and yield data are listed in Table II.

Trans-3,4-(N-Benzenesulfonylepimino)hexane. Prepared from *erythro*-3-bromo-4-(N-benzenesulfonamido)hexane, the product was purified by recrystallization from petroleum ether (bp 30–60 C) at −20 C, mp 28–29 C. Purity by titration was 101%.

Cis-2,3-(N-Benzenesulfonylepimino)heptane. Prepared from *threo*-2(3)-bromo-3(2)-(N-benzenesulfonamido)heptane, the product, an oil, was purified by chromatography on Florisil (1 g/30 g). Elution with benzene gave the aziridine as a clear liquid n_D^{27} 1.5141. Purity by titration was 98.7%.

Cis-5,6-(N-Benzenesulfonylepimino)decane. Prepared from *threo*-5-bromo-6-(N-benzenesulfonamido) decane, the product was purified by chromatography on Florisil (1 g/30 g). Elution with hexane gave the aziridine as a clear oil n_D^{27} 1.5039. Purity by titration was 99.2%.

Cis-9,10-(N-Benzenesulfonylepimino)octadecane. Prepared from *threo*-9-bromo-10-(N-benzenesulfonamido)octadecane, the product was recrystallized from hexane at −20 C, mp 30.0–30.5 C. Purity by titration was 99.0%.

Alternatively, the aziridine was prepared by the reaction of *cis*-9,10-epiminooctadecane with benzenesulfonylchloride in the presence of triethylamine, mp 30.0–30.3 C, purity by titration was 100%. The two samples were identical by TLC, infrared spectroscopy and mixed mp.

Trans-9,10-(N-Benzenesulfonylepimino)octadecane. Prepared from *erythro*-9-bromo-10-(N-benzenesulonamido)octadecane, the product was purified by chromatography on Florisil (1 g/30 g). Elution with 50% benzene-hexane gave the aziridine as a clear oil n_D^{27} 1.4938. Purity by titration was 99.1%.

Methyl cis-9,10-(N-benzenesulfonylepimino)octadecanoate. A solution of methyl *threo*-9(10)-bromo-10(9)-(N-benzenesulfonamido)octadecanoate in methanol was added in one portion to a solution of sodium methoxide in methanol and refluxed for 10 min. The crude reaction product was isolated as above. Column chromatography of the crude product on Florisil (1 g/30 g) with 10% ether-benzene gave the aziridine as a colorless oil n_D^{27} 1.4938. Purity by titration was 99.3%.

REFERENCES

1. Wolfe, S., and D. V. C. Awang, J. Am. Chem. Soc. *89*, 5287–88 (1967); Foglia, T. A., and D. Swern, J. Org. Chem. *31*, 3625–31 (1966); Schrage K., Tetrahedron *23*, 3033–38, 3039–42 (1967); Theilacker, W., and H. Wessel, Ann. Chem. *703*, 34–36 (1967); Ohashi, T., M. Sugie, M. Okahara and S. Komori, Tetrahedron Letters *1968*, 4195–97.
2. Kharasch, M. S., and H. M. Priestly, J. Am. Chem. Soc. *61*, 3425–32 (1939).
3. Buckles, R. E., and W. J. Probst, J. Org. Chem. *22*, 1728–29 (1957).
4. Oehlschlager, A. C., C. D. Kennedy and L. H. Zalkow, Ibid. *31*, 1682–88 (1966).
5. Ueno, Y., S. Takemura, Y. Ando and H. Teravchi, Chem. Pharm. Bull. *15*, 1193–97, 1198–1203 (1967); Ibid. *15*, 1328–30 (1967); Ibid. *13*, 1369–72 (1965).
6. Seden, T. P., and R. W. Turner, J. Chem. Soc. (Part C, Org. Chem. Section) *1968*, 876–78.
7. Daniher, F. A., and P. E. Butler, J. Org. Chem. *33*, 4336–40 (1968).
8. Daniher, F. A., M. T. Melchior and P. E. Butler, Chem. Commun. *1968*, 931–32.
9. Fanta, P. E., in "Heterocyclic Compounds With Three and Four Membered Rings," Part 1, Edited by A. Weissberger, Interscience Publishers, Inc., New York, 1964, p. 524–575.
10. Gebelein, C. G., G. Swift and D. Swern, J. Org. Chem. *32*, 3314–17 (1967).
11. Hassner, A., and C. Heathcock, Ibid. *29*, 3640–45 (1964); Ibid. *30*, 1748–52 (1965).
12. Hassner, A., M. E. Lorber and C. Heathcock, Ibid. *32*, 540–49 (1967).
13. Buckles, R. E., R. C. Johnson and W. J. Probst, Ibid. *22*, 55–59 (1957); Park, J. D., H. J. Gerjouich, W. R. Lycan and J. R. Lacher, J. Am. Chem. Soc. *74*, 2189–93 (1952).
14. Akiyoshi, S., and K. Okuno, Ibid. *76*, 693–94 (1954).
15. Dyen, M. E., H. C. Hamann and D. Swern, JAOCS *43*, 431–42 (1966).
16. Maerker, G., E. T. Haeberer, L. M. Gregory and T. A. Foglia, Anal. Chem. *41*, 1698–1700 (1969).

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