N-CHLORO-N-2,2,2-TRICHLOROETHYL-p-CHLOROBENZENESULFONAMIDE AND ITS REACTION WITH SOME UNSATURATED COMPOUNDS

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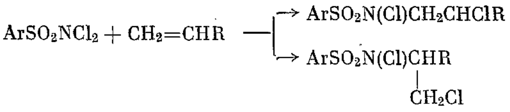
It was shown [1-5] on a number of examples that the addition of N,N-dichloroaryl(alkyl)sulfonamides to unsaturated compounds, containing electron-donor substituents, can be easily accomplished, both by the radical (A) and by the ionic (B) mechanism



$$ArSO_2NCl_2 + CH_2{=}CHR \rightarrow \begin{cases} ArSO_2N(Cl)CH_2CHClR \\ ArSO_2N(Cl)\underset{\displaystyle CH_2Cl}{\underset{|}{CHR}} \end{cases}$$

The addition of N,N-dichloroarylsulfonamides to compounds that contain electron-acceptor substituents at the double bond was studied to a less degree.

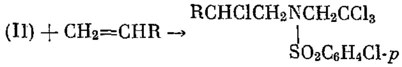
In the present paper, we studied both the radical and the ionic addition of N,N-dichloro-p-chlorobenzenesulfonamide (I) to vinylidene chloride. It was also interesting to study the addition of the obtained adduct to ethylene, styrene and allyl chloride, since only several examples are known [1, 4, 6] of the addition of N-halo-N-arylsulfonamides to unsaturated compounds

$$ArSO_2N(CH_2CHClX)Cl + CH_2{=}CHX \rightarrow ArSO_2N(CH_2CHClX)_2$$

The obtained data are summarized in Tables 1 and 2.

From the data in Table 1, it can be seen that the addition of (I) to vinylidene chloride in chlorobenzene at 95° goes under both radical and ionic conditions. The reaction goes much more rapidly in the presence of $SnCl_4$ (experiment 2) and benzoyl peroxide (experiment 4) and leads to high yields of N-chloro-N-2,2,2-trichloroethyl-p-chlorobenzenesulfonamide (II), the treatment of which with sodium bisulfite gives N-2,2,2-trichloroethyl-p-chlorobenzenesulfonamide (III).

The radical addition of (II) to ethylene, styrene and allyl chloride proceeded by the scheme:



$$(II) + CH_2{=}CHR \rightarrow RCHClCH_2\underset{\displaystyle SO_2C_6H_4Cl\text{-}p}{\underset{|}{N}}CH_2CCl_3$$

$R = H$ (IV); C_6H_5 (V); CH_2Cl (VI)

The conditions of this reaction are given in Table 2.

From Table 2 (experiment 2) it follows that the ionic addition of (II) to styrene does not go under the selected conditions. The radical addition under the same conditions led to N-2-chloro-2-phenylethyl-N-2',2',2'-trichloroethyl-p-chlorobenzenesulfonamide (V), i.e., the styrene fragment adds to the nitrogen atom contrary to the Markovnikov rule. The reactions with ethylene (experiment 1) and allyl chloride (experiment 4) were run under radical conditions and here the corresponding adducts (IV) and (VI) were isolated. The chloroallyl fragment also adds to the nitrogen atom contrary to the Markovnikov rule. As a result, (II) reacts more easily by the radical mechanism, both with electron-donor and with electron-acceptor unsaturated compounds, but, judging by the reaction conditions and the yields of the end products, this reaction goes with much greater difficulty than the analogous reactions of unsaturated compounds with N,N-dichloroarylsulfonamides [1-5].

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TABLE 1. Addition of N,N-Dichloro-p-chlorobenzenesulfonamide (I) to Vinylidene Chloride

$$\underset{\text{(I)}}{p\text{-}ClC_6H_4SO_2NCl_2} + CH_2{=}CCl_2 \xrightarrow{95°,\text{ in } C_6H_5Cl} \underset{\text{(II)}}{p\text{-}ClC_6H_4SO_2N(Cl)CH_2CCl_3}$$

Expt. No.	Medium	Catalyst (initiator)	Reaction time, h	Yield of adduct (II), % of theory	Amount of isolated unreacted (I), %
1	Air	None	4,0	52	39
2	"	$SnCl_4$	2,0	74	15
3	Nitrogen	None	3,5	8	82
4	"	$[C_6H_5COO—]_2$	2,0	75	15

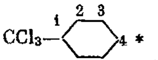
TABLE 2. Addition of N-Chloro-N-2,2,2-trichloroethyl-p-chlorobenzenesulfonamide (II) to Unsaturated Compounds

Expt. No.	Unsaturated compound	Formed adduct	Initiator, medium	T, °C	Reaction time, h	Yield of adduct, % theory	Amount of isolated unreacted (II), %
1	$CH_2{=}CH_2$	(IV)	$[C_6H_5COO—]_2$	95	3,0	21	20
2	$C_6H_5CH{=}CH_2$	(V)	Air	55	4,0	0	93
3	$C_6H_5CH{=}CH_2$	(V)	Nitrogen	55	1,5	27	60
4	$CH_2{=}CHCH_2Cl$	(VI)	Air $[C_6H_5COO—]_2$	95	3,0	10	75

TABLE 3. Melting Points and Elemental Analysis of Obtained Compounds

Compound	Mp, °C	Found/Calculated, %			Empirical formula
		C	H	Cl	
(II)	118 (from $CHCl_3$)	27,03/26,85	1,79/1,69	49,84/49,40	$C_8H_6Cl_5NO_2S$
(III)	179 (from $CHCl_3$)	29,34/29,41	2,02/2,16	44,05/44,00	$C_8H_9Cl_4NO_2S$
(IV)	106 (from $CCl_4-C_7H_{16}$)	31,41/31,20	2,61/2,56	45,02/45,63	$C_{10}H_{10}Cl_5NO_2S$
(V)	91 (from $CHCCl_3-C_7H_{16}$)	41,36/41,40	3,10/3,03	37,80/37,90	$C_{16}H_{12}Cl_5NO_2S$
(VI)	102 (from $CHCl_3-C_7H_{16}$)	30,60/30,50	2,45/2,54	49,27/49,02	$C_{11}H_{11}Cl_5NO_2S$

TABLE 4. Chemical Shifts of ^{13}C (ppm) with Suppression of the C–H Interaction

Compound	δ_{CCl_3}	δ_{CH_3}	δ_{CH_2}		
			1	2	3
$CCl_3—CH_3$	94,9	44,9			
$CCl_3—\overset{1}{C}H_2—CH_3$	100,8	10,8	48,5		
$CCl_3—\overset{1}{C}H_2—\overset{2}{C}H_2CH_3$	99,6	12,5	56,8	19,6	
$CCl_3—\overset{1}{C}H_2—\overset{2}{C}H_2—\overset{3}{C}H_2—CH_3$	99,8	13,4	54,4	21,3	30,4
 *	97,4				
$CCl_3—CH{=}CH_2$ †	93,7			115,1	

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* δ_{C^1} 143.8; δ_{C^2} and δ_{C^3} 121.1 and 128.0 (an accurate assignment is lacking), δ_{C^4} 229.9 ppm.

† δ_{CH} 140.3 ppm.

TABLE 5. Chemical Shifts (ppm) from TMS in NMR (δ_H) and ^{13}C NMR (δ_C) Spectra*

Compound	$ClCH_2$			$CHCl$			$CH-CH_2N$			NCH_2CCl_3				CCl_3
	δ_H	δ_C	J_{H-C}	δ_H	δ_C	J_{H-C}	δ_H	δ_C	J_{H-C}	δ_H		δ_C	J_{H-C}	δ_C
										δ_A	δ_B			
$\underset{SO_2PhCl\text{-}p}{\underset{\mid}{ClN}}CH_2CCl_3$ (II)										4,13	4,13	71,1	148	95,8
$Ph\underset{Cl}{\underset{\mid}{CH}}CH_2\underset{SO_2PhCl\text{-}p}{\underset{\mid}{N}}CH_2CCl_3$ (V)				5,30	60,0	153	4,00	55,5	144	4,50	3,76	63,5	146	97,9
$ClCH_2\underset{Cl}{\underset{\mid}{CH}}CH_2\underset{SO_2PhCl\text{-}p}{\underset{\mid}{N}}CH_2CCl_3$ (VI)	3,86	46,6	156	4,50†	58,3	160	3,61	52,8	143	4,52	4,28	65,2	146	97,6

*The δ_H values were determined with an accuracy of ± 0.03 ppm; the δ_C values were determined with an accuracy of ±0.1 ppm. The J_{H-C} values were determined with an accuracy of ±1.2 Hz.

†For compound (VI) the δ was determined hypothetically.

The melting points of compounds (II)-(VI) and the elemental analysis results are given in Table 3. In the IR spectra of compounds (II)-(VI) the SO_2 group was identified by the frequencies at 1340 and 1170 cm^{-1}. The presence of an NH group in compound (III) was identified by the frequency at 3260 cm^{-1}, which is absent in the IR spectra of (II) and (IV)-(VI).

The structure of compounds (II), (V), and (VI) was proved by the ^1H and ^{13}C NMR method. A single signal (in the 95.8-97.9 ppm region) was detected in the ^{13}C NMR spectrum of each compound, which corresponds to a carbon nucleus that is not attached to protons ("key" atom). The shape of the signal and its position in the spectrum can correspond only to the CCl_3 group in the $C-CCl_3$ fragment, since the chemical shift of the CCl_3 group is practically independent of the nature of the β-substituent in compounds of type CCl_3-R (Table 4).

In compound (V) the values of the $J_{^{13}C-^1H}$ constants (Table 5) make it possible to choose between the fragments $ClCH_2CH\cdot(Ph)\underset{\mid}{N}-$ and $Ph\underset{Cl}{\underset{\mid}{C}}HCH_2\underset{\mid}{N}-$ in favor of the latter, since the CH doublet has a higher constant (153) than the CH_2 triplet (144), which is in agreement with the presence of a chlorine on the methine carbon atom (CH-Cl). For the other structure the constant of the CH_2Cl triplet should be higher than the constants of the PhCHN doublet [7]. In the ^1H NMR spectrum of compounds (V) and (VI) the CH_2CCl_3 group corresponds to an AB quartet. The most probable explanation of this consists in a quite slow inversion of the nitrogen atom, as a result of which the CH_2 protons prove to be diastereotopic; the heating of a saturated solution of compound (V) in C_6H_5Cl from 50 up to 130° led to a decrease of the internal shift between the methylene protons from 35 to 28 Hz. The single signal of the analogous group in compound (II) does not contradict the retarded inversion of the nitrogen, since an averaging of the diastereotopic protons can occur due to the exchange of the chlorine atoms attached to the nitrogen. In view of the absence of alternate structures, the structure of compound (IV) does not evoke any doubts.

EXPERIMENTAL METHOD

The NMR spectra were taken on a Hitachi-Perkin-Elmer R-20 instrument, while the ^{13}C NMR spectra were taken on a Bruker-Physik HX-90 instrument. The spectra of all of the compounds were taken in chlorobenzene (as 15% solutions), using TMS as the internal standard. The chemical shifts are given on the δ scale (see Table 5).

After drying and distillation, the purity of the unsaturated compounds was verified by GLC. The N,N-dichloro-p-chlorobenzenesulfonamide (I) was subjected to additional recrystallization, after which its melting point agreed with the literature data.

N-Chloro-N-2,2,2-trichloroethyl-p-chlorobenzenesulfonamide (II). To a mixture of 26.0 g of (I) in 60 ml of chlorobenzene and 1.2 g of benzoyl peroxide was added 9.6 g of vinylidene chloride (see Table 1, experiment 4). The reaction mixture was cooled to give 27.2 g of adduct (II).

N-2,2,2-Trichloroethyl-N-2'-chloroethyl-p-chlorobenzenesulfonamide (IV). Into a 250 ml stainless steel autoclave were charged 17.8 g of adduct (II), 0.6 g of benzoyl chloride and 25 ml of CCl_4, and then ethylene was added up to a pressure of 25 atm (see Table 2, experiment 1). The reaction mixture on cooling deposited 3.5 g of unreacted (II). The CCl_4 was removed from the filrate under reduced pressure, and the residue was recrystallized from a 1: 1 CCl_4–heptane mixture. The insoluble syrupy mass (~10 g) was separated from the soluble portion by decantation. We obtained 4.8 g of (IV) from the solution.

N-2,2,2-Trichloroethyl-N-2'-chloro-2'-phenethyl-p-chlorobenzenesulfonamide (V). After cooling the reaction mixture, obtained from 14.3 g of adduct (II), 4.2 g of styrene and 50 ml of C_6H_5Cl (see Table 2, experiment 3), we separated 8.8 g of unreacted (II). A part of the chlorobenzene (~30%) was vacuum-distilled. The residual portion was passed through a column filled with Al_2O_3, followed by elution with a 1: 1 $CHCl_3$ $-C_7H_{16}$ mixture. From the eluate we isolated 8.8 g of pure (based on the TLC) (V).

N-2,2,2-Trichloroethyl-N-2',3'-dichloropropyl-p-chlorobenzenesulfonamide (VI). From 14.3 g of adduct (II), 0.48 g of benzoyl peroxide and 3.1 g of allyl chloride in 50 ml of C_6H_5Cl (see Table 2, experiment 4) were obtained 8.8 g of unreacted (II) and 6.8 g of (VI). Both the workup and the isolation of the products were carried out as described in the preceding experiment.

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CONCLUSIONS

1. N-Chloro-N-2,2,2-trichloroethyl-p-chlorobenzenesulfonamide (II) was obtained by the addition of N,N-dichloro-p-chlorobenzenesulfonamide to vinylidene chloride. The reaction is accelerated by the addition of either benzoyl peroxide (radical addition) or $SnCl_4$ (ionic addition).

2. Adduct (II) reacts with ethylene, styrene and allyl chloride under radical addition conditions to give the compounds $RCHClCH_2N(CH_2CCl_3)SO_2C_6H_4Cl$-p.

3. The data of the NMR spectra indicate that the obtained compounds are apparently characterized by a slow inversion of the nitrogen atom.

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