CONCLUSIONS

When perfluorinated tertiary cyclic amines containing a substituent at the nitrogen atom are heated with antimony pentafluoride, they isomerize to the corresponding azomethines.

LITERATURE CITED

1. V. A. Petrov, G. G. Belen'kii, and L. S. German, Izv. Akad. Nauk SSSR, Ser. Khim., 1935 (1985).
2. V. A. Petrov, V. K. Kunanets, K. N. Makarov, and L. S. German, Summary of the 5th All-Union Conference on the Chemistry of Organofluorine Compounds, Zvenigorod (1986), p. 51.
3. V. A. Petrov, V. K. Kunanets, B. A. Kvasov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 122 (1988).

POLYSULFONYLETHENES.

5. THE REACTIONS OF TRIS(ORGANOSULFONYL)CHLOROETHENES WITH AMINES AND THIOLS

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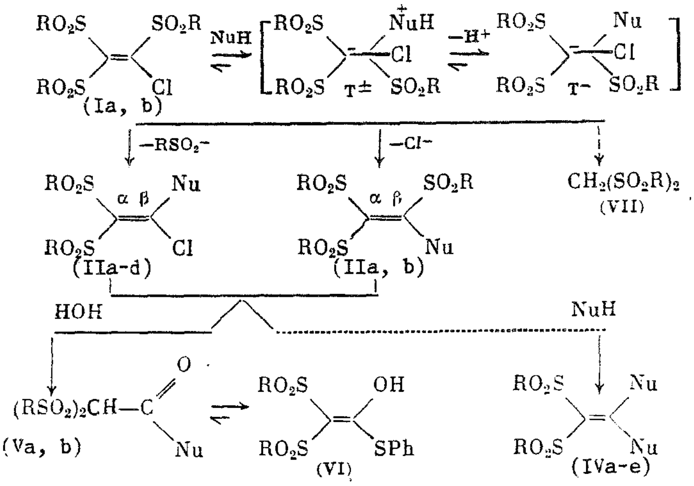
As a continuation of the systematic study of nucleophilic vinyl substitution in polysulfonylethenes [1-3], in the current work we investigate the interaction of tris(organosulfonyl)chloroethene (TSCE) (I), a new class of electron-deficient ethenes, with amines and thiols. In the previous report [3], we suggested that the formation of TSCE in the reaction of E-1,2-di(organosulfonyl)-1,2-dichloroethene (DSDCE) with amines apparently seemed to be caused by the "migration" of RSO_2-groups, forming products with a geminal arrangement of RSO_2-groups, N,N-aminyl disulfonylketenes.

Since the substitution reaction at the vinyl centre in tetrasubstituted, electronegative ethenes proceeds by a pathway of addition with elimination (Ad_N-E) [4-6], we propose a scheme for the interaction of TSCE (I) with the nucleophile which is supported by the compounds isolated, as described in the present work.



(I): R = Et (a); R = Ph (b); (II): R = Et, Nu = Et_2N (a), EtS (b), PhS (c): R = Ph, Nu = EtS(d); (III): R = Et, Nu = EtS (a), PhS (b); (IV): R = Et, Nu = n-BuHN (a), PhHN (b); R = Ph, Nu = PhHN (c); R = Et, Nu = EtS (d), PhS (e); (V): R = Et, Nu = Et_2N (a), PhS (b); (VI): R = Et, Nu = PhS; (VII): R = Et.

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TABLE 1. Conditions for the Reaction of TSCE (Ia, b) with Amines and Thiols in CH_2Cl_2, and Ratio of Products Obtained

Experiment No.	R	Nucleophile	Nucleophile/TSCE, mole/mole	T, °C; Time, h	Yield, %					
					(II)	(III)	(IV)	(V)	(VI)	(VII)
1	Et	n-$BuNH_2$	4.2	5(0.2)	–	–	71	–	–	12
2 *	Et	$PhNH_2$	1.0	5(0.25)	–	–	22	Trace	–	–
3	Et	$PhNH_2$	4.2	5(0,25)	–	–	92	–	–	–
4	Et	Et_2NH	2,0	30(0.25)	78	–	–	15	–	Trace
5	Ph	$PhNH_2$	4.2	5(0.25)	–	–	90	–	–	–
6	Et	EtSH	2,0	20(2,0)	35	43	13	–	–	–
7	Et	EtSH	3.0	30–35(1)	38	18	33	–	–	–
8	Et	PhSH	2.0	30–35(2)	88	–	–	–	6	6
9 **	Et	PhSH	2.0	30–35(2)	14	34	11	–	36	Trace
10 ***	Et	PhSH	2.0	50(2)	Trace	–	76	–	–	Trace
11	Ph	EtSH	2.0	30(2)	99	–	–	–	–	–

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*Minor bond conversion due to the availability of (Ia) in the reaction mixture, which is demonstrated by the appearance of the fragmentation product (VII).

**Reaction carried out in the presence of urea (2.5 moles/mole sulfone).

***Reaction carried out in MeCN.

As a result of the attack by the amine on the sulfone (I), the zwitterion $T^{\pm}$ is formed, which is deprotonated with the assistance of a second amine molecule to yield the anion T^-. Interaction of the same TSCE (I) with the nucleophilic anion, for example with thiols, is initiated immediately on the formation of the anion T^-. Subsequent conversion of the anion T^- can occur by the loss of either RSO_2^- or Cl^-, with the formation of the monosubstituted products (II) and (III), respectively. In an excess of the nucleophile, the ethenes (II) and (III) are converted to the disubstituted product (IV).

We have established that interaction of the sulfone (I) with nonionic nucleophiles, amines, depending on the natures of the latter, leads to the formation of 1-N-di(organo)-amino-1-chloro-2,2-di(organosulfonyl)ethene (II), N,N-aminyl disulfonylketene (IV), disulfonylacetamide (V) and disulfonylmethane (VII).

The reaction of the sulfones (Ia, b) with primary aliphatic and aromatic amines ($3.0 < pK_b < 9.4$) occurs exothermically, and, on cooling (to 5°C, in CH_2Cl_2) is completed in 15 min with the formation of N,N-aminyl ketones (IVa-c) in a yield of 70-92%. TSCE (Ia) reacts to such a weak extent with primary amines that, even with them in an equimolar ratio, only the disubstituted product is formed (IVb) (Table 1, experiment 2). For the reaction to progress to the full extent, excess amine is required (with 1 mole sulfone to 4.2 moles amine). We have obtained the same N,N-aminyl disulfonylketene previously from tetrasulfonyl-[2] and 1,2-disulfonyl-1,2-dichloroethenes [3].

The reaction of TSCE (I) with secondary aliphatic amines also proceeds exothermically, but leads only to monosubstituted products (II). From the mixture for the reaction of (Ia) with diethylamine, the ethene (IIa) (78%), the disulfonylacetamide (V) (15%), and the disulfonyl methane (VII) (<1%) were isolated, following chromatographic separation on an SiO_2 column. The disulfonylacetamide (V) is generated during the process of separating the reaction mixture, due to the hydrolysis of N-monosubstituted (IIa). This is proved by the fact that, in the ^{13}C NMR spectrum of the crude reaction mixture, there are two distinctive, weakly-coupled signals for compound (IIa), $C_\alpha = 113.4$ and $C_\beta = 166.6$ ppm, while the doublet for the CH group in (V), ($\delta = 82.91$ ppm, $J = 144.4$ Hz), is absent.

During the interaction of TSCE (Ia) with highly basic amines ($pK_b \sim 3$), together with N,N-aminyl (IV), the disulfonylmethane (VII) (1-12%) is isolated (Table 1, experiments 1, 4), which is probably generated due to decomposition of the zwitterion $T^{\pm}$ by the amines. It is common knowledge that nucleophilic substitution of electron-deficient ethylene is often accompanied by concurrent fragmentation of the molecule across multiple bonds [2-4].

TABLE 2. Optimized Yield of 1,1-Dianilinyl-2,2-diethylsulfonylethene from the Reaction of Polysulfonylethenes with Aniline

Substrate	Reaction temp. °C (time, h)	Yield, %
DSDCE	40(7)	57
TSCE	5(0,25)	92
TSE	40(0,7)	56

Thus, from studying the reaction of TSCE (I) with amines, we have corroborated the type of reaction mechanism, established by us previously, for other electrophilic ethenes [2, 3]. The structure and yield of reaction products are dependent upon the structure and basicity of the amines. During the interaction of polysulfonylethenes with primary amines, disubstituted products are formed (IV); but with secondary amines, only monosubstituted products are formed, all of which are frequently isolated in the form of amides (V). Nucleophilic substitution of (I) by strongly basic amines is accompanied by a fragmentation reaction. In the absence of kinetic data, even from a basic, qualitative comparison of the reactions of DSDCE, TSCE, and TSE with amines (Table 2) it can be confirmed that TSCE (I) possesses essentially the higher reactivity compared not only with DSDCE (which we suggested earlier in [3]), but also with tetrasulfonylethene (TSE).

During the interaction of the sulfone (I) with thiols, two types of monosubstituted product are formed, (II) and (III), which in an excess of thiol can be converted to dithioacetal disulfonylketenes (IV).

The reaction of TSCE (Ia) with the less nucleophilic thiophenol leads to monosubstituted (IIc) and the hydrolysis product, the thioester (Vb) (Table 1, experiment 8). As we have remarked upon previously, during an investigation into the reaction with thiols [1], in the case of the aromatic thiols, the thioesters (V) are found in the stable enol form (VI). Catalyzing the reaction of (Ia) and thiophenol with urea can displace the process towards formation of the disubstituted (IVe). However, obtaining the maximum yield of (IVe) only succeeds on use of high-grade acetonitrile as the solvent.

During the interaction of the more nucleophilic ethanethiol with the sulfone (Ia), not only the monosubstituted products (IIb) and (IIIa) are formed, but also the disubstituted product (IVd). Raising the temperature of the reaction can increase the yield of (IVd), and in addition (IVd) accumulates at the expense of the monosubstituted (IIIa) (analysis by GLC in the course of the reaction) (Table 1, experiments 6, 7). There is a connection between, on the one hand, the greater reactivity to nucleophilic substitution of (III) compared to (II), and, on the other hand, that in studying the system, RSO_2^- is shown to be a better leaving group than Cl^-. During the reaction with weaker nucleophilic reagents, conversion of the anion T^- is accomplished, as in the case also of secondary amines, with the loss of RSO_2^- to form the monosubstituted product (II).

The interaction of the arylsulfone (Ib) with ethanethiol is completed at the monosubstituted stage, with the formation of (IId) (Table 1, experiment 11). The reduction in reactivity of polyarylsulfonylethenes, compared with alkyl anologs, has been remarked upon previously [1, 3].

The structure of compounds obtained was confirmed by data from elemental analysis, IR and PMR spectra, and also ^{13}C NMR.

EXPERIMENTAL

IR-spectra were taken on a UR-20 instrument, using KBr discs. PMR spectra were obtained using a Tesla BS-467 instrument (60 MHz) with HMDS in $(CD_3)_2CO$ or $CDCl_3$, ^{13}C NMR spectra using a Bruker M-250 instrument (250 MHz) in $CDCl_3$. TSCE was synthesized as described in [7]. Amines were dried over KOH and distilled. SiO_2 40/100 μ was used for column chromatography. Anhydrous solvents were used.

General Method for the Reaction of TSCE (Ia, b) with Amines. To a cooled (5°C) solution of 5 mmoles of sulfone (Ia, b) in 10 ml CH_2Cl_2, the required quantity of amine (Table

1) was added, dropwise. The exothermic reaction was complete after 15 min. The mixture was evaporated down, the residue was washed with ether and recrystallized from a mixture of ether:CH_2Cl_2.

In the case of Et_2NH, the reaction was carried out at 30°C. The mixtures from the reactions of TSCE with Et_2NH or $BuNH_2$ were divided on an SiO_2 column. During gradient elution with a hexane—chloroform system, products were eluted in the order of separation (IIa), (IVa), (Va), (VII).

Compounds (IVa-c), (Va), and (VII) were the same as described in [2, 8]. (IIa), mp 112.5-113.5°C. Found: C 44.39; H 7.52; S 23.82; Cl 13.03%. $C_{10}H_{20}O_4S_2Cl$. Calculated: C 44.51; H 7.47; S 23.76; Cl 13.14%. IR-spectrum (ν, cm^{-1}): 1560 (C═C); 1325, 1120 (SO_2). ^{13}C NMR spectrum (δ, ppm): $C_\alpha = 113.4$, $C_\beta = 166.6$. PMR spectrum (δ, ppm): 1.25-1.58 m (12H, CH_3), 2.83-4.15 m (8H, $CH_2SO_2 + CH_2N$).

<u>General Method for the Reaction of TSCE (Ia, b) with Thiols.</u> To a solution of 3.0 mmoles (Ia, b) in 10 ml CH_2Cl_2 (MeCN) at 20°C, 6.2 mmoles thiol was added. It was warmed to 30-35 (50)°C for 2 h, evaporated down, and partitioned by chromatography on a column containing 80 g SiO_2. During gradient elution with a hexane—chloroform system, products were eluted in the order (IVd, e), (IIb-d), (IIIa, b), (VII), (VI).

Compounds (IVd, e), (IIIa, b), (VI) and (VII) are the same as described in [1, 8]. (IIb), mp 72-73°C (from ether). Found: C 46.11; H 3.81; S 24.70; Cl 9.00%. $C_8H_{15}O_4S_3Cl$. Calculated: C 46.09; H 3.87; S 24.61; Cl 9.07%. IR-spectrum (ν, cm^{-1}): 1450 (C═C), 1330, 1135 (SO_2). PMR spectrum (δ, ppm): 1.26 m (9H, CH_3), 3.01-3.76 m (6H, $CH_2S + CH_2SO_2$). ^{13}C NMR (δ, ppm): $C_\alpha = 131.4$, $C_\beta = 166.2$. (IIc), mp 139-140°C (from ether: CH_2Cl_2). Found: C 40.35; H 4.18; S 26.98; Cl 10.33%. $C_{12}H_{15}O_4S_3Cl$. Calculated: C 40.61; H 4.26; S 27.10; Cl 9.99%. IR-spectrum (ν, cm^{-1}): 1450 (C═C), 1330, 1140 (SO_2). PMR spectrum (δ, ppm): 1.20-1.55 m (6H, CH_3), 3.25-3.78 m (4H, CH_2SO_2), 7.58 m (5H, C_6H_5). (IId), mp 132-134°C (ether: CH_2Cl_2). Found: C 47.45; H 3.79; S 23.92; Cl 8.76%. $C_{16}H_{15}O_4S_3Cl$. Calculated: C 47.69; H 3.75; S 23.87; Cl 8.80%. IR-spectrum (ν, cm^{-1}): 1450 (C═C), 1335, 1150 (SO_2). PMR spectrum (δ, ppm): 1.30 t (3H, CH_3), 3.07 q (2H, CH_2SO_2), 7.41-8.32 m (10H, C_6H_5).

CONCLUSIONS

1. We have found that, in the process of nucleophilic substitution of vinyls with ionic and nonionic nucleophiles, the reactivity of tris(organosulfonyl)chloroethenes is considerably greater than that for tetrakis(organosulfonyl)ethenes, and, particularly, for 1,2-di(organosulfonyl)-1,2-dichloroethenes.

2. We have discovered multiple reaction pathways for substitution in tris(organosulfonyl)chloroethene, combined with the presence in the molecule of two other nucleophiles (RSO_2, Cl). We have demonstrated that, under weak nucleophilic conditions, substitution of the RSO_2-group is preferred.

LITERATURE CITED

1. N. P. Petukhova, N. E. Dontsova, and E. N. Prilezhaeva, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 194 (1984).
2. N. P. Petukhova, N. E. Dontsova, E. N. Prilezhaeva, and V. S. Bogdanova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 611 (1984).
3. N. E. Dontsova, N. P. Petukhova, E. N. Prilezhaeva, and V. S. Bogdanova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1104 (1988).
4. Z. Rappoport, Adv. Phys. Org. Chem., <u>7</u>, 1 (1969).
5. C. F. Bernasconi, D. Y. Carre, and A. Kanavarioti, J. Am. Chem. Soc., <u>103</u>, 4850 (1981).
6. Z. Rappoport and A. Topol, J. Chem. Soc. Perkin Trans. II, 863 (1975).
7. E. N. Prilezhaeva, N. E. Dontsova, N. P. Petukhova, et al., Dep. VINITI, No. 1903, 1388 (1988).
8. H. Böhme, Chem. Ber., <u>69</u>, 1610 (1936).