The Addition of N,N-Dichlorosulfonamides to Unsaturates

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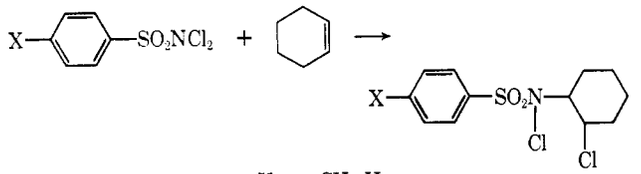
Received February 8, 1968

The addition of N,N-dichlorosulfonamides to olefins and conjugated dienes has been examined. The reaction of these reagents with propylene and styrene gives high yields of N-chloro-N-(β-chloroalkyl)sulfonamides which have predominantly anti-Markovnikov orientation. The reaction with isobutylene takes a different path to give 3-chloro-2-methyl-1-propene as the major product. Addition to 1,3-butadiene and chloroprene proceeds rapidly and exothermically to give high yields of 1,4 adducts. Reduction of the N-chloro adducts with sodium sulfite solution affords good yields of the corresponding sulfonamide derivatives.

In a study of the efficiency of N-chloramide derivatives as chlorinating agents, Ziegler[3] noted that N,N-dichloro-*p*-toluenesulfonamide rapidly lost about 50% of its active chlorine when treated with cyclohexene. The major product was not 3-chlorocyclohexene but an oil which was not further characterized. The major component of the oil was probably a 1:1 adduct since Thielacker[4] has reported that the addition of N,N-dichlorobenzenesulfonamide (Dichloramine B) to cyclohexene gives an 80% yield of addition product.



X = *p*-CH_3, H.

Russian workers have examined the reaction of Dichloramine B with alcohols,[5,6] carboxylic acids,[7] and phenols[8] as a method of generating hypohalite derivatives *in situ*. The reaction of these hypohalites with olefins or dienes produced chloro ether or ester derivatives.

The reaction of N,N-dichlorosulfonamides with styrene, propylene, isobutylene, 1,3-butadiene, and chloroprene has been examined. With the exception of isobutylene where chlorination is the principal reaction, good yields of 1:1 adducts are obtained. The behavior of the N,N-dichlorosulfonamides closely parallels the reactivity of the analogous N,N-dichlorocarbamates with olefins and conjugated dienes.[9]

Results

Generally, the reactions were performed by the dropwise addition of the N,N-dichlorosulfonamide in methylene chloride solution to a cooled solution of unsaturate in the same solvent. With gaseous unsaturates it was convenient to distil the reactant with nitrogen dilution into a cooled solution of the N,N-dichlorosulfonamide.

The reactions were spontaneous and quite exothermic when conjugated dienes were used. After an equimolar amount of diene had been introduced the exotherm abated. The reaction mixture was then warmed slowly to room temperature; the solvent was removed at aspirator pressure. The crude products were analyzed for isomer content by nmr spectroscopy.

The reaction with olefins was rapid, but not so exothermic as the diene reactions. Again the crude products were analyzed for isomer content by nmr spectroscopy.

An examination of the nmr spectra of the N–Cl adduct and its corresponding reduction product clearly indicates the mode of addition to the unsaturate (Table I). The chemical shift of the hydrogens on the carbon α to the sulfonamide group are very sensitive to changes in chemical environment. Upon reduction of the N-chloro function upfield shifts of approximately 0.3

$$>CH—NCl- \longrightarrow >CH—NH-$$

ppm are observed for the methylene hydrogens[9c] adjacent to the nitrogen. In addition, an increase in multiplicity of this group is observed due to coupling with the sulfonamide proton. This –CH—NH– coupling may be removed by treatment of the sample *in situ* with deuterium oxide, thereby exchanging the amide proton. The position of the hydrogens on the carbon α to the chloro group does not change significantly, shifting upfield anywhere from 0.01 to 0.20 ppm depending upon the particular compound.

Addition to Olefins.—The dropwise addition of styrene to a chilled solution of N,N-dichlorobenzenesulfonamide in methylene chloride proceeded spontaneously and exothermically to give the adduct II in nearly quantitative yield. In the nmr spectrum of II the

$$C_6H_5SO_2NCl_2 + C_6H_5CH{=}CH_2 \longrightarrow C_6H_5SO_2N(Cl)CH_2CH(Cl)C_6H_5$$
II

protons of the methylene group are nonequivalent and appear as an ABX pattern due to further coupling with the low field methine proton.

Treatment of II with aqueous sodium sulfite gave the reduction product III. Because of magnetic

$$II + Na_2SO_3 \longrightarrow C_6H_5SO_2NHCH_2CH(Cl)C_6H_5$$
III

symmetry the protons of the methylene group in III are equivalent and now appear as a triplet due to approximately equal coupling with both the methine proton and the NH proton. This signal changes to a doublet after exchange of the sulfonamide proton with deuterium oxide. The spectral data are consistent

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(8) M. V. Likhosherstov and R. A. Arkhangel'skaya, *ibid.*, **7**, 1914 (1937).
(9) (a) T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966); **33**, 766 (1968). (b) K. Schrage, *Tetrahedron Lett.*, 5975 (1966); *Tetrahedron*, 3033, 3039 (1967). (c) F. A. Daniher and P. E. Butler, *J. Org. Chem.*, **33**, 2637 (1968).

TABLE I
NMR PARAMETERS OF N,N-DICHLOROSULFONAMIDE-UNSATURATE ADDUCTS[a]

Propylene[b]

R	N-Chloro amides[f] RSO$_2$-NCl	CH$_2$	CH(Cl)	CH$_3$		Reduced N-chloro amides[g] RSO$_2$	NH	CH$_2$	CH(Cl)	CH$_3$	
C_6H_5	7.72 m[d] 8.00 m	3.47 d	4.26 h	1.60 d	$J_{CH_3-CH} = 6.5$ $J_{CH_3-CH} = 6.7$	7.55 m 7.92 m	5.54 t	3.17 m[c]	4.05 h	1.44 d	$J_{CH_3-CH} = 6.5$
p-ClC_6H_5	7.57 m[e] 7.90 m	3.46 d	4.22 h	1.60 d	$J_{CH_3-CH} = 6.5$ $J_{CH_3-CH} = 6.7$	7.49 m	5.38 t	3.17 m	4.08 h	1.47 d	$J_{CH_3-CH} = 6.5$
$(CH_3)_2N$	3.03 s	3.48 dd 3.61 dd	4.25 h	1.58 s	$J_{CH_3-CH} = 6.5$ $J_{AX} = 6.0$ $J_{BX} = 6.5$ $J_{gem} = 14.0$	2.81 s	5.28 t	3.28 m	4.16 m	1.53 d	$J_{CH_3-CH} = 6.5$

Styrene

	RSO$_2$	N-CH$_2$Cl	CH(Cl)	C_6H_5		RSO$_2$	N	CH$_2$	CH(Cl)	C_6H_5	
C_6H_5	7.58 m[d] 7.89 m	3.66 dd 3.93 dd	5.15 t	7.39 m	$J_{vic} = 7.0$ $J_{gem} = 14.0$	7.49 m 7.90 m	5.67 t	3.47 t	4.92 t	7.27 m	$J_{vic} = 7.0$ $J_{NH-CH} = 6.4$
$(CH_3)_2N$	2.79 s	3.90 d	5.16 t	7.37 m	$J_{vic} = 7.1$	2.74 s	4.98 b	3.54 t	5.98 t	7.41 m	$J_{vic} = 7.0$

Butadiene

	R-SO$_2$NCl	CH$_2$	CH=CH	CH$_2$Cl		R	SO$_2$NH	CH$_2$	CH=CH	CH$_2$Cl	
CH_3	3.12 s	4.13 m	5.98 m	4.12 m		3.01 s	5.32 t	3.80 m	5.94 m	4.11 m	$J_{NH-H} = 6.0$
C_6H_5	7.66 m[d] 7.95 m	4.01 m	5.83 m	3.90 m		7.63 m 7.92 m	5.60 b	3.60 m	5.70 m	3.90 m	
p-ClC_6H_5	7.58 d[e] 7.93 d	3.93 m	5.86 m	4.03 m		7.54 m 7.87 m	5.10 b	3.63 m	5.73 m	3.96 m	

Chloroprene

	R-SO$_2$NCl	CH$_2$	C(Cl)=CH	CH$_2$Cl		R	SO$_2$NH	CH$_2$	C(Cl)=CH	CH$_2$Cl	
CH_3	3.16 s	4.23 s	6.19 t	4.27 d	$J_{vic} = 7.5$	3.02 s	5.29 b	4.02 d	6.17 t	4.24 d	$J_{vic} = 7.5$ $J_{NH-H} = 6.2$
C_6H_5	7.80 m	4.01 s	6.05 t	4.16 d	$J_{vic} = 7.3$	7.75 m 7.87 m	5.70 t	3.84 d	5.94 t	4.00 d	$J_{vic} = 7.5$ $J_{NH-H} = 6.5$
p-ClC_6H_5	7.62 d[e]	4.08 s	6.10 t	4.22 d	$J_{vic} = 7.3$	7.53 m 7.87 m	5.62 t	3.88 d	5.96 t	4.05 d	$J_{vic} = 7.5$ $J_{NH-H} = 6.5$
$(CH_3)_2N$	3.06 s	4.22 s	6.18 t	4.28 d	$J_{vic} = 7.0$	3.03 s	5.32 b	3.96 d	6.18 t	4.20 d	$J_{vic} = 7.5$ $J_{NH-H} = 6.5$

[a] Notation: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, b = broad, m = multiplet. Chemical shifts are in parts per million from TMS; coupling constants, hertz. [b] The corresponding Markovnikov adducts of propylene were identified by the characteristic methyl doublets [$CH_3CH(NClR)$] at 1.22 (R = *p*-ClC_6H_4), 1.12 (R = C_6H_5), and 1.37 [R = $(CH_3)_2N$] ppm. [c] On D_2O treatment the NH proton is replaced and the NH–CH coupling is removed. This simplified the methylene–methine region to an ABX system with J_{vic} = 7.3, 5.3 Hz and J_{gem} = 13.8 Hz. [d] The *ortho* protons appear at lowest field. [e] These protons appear as a typical *p*-disubstituted benzene pattern (AA'BB'). [f] Respective registry numbers: 17396-55-3; 17448-28-1; 17396-56-4; 17414-51-6; 17396-57-5; 17396-58-6; 17396-59-7; 17396-60-0; 17396-61-1; 17396-62-2; 17396-63-3; 17396-64-4. [g] Respective registry number: 17396-65-5; 17396-66-6; 17396-67-7; 17396-68-8; 17396-69-9; 17396-70-2; 17396-71-3; 17396-72-4; 17396-73-5; 17396-74-6; 17396-75-7; 17414-52-7.

only with the anti-Markovnikov orientation for the adduct.

The reaction of N,N-dichloro-N',N'-dimethylsulfamide[10] with styrene gave a quantitative yield of crystalline adduct. Examination of the nmr spectra of both the N-chloro adduct and its reduction product indicated that anti-Markovnikov addition had occurred.

The reaction of propylene with the N,N-dichloroamide derivatives of benzenesulfonamide, *p*-chlorobenzenesulfonamide, or N,N-dimethylsulfamide afforded a mixture of anti-Markovnikov (IV) and Markovnikov (V) adducts. With these reagents, the anti-Markovnikov adducts predominated in a ratio of about 85:15.

$$RSO_2NCl_2 + CH_3CH{=}CH_2 \longrightarrow RSO_2N(Cl)CH_2CH(Cl)CH_3 + RSO_2N(Cl)CH(CH_3)CH_2Cl$$

IVa–c Va–c

R = (a) C_6H_5; (b) *p*-Cl-C_6H_4; (c) $(CH_3)_2N$

Pure samples of the anti-Markovnikov adducts IVa and IVb were obtained by fractional crystallization. The dimethylsulfamide derivative existed as an oil at room temperature, and all attempts to obtain a pure sample of one of the isomers were unsuccessful.

In the nmr spectra of IVa and IVb the methylene groups appear as doublets, while an ABX pattern is observed for the same group in IVc. Upon reduction the methylene group of IVa changes to a complex multiplet which simplifies to an ABX pattern when the sulfonamide proton is exchanged with deuterium oxide.

When the addition to isobutylene was examined, the reaction took a completely different course. The major product did not arise from addition but from chlorination. The chlorinated product was identified as 3-chloro-2-methyl-1-propene (VI) by comparison of its ir spectrum and vpc behavior with those of an authentic sample. This product was accompanied by the formation of an equivalent amount of benzenesulfonamide.

$$(H_3C)_2C{=}CH_2 + C_6H_5SO_2NCl_2 \longrightarrow ClCH_2C(CH_3){=}CH_2 + C_6H_5SO_2NH_2 + C_6H_5SO_2NHC(CH_3)_2CH_2Cl$$

VI VII

Further, a small amount of another material was also isolated and has been assigned the structure of N-(2-methyl-3-chloropropyl-2)benzenesulfonamide

(10) V. M. Cherkasov, T. A. Dashevskaya, and L. I. Baranova, *Ukr. Khim. Zh.*, **32**, 861 (1966); *Chem. Abstr.*, **66**, 2155 (1967).

(VII). The assignment is based upon elemental analysis, the failure of VII to give a positive potassium iodide–starch test, and spectral data. In the nmr spectrum of VII, the signals for the *gem*-dimethyl and methylene groups occur as sharp singlets at 1.25 and 3.60 ppm, respectively. The N–H proton appears as a broad singlet at 5.61 while the aromatic hydrogens occur as a pair of multiplets centered near 7.61 and 8.00 ppm.

Addition to Conjugated Dienes.—In this phase of the study, butadiene and chloroprene were chosen as the conjugated diolefins for examination. In addition to the N,N-dichlorosulfonamide derivatives employed in the propylene case, a simple aliphatic sulfonamide, N,N-dichloromethylsulfonamide, was also examined.

In all of these cases the addition reactions proceeded spontaneously and exothermically to afford high yields of the corresponding 1:1 adducts (VIII). The predominant mode of addition in each case was 1,4 with a selectivity of >95%. The high selectivity for 1,4

$$CH_2{=}C(R')CH{=}CH_2 + RSO_2NCl_2 \longrightarrow RSO_2N(Cl)CH_2C(R'){=}CHCH_2Cl \quad (VIII)$$

$R' = H, Cl$

addition is unusual since the addition of N,N-dichlorocarbamates to butadiene afforded significant amounts (15%) of 1,2 adducts.[9c]

The addition of N,N-dichlorobenzenesulfonamide to butadiene proceeded equally well in the dark. However, when the reaction was performed in the dark under an oxygen atmosphere, the adduct formation was inhibited.

The reduction of VIII with sodium sulfite solution proceeded smoothly to give the reduced sulfonamides (IX) in high yields.

$$VIII + Na_2SO_3 \longrightarrow RSO_2NHCH_2CH{=}CHCH_2Cl \quad (IX)$$

The structure of each of the adducts was established by nmr spectroscopy. The butadiene products (IX, R′ = H) are characterized by their nmr spectra which display proton signals (2 H apiece) for the methylene groups adjacent to chlorine and nitrogen (~4.0 ppm), respectively, and by the two-proton multiplet for the nearly equivalent olefin protons (~5.9 ppm). On reduction, the resonance position of the methylene group next to nitrogen moves upfield approximately 0.35 ppm and becomes more complicated owing to coupling with the amide proton. This coupling as well as the NH signal may be removed by treating the sample with deuterium oxide.

In the nmr spectra of the chloroprene adducts (VIII, R′ = Cl), the signal for the methylene group next to nitrogen is a broad singlet indicating the absence of an adjacent olefinic proton. The olefinic proton of the resultant internal olefin is a triplet near 6.10 ppm and is coupled to the adjacent methylene group which appears as a doublet at about 4.2 ppm. These assignments are confirmed by examining the nmr spectra of the reduction products (IX, R′ = Cl). The position of the methylene group adjacent to nitrogen moves upfield approximately 0.2 ppm and now appears as a doublet due to coupling with the amide proton. The amide proton appears as a triplet. Upon treatment with deuterium oxide this latter signal disappears, and the methylene doublet reverts to a singlet, while the multiplicity of the other signals remains unchanged. These data are consistent only with a 1,4 adduct.

Discussion

With simple olefins such as propylene and styrene, the addition of N,N-dichlorosulfonamides is predominantly anti-Markovnikov and consistent with a radical mechanism. The complete selectivity for anti-Markovnikov addition observed with styrene reflects the enhanced stability of the benzyl radical. The propylene adducts are predominantly anti-Markovnikov. The presence of some Markovnikov adduct may reflect the fact that the difference in stability of the two possible radicals is not so great that one is formed to the virtual exclusion of the other. Conversely it is possible that the Markovnikov adducts are being formed *via* a competing ionic mechanism.[11]

The propensity for isobutylene to undergo chlorination instead of addition with positive halogen compounds is well documented. Treatment of isobutylene with phenyl hypochlorite has been reported to yield[8] a large amount of chlorination product and a small percentage of adduct.

$$(CH_3)_2C{=}CH_2 + C_6H_5OCl \longrightarrow VI + C_6H_5OC(CH_3)_2CH_2Cl$$

The reaction of isobutylene with elemental chlorine has been shown to give an 87% yield of allylic chlorination product (VI) and a 13% yield of addition product.[12]

The formation of VII may arise by the interception of the chloronium ion (X) by benzenesulfonamide[13] and then subsequent proton loss as shown in Scheme I.

SCHEME I

REACTION OF ISOBUTYLENE WITH N,N-DICHLOROBENZENESULFONAMIDE

$$C_6H_5SO_2NCl_2 + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2\overset{Cl}{\overset{+}{C}}\!\!-\!\!CH_2 + C_6H_5SO_2N^-Cl \quad (X)$$

$$X \longrightarrow VI + H^+$$

$$C_6H_5SO_2NHCl \rightleftharpoons C_6H_5SO_2NCl_2 + C_6H_5SO_2NH_2$$

$$X + C_6H_5SO_2NH_2 \longrightarrow VII + H^+$$

The data obtained, however, do not rule out the possibility of the formation of VII by reaction of X with the N-chlorobenzenesulfonamide anion to give

(11) The reaction of propylene with N,N-dichlorobenzenesulfonamide has been examined both in the dark and in the dark under an oxygen atmosphere. The nmr spectra of the crude reaction mixture in both cases are identical and are significantly different from the spectrum of the crude product obtained in this study. In both of these cases the ratio of the C–CH_3 groups for anti-Markovnikov (1.60 ppm) and Markovnikov addition products (1.09 ppm) is about 1:1; in addition, the presence of other C–CH_3 groups is also noted. The structure of these other materials has not as yet been firmly established. In any event it is apparent that the course of the reaction changes drastically when performed under nonradical conditions.

The ionic addition of N,N-dichlorobenzenesulfonamide to olefins will be reported separately.

(12) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2172 (1965).

(13) The disproportionation two molecules of N-chlorobenzenesulfonamide into N,N-dichlorobenzenesulfonamide and benzenesulfonamide has been discussed by T. Higuchi, K. Ikeda, and A. Hussain, *J. Chem. Soc., B*, 546, 549 (1967).

XI and subsequent reaction of XI with isobutylene to give VII and VIII.[14]

$$X + C_6H_5SO_2^-NCl \longrightarrow C_6H_5SO_2N(Cl)C(CH_3)_2CH_2Cl$$

$$XI + (CH_3)_2C{=}CH_2 \longrightarrow VI \text{ and } VII$$

The data obtained for the addition of N,N-dichlorosulfonamides to conjugated dienes indicate that the reaction is occurring by a radical chain mechanism. The preference for 1,4 over 1,2 addition has been observed in the reaction of N,N-dichlorocarbamates,[9c] protonated N-chlorodialkylamines,[15] and chlorine[16] with conjugated dienes. In all of these cases a radical chain mechanism has been proposed for the addition reaction. Further support for the radical mechanism is the inhibition of the reaction by oxygen.

Since radical initiations are not required for the addition to occur, the generation of the radicals may be occurring *via* a process of "spontaneous" initiation.[9c,16,17] The reaction exhibits all of the characteristics which have been observed in other "spontaneously" initiated reactions, *i.e.*, lack of initiators, mild reaction conditions, and spontaneous reaction.

Experimental Section

Nuclear magnetic resonance spectra were run on a Varian A-60 spectrometer as *ca.* 50% solutions in deuteriochloroform with tetramethylsilane as an internal standard unless otherwise noted.

Infrared spectra were recorded on a Beckman Model IR-10 infrared spectrophotomer.

Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected.

Unsaturates.—The propylene used was Research Grade obtained from the Phillips Petroleum Co. The isobutylene and butadiene were CP grade (99%) obtained from the Matheson Co. The styrene was obtained from Matheson Coleman and Bell and was distilled prior to use. The chloroprene was obtained as a 50% solution in xylene from the E. I. du Pont de Nemours and Co., Inc., Elastomer Chemicals Department, Wilmington, Del. It was separated from the xylene by fractional distillation and then used immediately.

N,N-Dichlorosulfonamides.—N,N-Dichlorobenzenesulfonamide was obtained from Matheson Coleman and Bell. Before each run the appropriate amount of reagent was dissolved in methylene chloride and filtered through a bed of Filter Aid to remove dirt and other suspended particles. The clear filtrate was then used without further purification. The N,N-dichloroamide derivatives of methyl-[18] and *p*-chlorobenzenesulfonamide[19] and N,N-dimethylsulfamide[10] were prepared according to literature procedures.

General Procedure for the Addition of N,N-Dichlorosulfonamides to Unsaturates. Propylene.—Propylene (0.3 mol) was condensed at −78° into a Pyrex pressure tube fitted with a Teflon needle valve containing a solution of 0.1 mol of N,N-dichlorosulfonamide in 100 ml of methylene chloride. The needle valve was closed and the tube warmed to 0° and maintained at that temperature for 3 hr. The excess propylene was vented, and the solvent was removed at aspirator pressure at ambient temperature. The residue was then examined for isomer content by nmr spectroscopy. Recrystallization afforded the following anti-Markovnikov adducts: $C_6H_5SO_2N(Cl)CH_2CH(Cl)CH_3$ (cyclohexane), 53%, mp 69–70°. *Anal.* Calcd for $C_9H_{11}Cl_2NO_2S$: C, 40.32; H, 4.13; N, 5.22; S, 11.96. Found: C, 40.00; H, 4.40; N, 5.45; S, 12.47. *p*-$ClC_6H_4SO_2N(Cl)CH_2CH(Cl)CH_3$ (carbon tetrachloride), 54%, mp 90–92°. *Anal.* Calcd for $C_9H_{10}Cl_3NO_2S$: C, 35.72; H, 3.33; N, 4.63; S, 10.60. Found: C, 35.66; H, 3.47; N, 4.78; S, 10.87. The N,N-dimethylsulfamide adduct, $(CH_3)_2NSO_2N(Cl)CH_2CH(Cl)CH_3$, existed as an oil at room temperature. *Anal.* Calcd for $C_5H_{12}Cl_2N_2O_2S$: C, 25.53; H, 5.14; N, 11.91; S, 13.64. Found: C, 25.53; H, 5.30; N, 11.91; S, 13.59.

Styrene (0.1 mol) was added dropwise to a stirred solution of N,N-dichlorosulfonamide (0.1 mol) in 100 ml of methylene chloride cooled to 0° in an ice–water bath. After addition was complete the solution was warmed to room temperature, and then the solvent was evaporated at aspirator pressure at ambient temperature. Recrystallization gave the following adducts: $C_6H_5SO_2N(Cl)CH_2CH(Cl)C_6H_5$, 91%, mp 69–70°. *Anal.* Calcd for $C_{14}H_{13}Cl_2NO_2S$: C, 50.92; H, 3.97; N, 4.24; S, 9.71. Found: C, 50.62; H, 4.07; N, 4.12; S, 9.80. $(CH_3)_2NSO_2N(Cl)CH_2CH(Cl)C_6H_5$, 88%, mp 63–65°. *Anal.* Calcd for $C_{10}H_{14}Cl_2N_2O_2S$: C, 40.40; H, 4.75; N, 9.42; S, 10.79. Found: C, 40.46; H, 4.99; N, 9.52; S, 10.82.

Isobutylene (0.2 mol) was slowly distilled with nitrogen dilution into a stirred solution of N,N-dichlorobenzenesulfonamide (0.1 mol) in 100 ml of methylene chloride cooled to −15°. During addition benzenesulfonamide crystallized out of solution. After addition was complete the reaction mixture was warmed to room temperature and then filtered to give 4.5 g of benzenesulfonamide, mp 149–151°. The filtrate was evaporated at reduced pressure, and the volatiles were collected in a Dry Ice–acetone trap. The residue was triturated with carbon tetrachloride to give 4.2 g of crude benzenesulfonamide, mp 140–148°.

The volatiles were distilled at atmospheric pressure to give, in addition to methylene chloride, 3.6 g of 3-chloro-2-methyl-1-propene, bp 67–70°, $n^{25}D$ 1.4245. This material was identified by comparison of its glpc retention time and ir spectrum with those of an authentic sample.

The carbon tetrachloride solution was concentrated to a small volume and then taken to the cloud point with pentane. The crude solid which crystallized was recrystallized from carbon tetrachloride–cyclohexane to give 3.0 g, 10%, of N-(2-methyl-3-chloropropyl-2)benzenesulfonamide, mp 68–69°. *Anal.* Calcd for $C_{10}H_{14}ClNO_2S$: C, 48.47; H, 5.69; N, 5.68. Found: C, 48.94; H, 5.89; N, 5.51.

Butadiene (0.1 mol) was condensed into a Pyrex pressure tube fitted with a Teflon needle valve. The tube was then connected by way of a T-joint to a nitrogen source. The butadiene container was opened and distilled with nitrogen dilution into a stirred solution of N,N-dichlorosulfonamide (0.1 mol) in 100 ml of methylene chloride cooled to −10°. The addition rate was such that the internal temperature remained between 0 and 5°. After addition was complete the solution was warmed to room temperature, and the solvent was removed at aspirator pressure at ambient temperature. The adducts were generally recrystallized from carbon tetrachloride, chloroform, or a benzene–pentane mixture. The following adducts were prepared: $C_6H_5SO_2N(Cl)CH_2CH{=}CHCH_2Cl$, 77%, mp 53–55°. *Anal.* Calcd for $C_{10}H_{11}Cl_2NO_2S$: C, 42.87; H, 3.96; N, 5.00; S, 11.44. Found: C, 43.01; H, 3.92; N, 5.13; S, 11.47. *p*-$ClC_6H_4SO_2N(Cl)CH_2CH{=}CHCH_2Cl$, 85%, mp 126–127°. *Anal.* Calcd for $C_{10}H_{10}Cl_3NO_2S$: C, 38.17; H, 3.20; N, 4.45; S, 10.20. Found: C, 38.16; H, 3.26; N, 4.61; S, 10.18. $CH_3SO_2N(Cl)CH_2CH{=}CHCH_2Cl$, 85%, mp 48–51°. *Anal.* Calcd for $C_5H_9Cl_2NO_2S$: C, 27.53; H, 4.16; N, 6.42; S, 14.70. Found: C, 27.74; H, 4.05; N, 6.46; S, 14.73.

Chloroprene.—A solution of N,N-dichlorosulfonamide (0.1 mol) in 75 ml of methylene chloride was added dropwise to a stirred solution of freshly distilled chloroprene (0.1 mol) in 25 ml of methylene chloride cooled to −10°. After addition was complete the reaction was processed as above to isolate the addition products. The following adducts were prepared: $C_6H_5SO_2N(Cl)CH_2C(Cl){=}CHCH_2Cl$, 82%, mp 49–50°. *Anal.* Calcd for $C_{10}H_{10}Cl_3NO_2S$: C, 38.17; H, 3.20; N, 4.45; S, 10.20. Found: C, 38.46; H, 3.43; N, 5.28; S, 10.61. *p*-$ClC_6H_4SO_2N(Cl)CH_2C(Cl){=}CHCH_2Cl$, 85%, mp 87–88°. *Anal.* Calcd for $C_{10}H_9Cl_4NO_2S$: C, 34.40; H, 2.60; N, 4.01; S, 9.18. Found: C, 34.89; H, 2.56; N, 4.09; S, 9.17. $CH_3SO_2N(Cl)CH_2C(Cl){=}CHCH_2Cl$, 89%, mp 72–73°. *Anal.* Calcd for $C_5H_8Cl_3NO_2S$: C, 23.78; H, 3.19; N, 5.55; S, 12.70. Found: C, 24.28; H, 3.30; N, 5.61; S, 12.80. $(CH_3)_2NSO_2N(Cl)CH_2C(Cl){=}CHCH_2Cl$, 84%, mp 38–40°. *Anal.* Calcd for C_6H_{11}-

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General Procedure for the Reduction of the N,N-Dichlorosulfonamide–Unsaturate Adducts.—A solution of 0.1 mol of adduct in 100 ml of methylene chloride was vigorously stirred at ambient temperature with a solution of 0.3 mol of sodium sulfite in 150 ml of water for about 0.5 hr, or until the organic layer failed to give a positive test with potassium iodide–starch paper. The layers were then separated; the aqueous layer was extracted with methylene chloride. The organic extracts were combined and dried over sodium sulfate. The solvent was evaporated at aspirator pressure and ambient temperature to give the reduced sulfonamide. These materials were recrystallized from one or more of the following solvents or solvent pairs: benzene, carbon tetrachloride, cyclohexane, ether, and benzene–pentane. The following sulfonamides were prepared: $C_6H_5SO_2NHCH_2CH(Cl)CH_3$, 89%, mp 79–80°. *Anal.* Calcd for $C_9H_{12}ClNO_2S$: C, 46.25; H, 5.55; N, 6.00; S, 13.72. Found: C, 46.50; H, 5.55; N, 6.43; S, 13.55. *p*-$ClC_6H_4SO_2NHCH_2CH(Cl)CH_3$, 87%, mp 105–108°. *Anal.* Calcd for $C_9H_{11}Cl_2NO_2S$: C, 40.32; H, 4.13; N, 5.22; S, 11.96. Found: C, 40.09; H, 4.40; N, 5.26; S, 12.24. $(CH_3)_2NSO_2NHCH_2CH(Cl)CH_3$, 84%, mp 25–26°. *Anal.* Calcd for $C_5H_{13}ClN_2O_2S$: C, 29.92; H, 6.53; N, 13.95; S, 15.98. Found: C, 30.09; H, 6.69; N, 14.06; S, 15.97. $C_6H_5SO_2NHCH_2CH(Cl)C_6H_5$, 95%, mp 45–47°. *Anal.* Calcd for $C_{14}H_{14}ClNO_2S$: C, 56.85; H, 4.77; N, 4.73; S, 10.84. Found: C, 56.31; H, 4.97; N, 4.61; S, 10.54. $(CH_3)_2NSO_2NHCH_2CH(Cl)C_6H_5$, 92%, mp 69–70°. *Anal.* Calcd for $C_{10}H_{15}ClN_2O_2S$: C, 45.71; H, 5.75; N, 10.66; S, 12.20. Found: C, 45.71; H, 5.83; N, 10.53; S, 12.21. $C_6H_5SO_2NHCH_2CH{=}CHCH_2Cl$, 85%, oil. *Anal.* Calcd for $C_{10}H_{12}ClNO_2S$: C, 48.88; H, 4.92; N, 5.70; S, 13.05. Found: C, 49.10; H, 4.96; N, 5.71; S, 13.38. *p*-$ClC_6H_4SO_2NHCH_2CH{=}CHCH_2Cl$, 78%, mp 78–79°. *Anal.* Calcd for $C_{10}H_{11}Cl_2NO_2S$: C, 42.87; H, 3.96; N, 5.00; S, 11.44. Found: C, 42.71; H, 3.88; N, 4.98; S, 11.23. $CH_3SO_2NHCH_2CH{=}CHCH_2Cl$, 87%, mp 26–27°. *Anal.* Calcd for $C_5H_{10}ClNO_2S$: C, 32.69; H, 5.49; N, 7.63; S, 17.46. Found: C, 32.51; H, 5.60; N, 7.47; S, 17.96. $C_6H_5SO_2NHCH_2C(Cl){=}CHCH_2Cl$, 81%, mp 83–84°. *Anal.* Calcd for $C_{10}H_{11}Cl_2NO_2S$: C, 42.87; H, 3.96; N, 5.00; S, 11.44. Found: C, 42.96; H, 3.93; N, 5.02; S, 11.50. *p*-$ClC_6H_4SO_2NHCH_2C(Cl){=}CHCH_2Cl$, 78%, mp 78–80°. *Anal.* Calcd for $C_{10}H_{10}Cl_3NO_2S$: C, 38.17; H, 3.20; N, 4.45; S, 10.19. Found: C, 37.99; H, 3.05; N, 4.47; S, 10.20. $CH_3SO_2NHCH_2C(Cl){=}CHCH_2Cl$, 84%, mp 157–158°. *Anal.* Calcd for $C_5H_9Cl_2NO_2S$: C, 27.53; H, 4.16; N, 6.42; S, 14.70. Found: C, 27.49; H, 4.33; N, 6.47; S, 14.65. $(CH_3)_2NSO_2NHCH_2C(Cl){=}CHCH_2Cl$, 84%, mp 25–26°. *Anal.* Calcd for $C_6H_{12}Cl_2N_2O_2S$: C, 29.16; H, 4.99; N, 11.34; S, 12.97. Found: C, 29.65; H, 4.90; N, 11.24; S, 13.03.

Registry No.—Tropylene, 115-07-1; styrene, 100-42-5; butadiene, 106-99-0; chloroprene, 126-99-8; isobutylene, 115-11-7; 3-chloro-2-methyl-1-propene, 563-47-3; VII, 2948-79-0; N,N-dichlorobenzenesulfonamide, 473-29-0; N,N-dichloromethylsulfonamide, 17396-47-3; N,N-dichloro-*p*-chlorobenzenesulfonamide, 17260-65-0; N,N-dichloro-N,N-dimethylsulfamide, 13882-13-8.

Acknowledgment.—The authors wish to thank Miss M. Miciak and Mr. J. J. Clemens for their competent technical assistance.

Sulfilimines and Sulfoximines Derived from 4-*t*-Butylthiane[1,2a]

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Received May 13, 1968

The stereochemical course of the reactions of Chloramine-T with 4-*t*-butylthiane and of N-sulfinyl-*p*-toluenesulfonamide, *p*-toluenesulfonyl isocyanate, and *p*-toluenesulfonyl azide with 4-*t*-butylthiane 1-oxides was examined. The stereochemistry of the N-tosylsulfilimine grouping was correlated with the known configurations of the sulfoxide group in the 4-*t*-butylthiane system by N alkylation of the sulfilimine, followed by hydrolysis of the adduct salt to sulfoxide. New compounds prepared in this series include the isomeric N-tosylsulfilimines, the "free" sulfoximines, and the N-tosylsulfoximines.

The potential asymmetry at the sulfur atom in sulfilimines and sulfoximines has been established by the resolution of appropriately substituted examples.[3] A number of methods are now available for the preparation of sulfilimines and sulfoximines. Those of interest to the present work are briefly described. The well-known reaction of sulfides with chloramines, especially Chloramine-T, has been used in a typical preparation of sulfilimines by Leandri and Spinelli.[4] Recently the reactions of sulfoxides with *p*-toluenesulfonyl isocyanate[5] and N-sulfinyl-*p*-toluenesulfonamide to produce[6] sulfilimines have been described. The latter reaction is reported to proceed with inversion of configuration at the sulfur atom.[7] The most direct method for the synthesis of sulfoximines would appear to be the oxidation of sulfilimines. It is noteworthy that, at the present time, only potassium permanganate and the salts of per acids are known to effect this oxidation and, then, in the large majority of cases, only in low yield.[7b,8] A general method for the production of sulfoximines is given by the reaction of sulfoxides with hydrazoic acid (sodium azide in a mixture of sulfuric acid and chloroform).[9] Horner and Christmann[10] have obtained N-benzoyldimethylsulfoximine from the reaction of dimethyl sulfoxide and benzoyl azide under the influence of light. Very recently Kwart and Khan[11] have prepared N-benzenesulfonyldimethylsulfoximine by the use of di-

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