CONCLUSIONS

The synthesis and geometry of the sterically hindered meso-2,6-di(indanyl)phenol have been investigated.

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POLYSULFONYLETHENES.

4. REACTIONS OF E-1,2-DI(ORGANYLSULFONYL)DICHLOROETHENES WITH AMINES

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E-1,2-di(organylsulfonyl)dichloroethenes (I) have been previously described [1], however, their activity in nucleophilic vinyl substitution has not been studied. In this work reaction of (I) with primary and secondary aliphatic, alicyclic, and aromatic amines is discussed. It was established that together with aminals of disulfonylketenes (IIa-k), sulfonylchloroacetamides (Va-c) and in some cases disulfonylacetamides (IXa, b). N-monosubstituted 1,2-disulfonylchloroethenes (III), and disulfonylmethane (VIII) are also formed (see Scheme 1).

Reaction of (I) with primary aromatic amines results in products with geminal RSO_2 groups, i.e., N,N-aminals of disulfonylketones (II) in nearly quantitative yield. That is why at first this reaction appeared to be a rearrangement [2]. After more careful investigation of the reaction mixtures it turned out that also sulfonylchloroacetamides (Va-c) can always be isolated in small amounts. Moreover, upon reaction of an equimolar mixture of the two homologous sulfones (Ia) and (Ic) with aniline, together with the expected aminals of di(ethylsulfonyl)- and di(octylsulfonyl)ketenes (IIa) and (IIi) a third product, the aminal of ethyl(octyl)sulfonylketene (IIk), was also isolated in more than 30% yield (Scheme 2). The formation of a mixed aminal refutes the assumption of an intramolecular rearrangement and indicates this reaction to be an intermolecular process.

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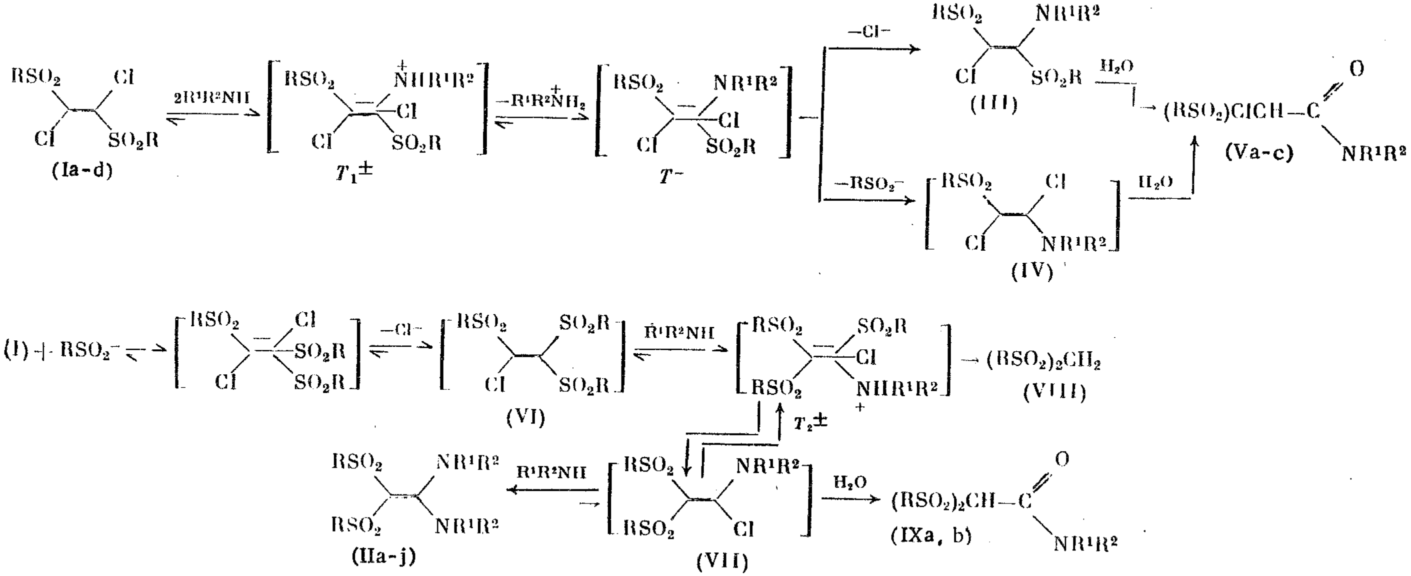
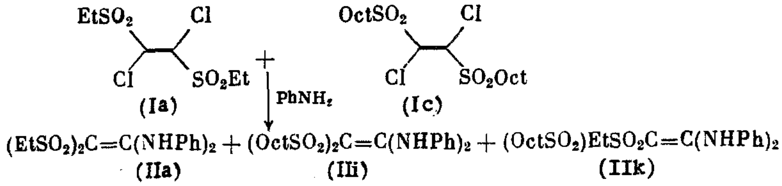
Scheme 1



(I): R = Et (a); R = n-Pr (b); R = n-Oct (c); R = Ph (d).
(II): R = Et, R^1 = Ph, R^2 = H (a); R = Et, R^1 = 4-$MeOC_6H_4$, R^2 = H (b); R = Et, R^1 = 4-HOC_6H_4, R^2 = H (c); R = Et, R^1 = 2-Nph, R^2 = H (d); R = Et, R^1 = 4-$NO_2C_6H_4$, R^2 = H (e); R = Ph, R^1 = Ph, R^2 = H (f); R = n-Pr, R^1 = Ph, R^2 = H (g); R = n-Pr, R^1 = 4-$MeOC_6H_4$, R^2 = H (h); R = n-Oct, R^1 = Ph, R^2 = H (i); R = Et, R^1 = n-Bu, R^2 = H (j).
(III): R = Et, R^1R^2 = $\underline{O(CH_2)_2NCH_2CH_2}$
(V): R = Et, R^1 = n-Bu, R^2 = H (a); R = Et, R^1R^2 = $\underline{O(CH_2)_2NCH_2CH_2}$ (b); R = Ph, R^1 = Ph, R^2 = H (c).
(VIII): R = Et
(IX): R = Et, R^1R^2 = $\underline{O(CH_2)_2NCH_2CH_2}$ (a); R = Et, R^1 = Et, R^2 = Ph (b).

Scheme 2



Assuming that substitution at the vinyl center (I) by amines proceeds by addition–elimination (Ad_N–E), characteristic of tetrasubstituted electrophilic olefins [3, 4], we propose the following scheme for the process (1). Attack of the amine on sulfone (I) gives the zwitterion $T_1^{\pm}$. Deprotonation of the latter with the aid of the second amine molecule leads to anion T^- which can lose a Cl^- or RSO_2^- anion to form (III) and (IV) respectively. The RSO_2^- anion, bound apparently in the form of an onium amine salt, is a fairly strong nucleophile. It is obvious that it will undergo nucleophilic vinyl substitution with (I) far more readily than the amine to form trisulfonylchloroethene (VI).† Reaction of the latter with amine will lead after several steps to formation of aminal (II) or to regeneration of anion RSO_2^-. This reaction scheme is proposed as a hypothesis which explains well the obtained results, although the anionic nature of the process requires additional evidence. An anion-radical mechanism can probably be excluded since no decrease of reaction rate of (Ia) with aniline was observed in the presence of 1,4-dinitrobenzene, a strong inhibitor of these reactions [6].

The aminals of disulfonylketones (IIa, e, j) and disulfonylacetamide (IXb) turned out to be completely identical with the ones obtained earlier from tetrasulfonylethenes [7]. In the ^{13}C NMR spectra (IIb-i, k) two different signals were obtained for the C=C bond carbon atoms [for example, 157 ppm for C^2 and 85 ppm for C^1 in compound (IIb)], which confirms

TABLE 1. Products of Reaction of $RSO_2ClC{=}C(Cl)SO_2R(I)$ with R^1R^2NH

Experiment No.	R	R¹	R²	Reaction conditions*	Time, h	pK_b of amine	Reaction products, %				
							(II)	(III)	(V)	(VIII)	(IX)
1	Et	Ph	H	A	1	9,4	86	–	—	–	—
2 **	Et	Ph	H	B	7	9,4	57	–	—	–	—
3	Et	Ph	H	C	7	9,4	77	–	—	–	—
4	*n*-Pr	Ph	H	A	1	9,4	91	–	—	–	—
5	*n*-Oct	Ph	H	A	1	9,4	91	–	—	–	—
6 **	Ph	Ph	H	A	4	9,4	53	–	—	–	—
7 **	Ph	Ph	H	B	8	9,4	14	–	—	–	—
8 **	Ph	Ph	H	D	10	9,4	35	–	14	–	—
9	Et	2-Nph	H	A	8	9,9	88	–	—	–	—
10	Et	$4\text{-}MeOC_6H_4$	H	A	1	8,7	95	–	—	–	—
11	*n*-Pr	$4\text{-}MeOC_6H_4$	H	A	1	8,7	92	–	—	–	—
12	Et	$4\text{-}HOC_6H_4$	H	A	1	8,5	94	–	—	–	—
13	Et	$4\text{-}O_2NC_6H_4$	H	E	18	12,0	48	–	—	–	—
14	Et	*n*-Bu	H	A	0,25	3,4	61	–	11	18	—
15	Et	*n*-Bu	H	B	0,25	3,4	39	–	21	13	—
16	Et	$O(CH_2)_2NCH_2$	CH_2	A	0,5	5,6	–	47	14	–	5
17 **	Et	Et	Ph	A	8	9,2	–	–	—	–	24

*A) 40°C, CH_2CL_2, 2.2 moles of amine, 2.2 moles of Et_3N per mole sulfone (I); B) 40°C, CH_2Cl_2, 4.2 moles of amine per mole of sulfone (I); C) 40°C, DMF, 4.2 moles of amine per mole of sulfone (I); D) 20°C, CH_2Cl_2, 2.2 moles of amine, 2.2 moles of Et_3N per mole of sulfone (I); E) 40°C, DMF, 2.2 moles of amine, 2.2 moles of Et_3N per mole of sulfone.

**Lower conversion associated with the presence in the reaction mixture of starting sulfone (Ia, d).

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†For example, it is known that reaction of dichlorofumaronitrile with sulfinic acid salts (40°C, DMF) gives good yields of compounds $RSO_2(CN)C{=}C(CN)SO_2R$ [5].

TABLE 2. Constants, Elemental Analysis Data, and Spectral Characteristics of the Synthesized Compounds

Compound	Mp, °C (solvent)	Found/Calculated, %					Molecular formula	IR spectra (ν, cm⁻¹)				PMR and ^{13}C NMR spectra (δ, ppm)
		C	H	N	S	Cl		SO_2	C=C	CO	NH	
(IIb)	163–165 (ether : $CHCl_3$ 1 : 1)	52,46 52,84	5,77 5,77	6,19 6,16	14,12 14,11	–	$C_{20}H_{26}O_6N_2S_2$	1345, 1120	1600	–	3300	1,28 t 6H (2Me), 3,38 q 4H($2CH_2SO_2$), 3,67 s 6H(2MeO), 6,48 and 6,88 dd 8H($2C_6H_4$), 9,55 s 2H(2NH); ^{13}C: 85,4 s (C^1), 157,4 s (C^2)
(IIc)	229–231 (CH_3OH : ether 1 : 2)	50,30 50,69	5,38 5,20	6,56 6,57	14,81 15,04	– –	$C_{18}H_{22}O_6N_2S_2$	1330, 1115	1585	–	3370	1,27 t 6H(2Me), 3,30 q 4H($2CH_2SO_2$), 6,47 and 6,81 dd 8H($2C_6H_4$), 6,67 s 2H(OH), 8,22 s 2H(2HN)
(IId)	178 (ether: $CHCl_3$ 1 : 2)	63,49 63,14	5,76 5,30	5,70 5,66	13,03 12,96	–	$C_{26}H_{26}O_4N_2S_2$	1325, 1105	1610	–	3300	1,47 t 6H(2Me), 3,56 q 4H($2CH_2SO_2$), 6,38–7,89 m 14H(2Nph), 8,05 s 2H(2NH)
(IIf)	169–170 ($CHCl_3$)	63,72 63,65	4,50 4,52	5,71 5,71	13,10 13,07	–	$C_{26}H_{22}O_4N_2S_2$	1350, 1130	1620	–	3280	^{13}C: 95,2 s (C^1), 155,5 s (C^2)
(IIg)	160,5–161 (ether: $CHCl_3$ 1 : 1)	57,00 56,84	6.64 6,20	6,50 6,63	14,84 15,18	– –	$C_{20}H_{26}O_4N_2S_2$	1350, 1110	1620	–	3300	0,99 t (6H(Me), 1,52–2,12 m 4H($2CH_2$), 3,25–3,52 m 4H($2CH_2SO_2$), 6,62–7,28 m 10H(2Ph), 9,83 s 2H (2NH)
(IIh)	124–126 (CH_2Cl_2)	48,81 48,49	6,07 6,27	5,72 5,80	13,10 13,29	–	$C_{22}H_{30}O_6N_2S_2$	1350, 1120	1600	–	3300	1,02 t 6H(2Me), 1,71–2,05 m4H($2CH_2$), 3,29–3,55 m 4H($2CH_2SO_2$), 3,64 s 6H(2MeO), 6,47 and 6,78 dd 8H($2C_6H_4$), 9,67 s 2H(2NH)
(IIi)	105–106 (ether: $CHCl_3$ 2 : 1)	63,90 64,00	8,39 8,24	5,08 4,98	11,27 11,40	–	$C_{30}H_{46}O_4N_2S_2$	1350, 1120	1620	–	3300	0,85 t 6H(2Me), 1,08–2,01 m (6CH_2), 3,18–3,54 m 4H($2CH_2SO_2$), 6,67–7,29 m 10H(2Ph), 9,71 s 2H(2NH); ^{13}C: 88,3 s (C^1), 155,8 s (C^2)
(IIk)	102–103 (ether : $CHCl_3$ 1 : 1)	59,94 60,22	7,13 7,16	5,81 5,85	12,83 13,40	– –	$C_{24}H_{34}O_4N_2S_2$	1360, 1110	1620	–	3300	0,78–1,53 m 18H(2Me+6CH_2), 3,13–3,62 m 4H($2CH_2SO_2$), 6,67–7,12 m 10H(2Ph), 9,93 s 2H(2NH)
(III)	103 (ether)	36,13 36,20	5,31 5,47	4,46 4,22	19,01 19,32	10,14 10,68	$C_{10}H_{18}O_5NS_2Cl$	1320, 1130	1610	–	–	1,39 t 6H(2Me), 3,10–3,88 m 12H($N(CH_2)_2$+$2CH_2SO_2$+$O(CH_2)_2$)
(Va)	117–118 (ether: $CHCl_3$ 1 : 1)	42,63 42,57	7,33 7,14	15,85 16,20	13,96 14,20	15,98 15,71	$C_8H_{16}O_2NSCl$	1330, 1120	–	1660	3330	1,33 t 6H(2Me), 2,80–3,02 m 4H($2CH_2$), 3,15–3,77 m 4H(CH_2SO_2+ +NCH_2), 5,53 s 1H(CH), 7,78 s 1H(NH)
(Vb)	96,5–97 (ether: $CHCl_3$ 1 : 1)	37,12 37,58	5,02 5,52	5,53 5,48	12,94 12,54	13,23 13,86	$C_8H_{14}O_4NSCl$	1320, 1140	–	1660	–	1,41 t 3H(Me), 3,23–3,90 m 10H($N(CH_2)_2$+CH_2SO_2+$O(CH_2)_2$), 5,54 s 1H(CH), 7,78 s 1H(NH)
(Vc)	169–170 ($CHCl_3$)	54,10 54,28	3,82 3,90	4,38 4,52	10,47 10,35	11,50 11,44	$C_{14}H_{12}O_3NSCl$	1340, 1150	–	1660	3310	5,57 s 1H(CH), 6,73–8,13 m 10H($PhSO_2$+PhN), 9,7 s 1H(NH)
(IXa)	175 ($CHCl_3$)	38,41 38,34	6.52 6,11	4,94 4,47	20,38 20,43	– –	$C_{10}H_{19}O_6NS_2$	1320, 1135		1670	–	1,30 t 6H(2Me), 3,38–3,80 m 12H($2CH_2SO_2$+$N(CH_2)_2$+$O(CH_2)_2$), 5,70 s 1H(CH)

their geminal structure (see experimental part of Table 2). Amides (Va-c) are evidently the hydrolysis products of (III) and (IV) and are formed either upon treatment of the reaction mixture with water, or during chromatographic separation on an SiO_2 column, which always contains water. This is confirmed by the absence in the PMR spectra of the crude reaction mixtures of (Ia) with n-$BuNH_2$ and morpholine and of (Id) with aniline of a singlet at 5.56 ppm characteristic of the CH groups in (Va-c). Upon standing (III) hydrolyzes into (Vb) due to atmospheric moisture. Compounds (VII) are more unstable; only their hydrolysis products [amides (IXa, b)] can be isolated, which is probably associated with their greater asymmetry compared to products (III). Compounds (II) do not undergo hydrolysis [7], which excludes the second possible route for formation of amides (IXa, b) from (II).

The reaction conditions and product yields depend substantially on the substrate and the nucleophile (Table 1). Reaction of sulfones (Ia-d) with primary aromatic amines leads to formation of aminals of ketones (IIa-i, k) in 50-95% yield.

Alkylsulfones (Ia-c) react equally well under mild conditions (40°C, 7-8 h) in CH_2Cl_2 (or DMF) solution with the majority of amines ($7 < pK_b < 10$). Under the same conditions arylsulfones give only 50% of aminal (II) (Table 1, experiments 1, 4-6). This is associated probably with a decrease of $ArSO_2^-$ activity compared with $AlkSO_2^-$ anion.

Increase of nucleophile volume at the same basicity [for example, reaction of sulfone (Ia) with 2-naphtylamine (pK 9.9) instead of aniline] significantly increases the time necessary to obtain high yields of disubstituted (IId) (Table 1, experiments 1 and 9). Even reaction of this amine with such a reactive electrophilic olefin as tetrasulfonylethylene does not proceed further than monosubstitution [7]. This is probably caused by higher steric hindrance in the substitution product of tetrasulfonylethene than in the product of type (VII). With weakly basic amines (4-$NO_2C_6H_4NH_2$, $pK_b \sim 12$) even after prolonged heating, together with (IIe) starting sulfone (Ia) is found by TLC (Table 1, experiment 13). Substitution in (I) under the action of strongly basic primary aliphatic amines, on the contrary, proceeds exothermically. For example, reaction of sulfone (Ia) with n-butylamine ($pK_b \sim 3.4$) is complete in 15-20 min and gives a mixture of aminal (IIj), ethylsulfonylchloroacetamide (Va), and disulfonylmethane (VIII) (Table 1, experiment 14). Disulfonylmethane (VIII) is probably formed by cleavage of zwitterion $T_2^{\pm}$ by amines (Scheme 1). This is confirmed by the presence of a singlet at 4.6 ppm in the PMR spectrum of the crude mixture from reaction of (Ia) with n-$BuNH_2$, which corresponds to the CH_2 group in methane (VIII). It is known that upon nucleophilic attack of alkene, together with formation of nucleophilic substitution products, a competing molecular fragmentation at the multiple bond is also possible [7, 8].

Reaction of sulfones (I) with primary amines in the presence of triethylamine (conditions of reaction A are in Table 1) proceeds at increased rate and the yield of aminals (II) is quantitative. On one hand, the strongly basic triethylamine deprotonates a zwitterion of type $T_1^{\pm}$ and $T_2^{\pm}$, which also leads in the case of primary aromatic amines to increased reaction rate. On the other hand, it plays a great role in binding the RSO_2^- anion. Upon reaction of sulfone (Ia) with n-butylamine ($pK_b \sim 3.4$) in the presence of Et_3N ($pK_b \sim 3.3$) the yield of amide (Va) decreases twofold due to the increased yield of aminal (IIj).

Secondary aromatic amines, unlike primary aromatic amines, react with (Ia) with extreme difficulty to give disulfonylacetamide (IXb) in 25% yield (Table 1, experiment 17). Highly basic secondary amines, like primary amines, react with sulfones (I) exothermically. For example, reaction of (Ia) with morpholine is complete in 0.5 h and results in a mixture of (III) and amides (Vb) and (IXa). Thus, compounds (I), as well as tetrasulfonylethenes [7], upon reaction with secondary amines do not form aminals of ketenes (II). This is very likely caused by steric hindrance to the addition of a bulky amine molecule to substituted ethylene (VII) and to deprotonation of the resultant zwitterion.

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument using KBr pellets, PMR spectra on a DA60IL instrument (60 MHz) and a Tesla BS-497 (100 MHz) in $(CD_3)_2CO$ or $CDCl_3$ with HMDS as standard, and ^{13}C NMR spectra on a Bruker-250 (250 MHz) instrument in $CDCl_3$. Starting compounds (I) were synthesized by oxidation of E-1,2-di(organylthio)dichloroethenes, obtained by nucleophilic substitution of chlorine in tetrachloroethylene by thiolate anion [1]. Amines were dried with KOH and distilled. For column chromatography SiO_2 L40/100 μ was used. Absolute solvents were used.

General Reaction Method of (Ia-d) with Amines. To a solution of 7 mmoles sulfone (Ia-d) in 10 ml of CH_2Cl_2 a mixture of 15.6 mmoles of amine and 15.6 mmoles of Et_3N was added dropwise with stirring. The reaction mixture was kept at 20-40°C for 0.25-18 h (Table 1). After solvent removal the residue was separated on a column (SiO_2). By gradient elution with a hexane—chloroform system the products were isolated in the following order: (II), (I), (VIII), (III), (V), (VI).

Properties of the obtained compounds are shown in Table 2. Aminals (IIa, e, j) and amide (IXb) were identified according to [7], and disulfonylmethane (VIII) according to [9].

Reaction of (Ia) and (Ic) with Aniline. To a solution of 1 g (3.6 mmoles) of (Ia) and 1.62 g (3.6 mmoles) of (Ic) in 15 ml CH_2Cl_2 a mixture of 1.41 g (14 mmoles) of Et_3N and 1.3 g (14 mmoles) of aniline was added dropwise with stirring and the reaction mixture was heated for 1 h at 40°C. After solvent removal the residue was separated on a column (100 g SiO_2). By gradient elution with a hexane—hexane:$CHCl_3$ system there was isolated 0.87 g (22%) of (IIi), 1.01 g (30%) of (IIk), and 0.59 g (21%) of (IIa).

CONCLUSIONS

1. Reaction of 1,2-di(organylsulfonyl)dichloroethenes with primary amines results in quantitative yields of products with geminal sulfonyl groups, namely N,N-aminals of di(organylsulfonyl)ketenes.

2. In reaction of E-1,2-di(organylsulfonyl)dichloroethenes with secondary amines only products with one chlorine atom replaced by an amino group are formed and during reaction they partially hydrolyze.

3. A mechanism based on reaction of RSO_2^- anion with the starting sulfone giving trisulfonylchloroethene as an intermediate was proposed.

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