NUCLEOPHILIC ADDITION OF N-CHLORO-N-SODIO-p-CHLOROBENZENESULFONAMIDE TO 1,1,3- AND 3,3,3-TRICHLOROPROPENES

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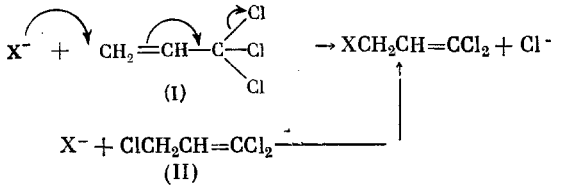
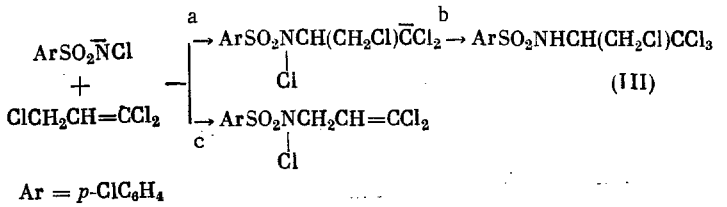
The accessibility of N-chloro-N-sodioarenesulfonamides and the potential use of their derivatives as physiologically active substances confers interest on any study of their synthetic possibilities. The majority of known reactions [1-5] of N-halo-N-sodioarenesulfonamides involve cleavage of the N–Hal bond. The nucleophilic character of the N-halosulfonamide ion has been established [6]. Nucleophilic addition of N-chloroarenesulfonamides to olefins is unknown.

Here we report a study of the reaction of N-chloro-N-sodio-p-chlorobenzenesulfonamide (p-$ClC_6H_4SO_2NClNa \cdot H_2O$, Chloramine "KhB") with 3,3,3-trichloropropene (I) and 1,1,3-trichloropropene (II) in the presence of water.

All reactions of nucleophiles with (II) that have been studied have involved allylic rearrangement. The reaction products are identical to compounds derived from the reaction of the same nucleophiles with (I) [7]. The nucleophiles included diethylamine, sodiomalonic ester, sodium sulfide, sodium methoxide, etc. The reactions of nucleophiles with (I) are stated [7] to take place under conditions that exclude preliminary isomerization of (I) to (II) by the scheme



Our studies of the reactions of (I) and (II) with a nucleophile containing an active N-Cl bond in aqueous medium gave results in conflict with the literature. The major product from the reaction of (II) with Chloramine KhB (Table 1) is 1,3,3,3-tetrachloro-2-(p-chlorobenzenesulfonamido)propane (III). Thus, addition of Chloramine KhB to the dichlorovinyl group is more rapid than substitution of the allylic chlorine; the reaction can be described by the scheme given below. The anionic adduct formed in step a abstracts chlorine from the Chloramine KhB molecule and in the presence of water (step b) gives (III). Compounds (IV), (V), and (VI) seem to be formed, in low yield, via step c, substitution of the allylic chlorine: we discuss their structures and assumed mode of formation below.



Such a course for the principal reaction finds support in the ease of addition of N,N-dichloro-p-chlorobenzenesulfonamide to (II) as a consequence of the N-Cl bond [8], forming adduct (III) in good yield.

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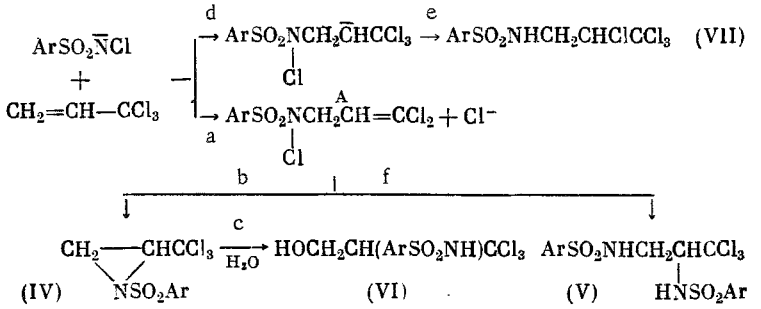
TABLE 1. Product Yields from the Reaction of N-Chloro-N-sodio-p-chlorobenzenesulfonamide with 3,3,3-Trichloropropene (I) and 1,1,3-Trichloropropene (II) for Various Reactant Ratios

Unsaturated compound	Ratio of (I) or (II) to Chloramine KhB (moles)	Yield, % (based on Chloramine KhB)				
		(III)	(IV)	(V)	(VI)	(VII)
(I)	1:1	–	0,6	4	37	2
	3:1	–	1	8	51	8
(II)	1:1	22	7	1	3	–
	3:1	49	12	4	5	–

The reaction with (I) proceeds differently. The major product is 1-hydroxy-2-(p-chlorobenzenesulfonamido)-3,3,3-trichloropropane (VI) (Table 1); its formation can be described by the scheme given below. The scheme supposes that initial addition of Chloramine KhB involves transfer of the reaction center [7] (step a). Compound (A), which is formed in this step, undergoes intramolecular addition of the N-Cl group to the double bond (b) to form aziridine (IV), hydrolysis of which (c) apparently gives (VI). Indeed we found that ring opening in aziridine (IV) is easily induced by acidified water, resulting in rearrangement to (VI). Compound (VII) is the product of addition without transfer of the reaction center (d, e) and is also formed in low yield. Compound (A) forms diamide (V) in low yield (Table 1) by addition to a second Chloramine KhB molecule (f).



The identity of compounds (III), (IV), and (VII) with those prepared earlier [8, 9] was confirmed by the absence of freezing point depression of a mixed sample and by the PMR spectra.

Evidence for the structures of compounds (V) and (VI) is provided by their IR and ^1H and ^{13}C NMR spectra. The IR spectra of compounds (V) and (VI) contain bands characteristic for the SO_2 group (1340, 1165 cm^{-1}) and CCl_3 group (790, 710, 570, 565 cm^{-1}) [10]. The IR spectrum of compound (V) shows bands characteristic for two NH groups (3320 and 3240 cm^{-1}), while that of (VI) indicates an NH group (3280 cm^{-1}) and OH group (3540 cm^{-1}). The ^1H NMR spectrum of (V) in $(CD_3)_2CO$ contains five groups of signals: CH_2 and CH multiplets at (δ, ppm): 3.38 (CH_2) and 4.60 (CH), two unresolved NH signals at 6.80 and 7.33, and a multiplet of phenyl protons centered at 7.87. The integrated intensities correspond to the assumed structure. The $^{13}C-\{^1H\}$ NMR spectra of (V) and (VI) contain three singlets in the aliphatic part [Table 2, compounds (VI) and (V)]. The multiplicities of the $^{13}C-^1H$ NMR spectra correspond to the structures in question.

The ^1H NMR spectrum of (VI) in $(CD_3)_2CO$ contains four groups of signals: a broad OH singlet at 3.01 ppm; an unresolved CH_2CH multiplet at 4.01 ppm; a broad NH doublet at 7.45; and a C_6H_4 quadruplet at 7.80 ppm. The ratio of the integrated intensities corresponds to the cited formula. Addition of a small amount of CF_3COOH to the sample causes exchange of the OH and COOH protons; as a result, they and the NH proton give a common signal at 7.33 ppm, and the unresolved CH_2CH multiplet appears as a strongly coupled ABC system: 3.90 (CH_2) and 4.23 ppm (CH).

Table 2 summarizes the $^{13}C-\{^1H\}$ and $^{13}C-^1H$ NMR parameters of (V) and (VI) and of several related compounds. The ^{13}C chemical shift of the CCl_3 group lies in the 95-103 ppm range,

TABLE 2. $^{13}C-\{^1H\}$ and $^{13}C-^1H$ NMR Parameters

Number	Compound	δ, ppm			$^1J_{(^{13}C-^1H)}$, Hz	
		CCl_3	CH_2	CH	CH_2	CH
1	$CCl_3CH_2N(Cl)SO_2PhCl\text{-}p$	95,8	71,1	–	148	–
2	$CCl_3CH_2N(CH_2CHClC_6H_5)SO_2PhCl\text{-}p$	97,9	63,5	–	146	–
3	$CCl_3CHClCH_2N(H)SO_2PhCl\text{-}p$	98,9	47,7	73,1	142	158
4	$CCl_3CH(HNSO_2Ph)-CH_2Cl$	100,8	43,7	71,0	153	146
5	$CCl_3CH(HNSO_2PhCl\text{-}p)CH_2Cl$	101,2	44,7	69,6	152	146
6	$CCl_3CH(HNSO_2PhCl\text{-}p)CH_2OH$ (VI)	101,2	61,9	71,0	142	145
7	$CCl_3CH(HNSO_2PhCl\text{-}p)CH_2N(H)SO_2PhCl\text{-}p$ (V)	101,5	62,2	71,2	140	144
8	$CCl_3CH(NEt_2)CH_2N(H)SO_2PhCl\text{-}p$	102,9	54,7	68,0	139	147

which is characteristic for many derivatives of the type $Cl_3C-C\langle$ [11]. The ^{13}C signal of the CH_2—N group is visible over a wider range of the spectrum (71–47.7 ppm), and its position depends significantly on the combination of substituents on neighboring atoms. Thus in compounds containing the $CCl_3CH_2N\langle$, moiety, $\delta(^{13}CH_2)$ is 63–72 ppm (Table 2, Nos. 1 and 2), whereas in derivatives of the type $CCl_3-CHX-CH_2N\langle$ (Nos. 3, 6–8) the deshielding effect of the strongly electronegative CCl_3 group is significantly attenuated; consequently, the ^{13}C signal of the CH_2N group is shifted slightly downfield, $\delta(CH_2N)$ 47–62 ppm. We note that in compounds of this type (Table 2), $^1J(^{13}C-^1H)$ remains within the limits characteristic for such structures [11]. Thus, for the compounds CCl_3CHXCH_2E, $^1J(^{13}C-^1H)$ in the CH_2 group is 139–142 Hz when E = N (Table 2, Nos. 3, 7, and 8) and O (No. 6), and 152–153 Hz when E = Cl (Nos. 4 and 5). In the compounds $CCl_3CH_2N\langle$ this constant becomes 146–148 Hz (Table 2, Nos. 1 and 2).

The ^{13}C signal of the methine carbon in the $CCl_3CHX-CH_2$ moiety of these compounds is visible over quite a narrow range of the spectrum (73.1–68.0 ppm). Its position seems to be determined primarily by the effect of the CCl_3 group and by the presence of an attached electronegative substituent, and to a lesser extent by the specific nature of this substituent. The effect of the various substituents is particularly noticeable in $^1J(^{13}C-^1H)$ (Table 2, Nos. 3–8), which is 145 ± 2 Hz with hydroxyl, sulfonamide, or alkylamine, but increases to 158 Hz with chlorine.

EXPERIMENTAL

The IR spectra were recorded in KBr tablets (concentration 0.5%) with a UR-10 spectrometer. The ^{13}C NMR spectra were recorded with a Bruker–Physik HX-90 spectrometer, and the PMR spectra with a Hitachi–Perkin–Elmer R-20 spectrometer. The purity of 3,3,3-trichloropropene and 1,1,3-trichloropropene was checked by GLC. N-Chloro-N-sodio-p-chlorobenzenesulfonamide was recrystallized from water, whereupon its decomposition temperature of 190°C was in agreement with the literature, and its active chlorine content with the calculated value.

Reaction of 1,1,3-Trichloropropene (II) with N-Chloro-N-sodio-p-chlorobenzenesulfonamide. A mixture of N-sodio-N-chloro-p-chlorobenzenesulfonamide (6.7 g), (II) (10.9 g), water (25 ml), and CCl_4 (40 ml) was refluxed (75°C) with stirring for 5 h, whereupon the organic layer was removed, dried over $CaCl_2$, and left to stand at 20°C. 1,3,3,3-Tetrachloro-2-(p-chlorobenzenesulfonamido)propane (III) (4.4 g) was precipitated, mp 163°C (from $CHCl_3$) [8]. Carbon tetrachloride was removed from the filtrate under vacuum. Column chromatography on Al_2O_3 of the residue (10.3 g) eluted successively n-C_7H_{16}, $CHCl_3$, and CH_3COCH_3, and then 1-(p-chlorobenzenesulfonyl)aziridine (IV) (1.0 g), mp 116°C (from CCl_4) [8]; (III) (0.2 g); 1,2-bis(p-chlorobenzenesulfonamido)-3,3,3-trichloropropane (V) (0.3 g), mp 214°C (from $CHCl_3$). [Found: C 34.05; H 2.40; N 5.16%. $C_{15}H_{13}Cl_5N_2S_2O_4$. Calculated: C 34.20; H 2.48; N 5.30%]; 1-hydroxy-2-(p-chlorobenzenesulfonamido)-3,3,3-trichloropropane (VI) (0.3 g), mp 147-148°C. [Found: C 30.74; H 2.45; N 4.01; Cl 40.43%. $C_9H_9Cl_4NO_3S$. Calculated: C 30.60; H 2.46; N 3.96; Cl 40.23%]; p-chlorobenzenesulfonamide (0.7 g). The course of the separation on the Al_2O_3 column was followed by TLC on Silufol UV-254 using the system n-C_7H_{16}–$CHCl_3$–C_2H_5OH (7:3:1). The compounds had the following R_f values: 0.67 (IV); 0.46 (III); 0.31 (V); 0.29 (VI), 0.25 [p-$ClC_6H_4SO_2NH_2$ (VIII)].

The aqueous layer gave a mixture (2.1 g) of the original Chloramine KhB, p-chlorobenzenesulfonamide, and NaCl.

Reaction of 3,3,3-Trichloropropene (I) with N-Chloro-N-sodio-p-chlorobenzenesulfonamide. The procedure was that of the preceeding experiment. The organic layer yielded a precipitate of (VI) (3.9 g). After removal of CCl_4 under vacuum, column chromatography on Al_2O_3 of the residue (10.2 g) gave (IV) (0.1 g); 1-(p-chlorobenzenesulfonamido)-2,3,3,3-tetrachloropropane (VII) (0.7 g), mp 139°C (from CCl_4) [9]; (V) (0.5 g); (VI) (0.6 g); (VIII) (0.8 g). The separation was followed by TLC. Compound (VII) had R_f 0.43, while (IV), (V), (VI), and (VIII) R_f and the mp for (IV), (V), (VI), and (VIII) were identical to those in the preceding experiment. The solid residue from the aqueous layer (1.8 g) was a mixture of p-chlorobenzenesulfonamide, NaCl, and original Chloramine KhB (TLC).

Synthesis of 1-Hydroxy-2-(p-chlorobenzenesulfonamido)-3,3,3-trichloropropane (VI) from 1-(p-Chlorobenzenesulfonyl)-2-(trichloromethyl)-ziridine (IV). After addition of one drop of 70% H_2SO_4 to (IV) (2.0 g) in water (20 ml), the mixture was heated at 75-80°C for 5 h. It was then filtered hot, giving a mixture (1.2 g) of the original aziridine and (VI). The aziridine was rinsed off with $CHCl_3$, leaving (VI) (0.6 g) as the residue. On cooling the filtrate gave more (VI) (0.6 g), total yield 57%.

CONCLUSIONS

1. The reaction of N-chloro-N-sodio-p-chlorobenzenesulfonamide with 1,1,3-trichloropropene in aqueous medium forms 1,3,3,3-tetrachloro-2-(p-chlorobenzenesulfonamido)propane as the major reaction product, indicating that addition of N-chloro-N-sodio-p-chlorobenzenesulfonamide to the dichlorovinyl group is favored over substitution of the allylic chlorine.

2. The reaction of Chloramine KhB with 3,3,3-trichloropropene in aqueous medium forms 1-hydroxy-2-(p-chlorobenzenesulfonamido)-3,3,3-trichloropropane as the major reaction product. We suggest that its formation involves the intermediacy of 1-(p-chlorobenzenesulfonyl)-2-(trichloromethyl)aziridine with subsequent opening of the aziridine ring under the reaction conditions.

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COMPARISON OF THE ELECTRONIC EFFECTS OF THE NITRILE AND TRIFLUOROMETHYL GROUPS

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α-Hydrohexafluoroisobutyronitrile is a strong CH acid ($pK_\alpha = 0 \pm 2$ [1]) as a consequence of the coordinated electron-withdrawing effects of the three geminal groups, one nitrile and two trifluoromethyl. We decided to evaluate the relative contribution of each of these groups to the total effect in question. We therefore undertook a comparison of the properties of 2,2-dihydrohexafluoropropane, $(CF_3)_2CH_2$ (I), 2-hydro-2-chlorohexafluoropropane, $(CF_3)_2CHCl$ (II), and β,β,β-trifluoropropionitrile, CF_3CH_2CN (III).

Compound (I) was prepared by decarboxylation of α-hydrohexafluoroisobutyric acid, but in contrast to the published procedure [2] the reaction was carried out by heating the acid in DMF. Chloropropane (II) was prepared by chlorination of the same acid, and nitrile (III) by controlled alkaline hydrolysis of α-hydrohexafluoroisobutyronitrile.

We found that propane (I) is inert to caustic alkali solutions and to tertiary amines even at 100°C (in an autoclave). We were also unable to accomplish electrophilic substitution of the H atoms under ionic conditions: by treating (I) with mercuric acetate solution (in water, in water–dioxane, in DMF), by heating with chlorine or bromine in the presence of triethylamine (to 150°C), and even by heating with SO_3 (to 180°C). The CH bond in (I) is plainly nonpolar, and the compound itself seems to be susceptible only to radical reactions. Indeed, propane (I) reacts with fluorosulfonyl peroxide even at −5°C to form hexafluoroacetone, pyrosulfuryl fluoride, and fluorosulfonic acid. The fluorosulfonate radical obviously initiates homolysis of first one and then the second CH bond

$$(I) \xrightarrow[-HOSO_2F]{\cdot OSO_2F} (CF_3)_2\dot{C}H \xrightarrow{\cdot OSO_2F} (CF_3)_2CHOSO_2F \xrightarrow[-HOSO_2F]{\cdot OSO_2F} (CF_3)_2\dot{C}OSO_2F \xrightarrow[-O(SO_2F)_2]{\cdot OSO_2F} (CF_3)_2CO$$

We think it important that the polarity of the CH bond remains essentially unchanged even by introduction of the fluorosulfonate group, which correlates completely with an assessment of the reactivity of its chlorine analog, chloropropane (II). This compound is also inert to caustic alkali solutions and to tertiary amines; nor does it undergo mercuration, chlorination in the presence of amines, or sulfonation even on heating. On the other hand, (II) reacts vigorously with fluorosulfonyl peroxide to form the stable α-chlorohexafluoroisopropyl fluorosulfate (IV)

$$(II) + (OSO_2F)_2 \rightarrow (CF_3)_2CClOSO_2F\ (IV) + HOSO_2F$$

Thus, the polarity of the CH bond in propane (I) scarcely differs from that in chloropropane (II): both compounds are characterized by susceptibility only to S_R reactions. Even the total electron-withdrawing effect of the two CF_3 groups and the chlorine seems insufficient to displace the σ electrons of the CH bond.

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