

# Induced Alkene Reactions with Sulfur Dichloride. System Sulfur Dichloride—Dimethyl Sulfide as a Reagent for Polysulfonation and Conjugate Chlorination of Alkenes

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**Abstract**—In reaction of unsaturated compounds with sulfur dichloride in the presence of dimethyl sulfide radically new induced directions are realized: the reagent is involved as dimer or trimer (formation of di- and trisulfides). Alongside this process a conjugate chlorination occurred with participation of external nucleophiles, dimethyl sulfide and acetonitrile, furnishing sulfonium chlorides and N-substituted acetamides respectively. The relative importance of these alternative reactions depends on solvent, alkene structure, and order of reagents addition.

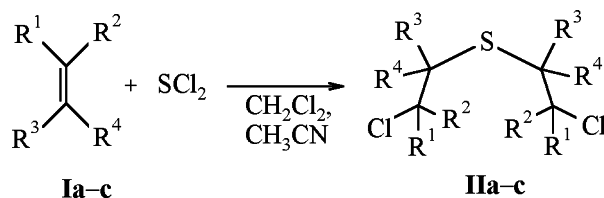
The sulfur dichloride in reactions with unsaturated compounds behaves as bielectrophile providing products of double addition,  $\beta, \beta'$ -dichlorodialkyl sulfides [1, 2]. Other directions were observed only in single cases of unsaturated compounds with uncommon structure (allyl phenolate [3], adamantylidene-adamantane [4], allene [5]) or in reactions carried out under homolytic conditions [6].

Up till now the  $Ad_E$ -reactions of alkenes with compounds of bivalent sulfur in the presence of donor agents were investigated only for systems aryl-, phosphorylsulfonyl chloride – dimethyl sulfide [7, 8]. In reaction of these systems with alkenes prevailed a substitution of an allyl hydrogen of the internal alkenes by electrophilic moiety of the reagent. The role of the donor agent is therewith limited to conversion of the reagent into a new electrophile which instead of reacting along addition mechanism as should be expected takes the other routes. This procedure for modification of various weak electrophiles is interesting both from theoretical and practical viewpoint for it provides an efficient method for extending synthetic potential of alkene chemistry.

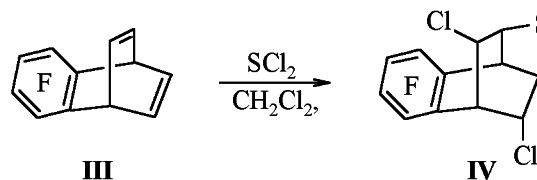
As known from the literature [1, 9], the sulfur dichloride in reactions with alkenes **Ia–c** in dichloromethane\* behaves as a bielectrophile: It adds two

\* We showed that the reaction proceeded similarly in acetonitrile.

molecules of substrate to afford  $\beta, \beta'$ -dichlorodialkyl sulfides (**II**).



In reaction with sulfur dichloride of bicyclic diene, tetrafluorobenzobarrelene (**III**), both  $\pi$ -bonds of the substrate take part yielding a product of intramolecular cyclization **IV** [10].

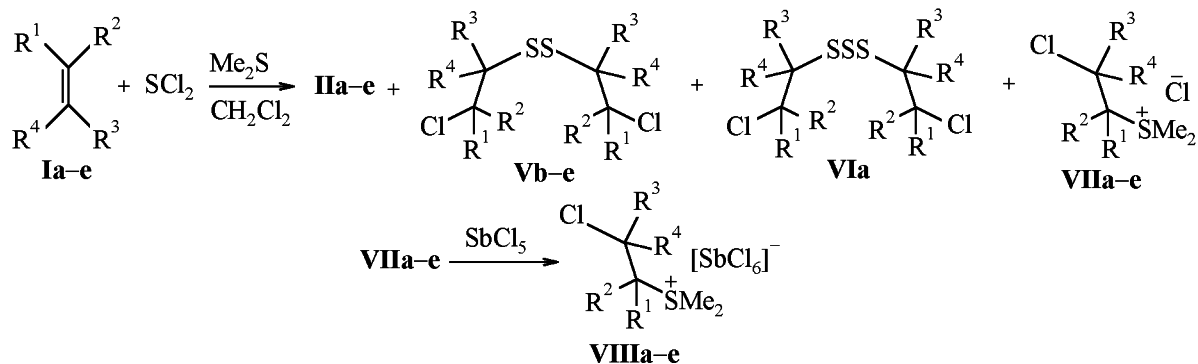


We were first to establish that in reaction of sulfur dichloride with alkenes **Ia–e**, **III** in the presence of dimethyl sulfide in the same solvents (dichloromethane, acetonitrile) occurred also as a novel process where the reagent operated in the form of dimer or trimer. Another uncommon reaction of sulfur dichloride also proceeded in this system, namely, conjugate chlorination of alkenes involving

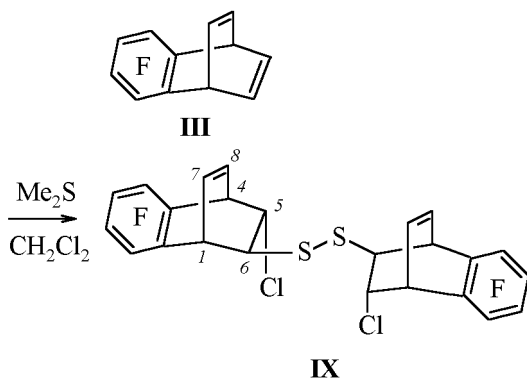
external nucleophiles. The relative importance of these processes depended on solvent, alkene structure, and the order of reagents introduction.

The reagent enters into the reaction in polysulfide form on addition of sulfur dichloride solution in dichloromethane or acetonitrile to the solution of alkene and dimethyl sulfide in the same solvent (procedure a). Therewith from alkenes **Ia-e** formed disulfides

**Vb-e** and trisulfide **VIa**. Alongside polysulfides **V** and **VI** in dichloromethane arose products of conjugate addition of chlorine and dimethyl sulfide, *trans*- $\beta$ -chloroalkylmethylsulfonium chlorides **VIIa-e**, that we converted into more stable hexachloroantimonates **VIIIa-e**. Simultaneously with these induced processes the common addition of the reagent across the multiple bond also occurred yielding  $\beta,\beta'$ -dichlorodialkyl sulfides **II** (Table 1).

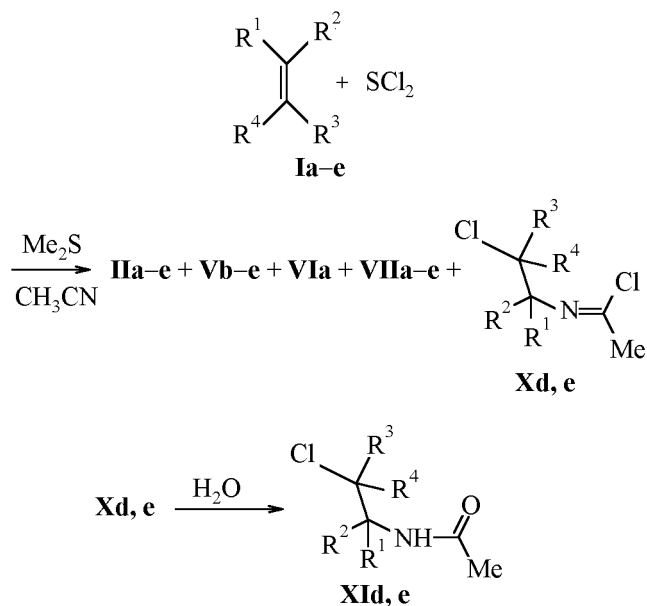


Under the same conditions the sulfur dichloride reacts with tetrafluorobenzobarrelene (**III**) along the pattern of additive heterodimerization providing in virtually quantitative yield (*d,l*)-bis(5-*endo*-chloro-2,3-tetrafluorobenzobicyclo[2.2.2]octadien-6-*exo*-yl) disulfide (**IX**).



In acetonitrile alongside the processes furnishing sulfides **II** and polysulfides **V** and **VI** concurrent conjugate chlorination of alkenes **I** proceeded that was completed by taking up acetonitrile and dimethyl sulfide to yield iminochlorides **Xd, e** and sulfonium chlorides **VIIa-c** respectively. Compounds **Xd, e** arise in reaction of sulfur dichloride with sterically

hindered alkenes **Id, e**, and reaction of alkenes **Ia-e** with less screened multiple bonds results in compounds **VIIa-c**. Compounds **X** are readily hydrolyzed to the corresponding *N*-substituted acetamides **XI**.



The conjugate chlorination becomes virtually the only reaction pathway at addition of alkene **I** solution

**Table 1.** Products of reaction between alkenes **I** and sulfur dichloride prepared by procedure A

Compd. no.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Solvent	Reaction products, yield, %				
						II	V	VI	VII	X
<b>Ia</b>	H	(CH <sub>2</sub> ) <sub>4</sub>		H	CH <sub>2</sub> Cl <sub>2</sub>	25	0	35	40	0
					MeCN	4	0	32	16	0
<b>Ib</b>	Ph	H	H	H	CH <sub>2</sub> Cl <sub>2</sub>	8	26	0	46	0
<b>Ic</b>	Me	Me	H	H	CH <sub>2</sub> Cl <sub>2</sub>	39	44	0	17	0
					MeCN	4	73	0	23	0
<b>Id</b>	Me	Me	Me	Me	CH <sub>2</sub> Cl <sub>2</sub>	17	66	0	17	0
					MeCN	9	63	0	0	28
<b>Ie</b>	Me	Me	Me	H	CH <sub>2</sub> Cl <sub>2</sub>	47	43	0	10	0
					MeCN	8	53	0	0	39

in dichloromethane or acetonitrile to a solution of sulfur dichloride and dimethyl sulfide in the same solvent (procedure b). Under these conditions preliminary liberation of sulfur from the reagent occurs in the form of dichloropolysulfanes in the quantitative yield. Therewith the reaction of alkenes **I** with the system sulfur dichloride-dimethyl sulfide in dichloromethane furnishes only sulfonium chlorides **VII**, and in acetonitrile depending on the alkene affords either amides **XId, e** or sulfonium chlorides **VIIa-c** (Table 2). The low yields of sulfonium chlorides **VII** are due apparently to the low stability of the modified reagent.

The structure and composition of reaction products was proved by IR and NMR spectroscopy, by X-ray diffraction study, and elemental analysis. Physical constants of sulfides **IIa-c** are consistent with the published data [4, 8]. Characteristics of polysulfides **V, VI** and newly prepared sulfides **IId, e** are listed in Table 3. Sulfides **II** and disulfides **Vb-e** were also prepared by independent syntheses.

In the <sup>1</sup>H NMR spectra of all compounds **VIII** appear characteristic signals of methyl groups from (CH<sub>3</sub>)<sub>2</sub>S<sup>+</sup> fragment in the region 2.6–3.1 ppm; the carbon signals from the fragment in the <sup>13</sup>C NMR spectra are observed in the 19.0–32.0 ppm range. The <sup>1</sup>H NMR spectra of amides **XI** contain a broadened signal of amide proton in the region 5.5–8.5 ppm and a singlet from the acetyl group at 2.0 ppm. All absorption bands in the IR spectra of compounds **XI** are typical of secondary amines: 1660 cm<sup>-1</sup> (band amide I, ν<sub>C=O</sub>), 1500 cm<sup>-1</sup> (band amide II, ν<sub>N-H</sub>), stretching vibrations of N–H bond in the free and associated forms in the 3300–3450 cm<sup>-1</sup> region. Characteristics of compounds **VIII** and **XI** are presented in Table 4. <sup>1</sup>H NMR spectrum of disulfide **IX** (δ, ppm): 2.98 d.d (H<sup>6n</sup>, J<sub>6n,5k</sub> 3.5, J<sub>6n,1</sub> 2.5 Hz), 3.95 d.d (H<sup>5k</sup>, J<sub>5k,6n</sub>

3.5, J<sub>5k,4</sub> 3 Hz), 4.53 m and 4.60 m (n<sup>1</sup> and n<sup>4</sup>), 6.61 m (H<sup>7</sup> and H<sup>8</sup>). <sup>13</sup>C NMR spectrum (δ<sub>C</sub>, ppm): 37.36 d and 42.01 d (C<sup>1</sup> and C<sup>8</sup>). <sup>19</sup>F NMR spectrum (δ<sub>F</sub>, ppm from C<sub>6</sub>F<sub>6</sub>): 3.69 (1F), 4.21 (1F), 14.67 (2F). The crystal of disulfide **IX** is built up of two crystallographically independent molecules, and each one is located on a second order rotational axis. The geometrical structure of both independent molecules is virtually identical and coincides with that described in the literature [11]. The structure of one of the molecules **IX** is shown in a figure. The *trans*-position of substituents located at carbons 5 and 6 results in a slight twist of the bicyclo[2.2.2]octene skeleton: the torsional angles C<sup>4</sup>C<sup>5</sup>C<sup>6</sup>C<sup>1</sup> are equal to 6.0(7) and 3.8(7)° for the two molecules respectively. In the packing of the molecules several slightly shortened [12] contacts are present: C–H...S (2.82(5), 2.89(7) Å), C–H...Cl (2.84(6) Å), C–H...F (2.52(6) Å), S...F (3.179(3) Å).

The above results show that dimethyl sulfide used as co-reagent in reactions of sulfur dichloride with

**Table 2.** Products of reaction between alkenes **I** and sulfur dichloride prepared by procedure B

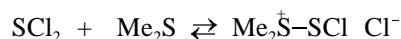
Alkene no.	Solvent	Reaction products, yield, %	
		VII	X
<b>Ia</b>	CH <sub>2</sub> Cl <sub>2</sub>	40	0
	MeCN	65	0
<b>Ib</b>	MeCN	76	0
<b>Ic</b>	MeCN	64	0
<b>Id</b>	CH <sub>2</sub> Cl <sub>2</sub>	31	0
	MeCN	0	72
<b>Ie</b>	CH <sub>2</sub> Cl <sub>2</sub>	23	0
	MeCN	0	63

**Table 3.** Melting points, refractive indices, <sup>1</sup>H NMR spectra and elemental analyses of compounds **II**, **V**, and **VI**

Compd. no.	Name	mp, °C ( <i>n</i> <sub>D</sub> <sup>20</sup> )	<sup>1</sup> H NMR spectrum, δ, ppm	Found, %				Formula	Calculated, %			
				C	H	Cl	S		C	H	Cl	S
<b>IId</b>	Bis(1,1,2-trimethyl-2-chloropropyl) sulfide	59–60	1.20 s (12H, 2C <sup>1</sup> Me <sub>2</sub> ), 1.63 s (12H, 2C <sup>2</sup> Me <sub>2</sub> )	52.85	8.48	26.37	12.30	C <sub>12</sub> H <sub>24</sub> Cl <sub>2</sub> S	53.13	8.92	26.14	11.82
<b>IIE</b>	Bis(1,2-dimethyl-2-chloropropyl) sulfide	(1.4980)	1.49 s (12H, 2C <sup>2</sup> Me <sub>2</sub> ), 1.28 d (6H, 2C <sup>1</sup> Me), 3.31 q (2H, 2C <sup>1</sup> H)	48.90	8.12	30.06	12.92	C <sub>10</sub> H <sub>20</sub> Cl <sub>2</sub> S	49.38	8.29	29.15	13.18
<b>Vb</b>	Bis(2-phenyl-2-chloroethyl) disulfide	(1.6220)	3.30 m (4H, 2C <sup>1</sup> H <sub>2</sub> ), 5.26 m (2H, 2C <sup>2</sup> H), 7.30–7.80 m (10H, 2Ph)	55.29	4.62	20.91	19.18	C <sub>16</sub> H <sub>16</sub> Cl <sub>2</sub> S <sub>2</sub>	55.97	4.70	20.65	18.68
<b>Vc</b>	Bis(2-methyl-2-chloropropyl) disulfide	(1.5292)	1.65 s (12H, 2C <sup>2</sup> Me <sub>2</sub> ), 3.04 s (4H, 2C <sup>1</sup> H <sub>2</sub> )	39.10	6.73	28.51	25.66	C <sub>8</sub> H <sub>16</sub> Cl <sub>2</sub> S <sub>2</sub>	38.86	6.52	28.68	25.93
<b>Vd</b>	Bis(1,1,2-trimethyl-2-chloropropyl) disulfide	(1.5360)	1.28 s (12H, 2C <sup>1</sup> Me <sub>2</sub> ), 1.71 s (12H, 2C <sup>2</sup> Me <sub>2</sub> )	48.02	7.54	23.11	21.33	C <sub>12</sub> H <sub>24</sub> Cl <sub>2</sub> S <sub>2</sub>	47.51	7.97	23.37	21.14
<b>Ve</b>	Bis(1,2-dimethyl-2-chloropropyl) disulfide	(1.5310)	1.58 s (12H, 2C <sup>2</sup> Me <sub>2</sub> ), 1.37 d (6H, 2C <sup>1</sup> Me), 3.49 q (2H, 2C <sup>1</sup> H)	43.14	7.11	26.28	23.47	C <sub>10</sub> H <sub>20</sub> Cl <sub>2</sub> S <sub>2</sub>	43.63	7.32	25.76	23.29
<b>VIa</b>	Bis(2-chlorocyclohexyl) trisulfide	(1.5734)	3.16, 3.17 m (2H, 2C <sup>1</sup> H), 4.05, 4.15 m (2H, 2C <sup>2</sup> H), 1.30–1.90 m (16H, 8CH <sub>2</sub> )	43.96	6.17	20.96	28.91	C <sub>12</sub> H <sub>20</sub> Cl <sub>2</sub> S <sub>3</sub>	43.49	6.08	21.40	29.02

alkenes encourages proceeding of a number of new processes. The most significant among the arising uncommon reaction paths is formation of di- and trisulfides. The function of electrophilic chlorinating agent for unsaturated compounds is unconventional for sulfur dichloride and sulfonyl chlorides. The dependence of competing reactions of polysulfination and conjugate chlorination on the order of reagents mixing is also uncommon for alkenes. The occurrence of these processes induced by dimethyl sulfide and also the influence thereon of the order of reagents mixing is apparently due to different extent of sulfur dichloride transformation preceding the reaction and effected by the donor reagent. In the system sulfur dichloride–dimethyl sulfide in dichloromethane or acetonitrile analogously to the system sulfur dichloride–pyridine [13] a structure of sulfonium salt

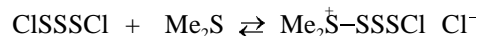
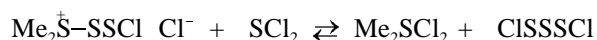
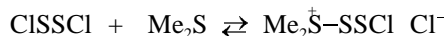
**XII** is apparently generated that further undergoes oligomerization into dichloropolysulfanes with conversion of the dimethyl sulfide into sulfuran-like compound **XIII**.



**XII**



**XIII**



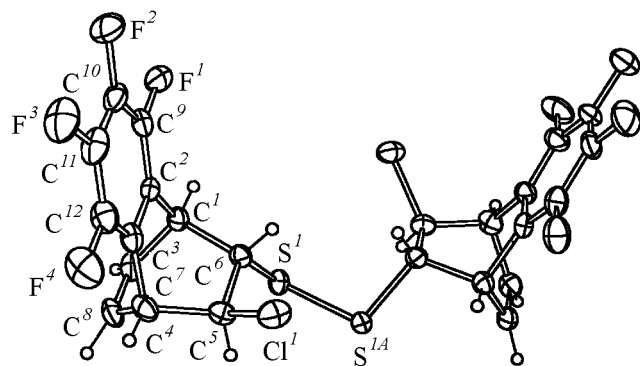
**Table 4.** Yields, melting points,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, elemental analyses of compounds **VIII** and **XI**

Compd. no.	Name	Yield %	mp, °C	$^1\text{H}$ NMR spectrum, $\delta$ , ppm	$^{13}\text{C}$ NMR spectrum, $\delta_{\text{C}}$ , ppm				Found, %			Formula	Calculated, %		
					$\text{C}^1$	$\text{C}^2$	$\text{Me}_2\text{S}$	other signals	C	H	Cl		C	H	Cl
<b>VIIIa</b>	Dimethyl(2-chloro-cyclohexyl)-sulfonium hexachloroantimonate	81	115	1.3÷2.5 m (8H, 4CH <sub>2</sub> ), 2.81 s, 2.84 s (6H, SMe <sub>2</sub> ), 4.59 m (1H, C <sup>2</sup> Cl), 4.94 · (1H, C <sup>1</sup> S)	52.9	58.7	19.0	24.3, 23.9, 23.6, 36.6 [(CH <sub>2</sub> ) <sub>4</sub> ]	21.94	2.71	46.63	C <sub>10</sub> H <sub>16</sub> Cl <sub>7</sub> SSb	22.40	2.63	46.28
<b>VIIIb</b>	Dimethyl(1-phenyl-2-chloroethyl)sulfonium hexachloroantimonate	78	94	2.62 s, 2.86 s (6H, SMe <sub>2</sub> ), 3.75 d.d (2H, C <sup>2</sup> H <sub>2</sub> ), 5.20 d.d (1H, C <sup>1</sup> H), 7.52 · (5H, Ph)	57.4	37.2	22.1, 23.8	130.3, 129.9, 129.3, 129.7 (Ph)	18.91	3.05	48.65	C <sub>8</sub> H <sub>16</sub> Cl <sub>7</sub> SSb	18.69	3.14	48.26
<b>VIIIc</b>	Dimethyl(1,1-dimethyl-2-chloroethyl)-sulfonium hexachloroantimonate	91	117	1.71 s (6H, Me <sub>2</sub> C <sup>1</sup> ), 3.03 s (6H, SMe <sub>2</sub> ), 3.98 s (2H, C <sup>2</sup> H <sub>2</sub> )	57.3	67.3	31.9	27.4 (Me <sub>2</sub> C <sup>1</sup> )	14.51	3.02	51.21	C <sub>6</sub> H <sub>14</sub> Cl <sub>7</sub> SSb	14.76	2.89	50.84
<b>VIII d</b>	Dimethyl(1,1,2-trimethyl-2-chloropropyl)sulfonium hexachloroantimonate	77	159	1.57 s (6H, Me <sub>2</sub> C <sup>2</sup> ), 1.74 s (6H, Me <sub>2</sub> C <sup>1</sup> ), 2.95 s (6H, SMe <sub>2</sub> )	76.6	68.0	19.9	23.6 (Me <sub>2</sub> C <sup>1</sup> ), 28.6 (Me <sub>2</sub> C <sup>2</sup> )	18.98	3.66	47.83	C <sub>8</sub> H <sub>18</sub> Cl <sub>7</sub> SSb	18.61	3.51	48.08
<b>VIII e</b>	Dimethyl(1,1-dimethyl-2-chloropropyl)sulfonium hexachloroantimonate	69	167	1.49 d (3H, MeC <sup>2</sup> ), 1.55, 1.58 s (6H, Me <sub>2</sub> C <sup>1</sup> ), 2.89 s (6H, SMe <sub>2</sub> ), 4.68 q (1H, C <sup>2</sup> H)	62.4	61.1	20.3, 20.2	18.5, 17.9 (Me <sub>2</sub> C <sup>1</sup> ), 19.7 (MeC <sup>2</sup> )	17.10	3.14	48.96	C <sub>7</sub> H <sub>16</sub> Cl <sub>7</sub> SSb	16.74	3.21	49.42
<b>XI d</b>	N-(1,1,2-Trimethyl-2-chloropropyl)acetamide	98	130	5.88 s (1H, N-H), 1.91 s (3H, MeCO), 1.62 s (6H, Me <sub>2</sub> C <sup>2</sup> ), 1.49 s (6H, Me <sub>2</sub> C <sup>1</sup> )	-	-	-	-	54.66	9.31	20.30	C <sub>8</sub> H <sub>16</sub> ClNO	54.21	9.11	19.75
<b>XI e</b>	N-(1,1-Dimethyl-2-chloropropyl)-acetamide	96	74	8.54 s (1H, N-H), 4.96 q (1H, C <sup>2</sup> H), 2.17 s (3H, MeCO), 1.45 d (3H, MeC <sup>2</sup> ), 1.42 s, 1.40 s (6H, Me <sub>2</sub> C <sup>1</sup> )	-	-	-	-	51.56	8.73	21.49	C <sub>7</sub> H <sub>14</sub> ClNO	51.51	8.65	21.44

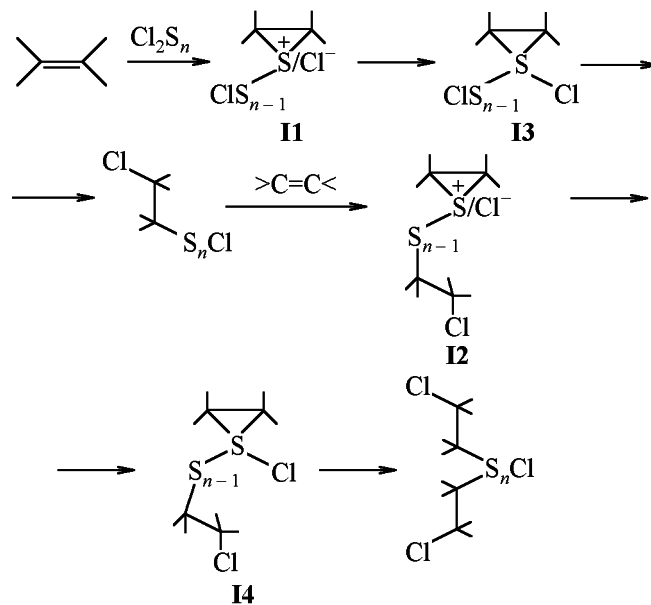
On adding sulfur dichloride into the solution of alkene and dimethyl sulfide in dichloromethane or acetonitrile the short contact of the reagent with dimethyl sulfide results in involving the system sulfur dichloride-donor in the reaction with alkenes as a monomer, a dimer, or a trimer. The reaction with a definite form of the reagent is controlled by the reactivity of alkene and the steric effect of the substituents in the alkene. At the relatively long contact of sulfur dichloride and dimethyl sulfide in dichloromethane or acetonitrile the sulfur dichloride virtually completely is converted into dichloropolysulfanes insoluble in both solvents and not reacting with alkenes. In this case reaction with alkenes is effected by sulfuran structure **XIII** operating as chlorination agent.

In the above forms the sulfur chlorides behave as weak electrophiles, and both stages are typical addition reactions (the addition completes only with the proper nucleophile). In keeping with the ion-pair mechanism of reactions between bivalent sulfur compounds and alkenes [14, 15] and according to the results of quantum-chemical calculations [16] the intermediates ensuring the development of the two-stage processes along these paths may be represented as tight ion pairs (11, 12) and sulfuranes (13, 14). The most compelling evidence supporting this assumption is the lack of products from skeleton rearrangements in the reaction of sulfur dichloride with tetrafluorobenzobarrelene in the presence of dimethyl sulfide.

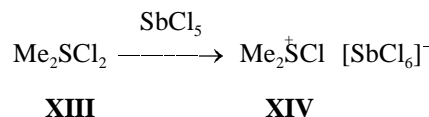
The results cited show that the products of conjugate chlorination obtained in reactions between alkenes and sulfur dichloride in the presence of dimethyl sulfide originate from the action of sulfuran



The structure of disulfide **IX** molecule according to X-ray diffraction analysis. Selected bond lengths (Å), bond and torsional angles (deg):  $S^I-C^6$  1.835(6), 1.835(6),  $S^I-S^{IA}$  2.027(3), 2.021(3),  $Cl^I-C^5$  1.789(6), 1.785(6),  $C^6-S^I-S^{IA}$  104.3(2), 103.3(2),  $C^5-C^6-S^I-S^{IA}$  63.1(4), 66.3(4),  $C^6-S^I-S^{IA}-C^{6A}$  83.0(3), -83.8(3).



**XIII**. Its formation in reaction of sulfur dichloride with dimethyl sulfide in the absence of alkene was fixed by conversion into stable dimethylchlorosulfonium hexachloroantimonate **XIV** that was also prepared by an independent synthesis [17].



The electrophilic part of these species is formally chlorine. It is known that in reactions of branched alkenes with molecular chlorine or the other chlorinating agents deprotonation commonly occurs (L'vov-Sheshukov reaction). The coordination of chlorine with the donor component similarly to behavior of coordinated bromine [18] apparently sharply reduces the electrophilicity and reactivity of chlorine. The low electrophilicity of chlorine in this form of the reagent is evidenced by occurrence only of the processes completed either by the formally proper nucleophile (dimethyl sulfide), or external nucleophile (acetonitrile). Thus the nucleophilic components play significant role in completing the addition, and this fact indirectly testifies to low degree of charge separation in the transition state of the reacting system.

## EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from solutions in  $\text{CH}_2\text{Cl}_2$  with compensation.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were registered on

spectrometer Gemini-300 (300 MHz) from solutions in  $\text{CD}_2\text{Cl}_2$  or  $\text{DMSO}-d_6$ , internal reference TMS. The reaction progress was monitored and purity of compounds was checked by TLC on Silufol plates. The yield of reaction products obtained from alkenes **I** are listed in Tables 1 and 2, and physico-chemical and spectral characteristics of compounds obtained are given in Tables 3 and 4. X-ray diffraction analysis on a single crystal of disulfide **IX** was performed on diffractometer Syntex P21 (Cu  $K_\alpha$ -radiation, graphite monochromator). Monoclinic crystals with the following unit cell parameters:  $a$  12.116(2),  $b$  9.582(2),  $c$  20.149(4) Å,  $\beta$  96.83(3)°,  $V$  2322.6(8) Å<sup>3</sup>, space group P2/n.  $\text{C}_{24}\text{H}_{12}\text{Cl}_2\text{F}_8\text{S}_2$ .  $M$  587.36.  $Z$  4,  $d_{\text{calc}}$  1.680,  $\mu$  4.920  $\text{mm}^{-1}$ , crystal habit  $0.05 \times 0.06 \times 1.5$  mm. Intensities of 3367 independent reflections with  $2\theta < 114^\circ$  were measured by  $\theta/2\theta$ -scanning. In calculations 3127 independent reflections ( $R_{\text{int}}$  0.014) were used after making corrections for absorption by integration method for the real crystal faces. The structure was solved by the direct method with the use of SHELXS-86 software and refined by the least-squares procedure (SHELXS-93 software) in the anisotropic-isotropic approximation to  $wR^2$  0.1818,  $S$  1.02 ( $R$  0.0646 for 2109  $F > 4\sigma$ ). The coordinates of hydrogen atoms were found from the difference synthesis. The coordinates of nonhydrogen atoms are listed in Table 5.

**Reactions of sulfur dichloride with alkenes I in the presence of dimethyl sulfide.** (a) In a flow of dried nitrogen to a solution of 39 mmol of alkene **I** and 3.50 ml (47.1 mmol) of dimethyl sulfide in 20 ml of an appropriate solvent cooled to  $-40^\circ\text{C}$  was added dropwise a solution of 1.00 ml (15.7 mmol) of sulfur dichloride in 5 ml of the same solvent. The mixture was stirred for 4 h, then warmed to room temperature, evaporated in a vacuum, and treated with hexane (4×5 ml) separating the insoluble residue. The crystalline substance obtained consisted of sulfonium chloride **VII** after reaction in dichloromethane, or after reaction in acetonitrile contained either iminochloride **X** or sulfonium chloride **VII**. The hexane extracts were combined and evaporated in a vacuum to obtain a mixture of compounds **II** and **V** or **VI**. In reaction with alkenes **Ia**, **Ib**, or **Ic** on keeping the mixture obtained for 15 days at  $5^\circ\text{C}$  the corresponding sulfides completely separated in crystalline state. For the other alkenes the simultaneous presence in the mixture of compounds **II** and **V** was determined from the results of bromometric titration [19]. Compounds **VII** and **X** were subjected to further reactions. To a solution of 5.0 mmol of sulfonium chloride **VII** in 5 ml of anhydrous dichloromethane in a stream of dried nitrogen at  $-60^\circ\text{C}$  was added a solution of

**Table 5.** Coordinates ( $\times 10^4$ ) and equivalent thermal factors ( $\text{Å}^2$ ,  $\times 10^3$ ) of nonhydrogen atoms in disulfide **IX**

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$
Molecule 1				
$\text{C}^1$	3353(5)	2433(6)	1041(3)	45(1)
$\text{C}^2$	4058(5)	1176(6)	940(3)	44(1)
$\text{C}^3$	5167(5)	1353(6)	1215(3)	49(2)
$\text{C}^4$	5382(6)	2762(7)	1524(4)	55(2)
$\text{C}^5$	4645(5)	2888(7)	2094(3)	48(2)
$\text{C}^6$	3425(5)	2594(7)	1810(3)	41(1)
$\text{C}^7$	3905(6)	3700(7)	774(4)	54(2)
$\text{C}^8$	4962(6)	3862(7)	1025(4)	57(2)
$\text{C}^9$	3736(5)	-67(8)	648(3)	57(2)
$\text{C}^{10}$	4467(7)	-1146(7)	615(4)	62(2)
$\text{C}^{11}$	5564(7)	-958(7)	890(4)	67(2)
$\text{C}^{12}$	5894(6)	262(7)	1189(4)	60(2)
$\text{F}^1$	2671(3)	-269(4)	377(2)	74(1)
$\text{F}^2$	4141(4)	-2357(4)	334(2)	90(1)
$\text{F}^3$	6287(4)	-2011(5)	839(2)	93(2)
$\text{F}^4$	6972(3)	392(5)	1464(3)	88(1)
$\text{Cl}^1$	5109(2)	1715(2)	2760(1)	62(1)
$\text{S}^1$	2458(1)	3975(2)	1995(1)	45(1)
Molecule 2				
$\text{C}^{1A}$	942(5)	-2575(6)	1112(3)	43(1)
$\text{C}^{2A}$	176(5)	-3875(6)	1048(3)	42(1)
$\text{C}^{3A}$	-791(4)	-3576(6)	1339(3)	44(1)
$\text{C}^{4A}$	-849(5)	-2166(6)	1639(3)	48(2)
$\text{C}^{5A}$	164(5)	-2075(7)	2189(3)	45(2)
$\text{C}^{6A}$	1234(5)	-2378(6)	1882(3)	42(1)
$\text{C}^{7A}$	298(5)	-1298(6)	854(3)	47(2)
$\text{C}^{8A}$	-626(5)	-1086(7)	1125(3)	53(2)
$\text{C}^{9A}$	372(5)	-5095(6)	795(3)	44(1)
$\text{C}^{10A}$	-390(6)	-6147(7)	793(3)	54(2)
$\text{C}^{11A}$	-1353(6)	-5921(7)	1059(3)	59(2)
$\text{C}^{12A}$	-1559(5)	-4650(8)	1339(3)	58(2)
$\text{F}^{1A}$	1331(3)	-5354(4)	523(2)	58(1)
$\text{F}^{2A}$	-193(4)	-7403(4)	536(2)	78(1)
$\text{F}^{3A}$	-2118(4)	-6950(5)	1044(3)	90(1)
$\text{F}^{4A}$	-2522(3)	-4479(5)	1612(2)	81(1)
$\text{Cl}^{1A}$	-4(2)	-3251(2)	2857(1)	62(1)
$\text{S}^{1A}$	2276(1)	-982(2)	2001(1)	46(1)

0.64 ml (5.0 mmol) of antimony pentachloride in 5 ml of the same solvent. The mixture was vigorously stirred for 1 h and gradually warmed to room temperature. Then 20 ml of carbon tetrachloride was added to the solution, and the mixture was stirred for 15 min more. The precipitate was filtered off, and hexachloroantimonate **VIII** obtained was purified by

reprecipitation from acetonitrile solution with ethyl ether. Iminochloride **X** was dissolved in 10 ml of dichloromethane, treated with 5 ml of water for 15 min, the organic layer was separated, dried on  $\text{CaCl}_2$ , and evaporated in a vacuum. Amide **XI** obtained was recrystallized from hot hexane.

(b) To a solution of 3.5 ml (47.2 mmol) of dimethyl sulfide in 10 ml of an appropriate solvent cooled to  $-40^\circ\text{C}$  in a flow of dried nitrogen was added a solution of 1.0 ml (15.5 mmol) of  $\text{SCl}_2$  in 5 ml of the same solvent. The mixture was stirred for 15 min, and then dropwise a solution of 18.0 mmol of alkene **Ia**, **Ib**, **Id**, or **Ie** in 10 ml of the same solvent was added thereto. Alkene **Ic** in a preliminary measured amount (18.0 mmol) was condensed into the reaction mixture. The mixture was stirred for 4 h, warmed to the room temperature, evaporated in a vacuum, and 15 ml of acetonitrile was added. The solution was separated from the precipitate that according to analysis consisted of dichloropolysulfane of an average composition  $\text{S}_{70}\text{Cl}_2$  (0.5 g, yield 99%). The filtrate was evaporated in a vacuum to obtain either crystalline sulfonium chloride **VII** or iminochloride **X** that were worked up as described above.

**Reaction of tetrafluorobenzobarrelelene (III) with sulfur dichloride in the presence of dimethyl sulfide.** To a solution of 1.0 g of tetrafluorobenzobarrelelene (**III**) and 0.4 ml of dimethyl sulfide in 80 ml of dichloromethane at  $-20^\circ\text{C}$  in a stream of dried nitrogen was added dropwise a solution of 0.14 ml of sulfur dichloride in 20 ml of dichloromethane. The reaction mixture was maintained for 15 h at room temperature, then the solvent was removed in a vacuum. Disulfide **IX** was purified by reprecipitation from hexane, mp  $154\text{--}156^\circ\text{C}$ .

**Reaction of sulfur dichloride with dimethyl sulfide.** In a stream of dry nitrogen to a solution of 0.25 ml (3.3 mmol) in 3 ml of anhydrous dichloromethane at  $-65^\circ\text{C}$  while vigorous stirring was slowly added a solution of 0.20 ml (3.2 mmol) of sulfur dichloride in 3 ml of the same solvent. A precipitate formed in the course of reaction. The mixture was maintained for 15 min at low temperature and at the same temperature the precipitate of dichloropolysulfane (0.1 g, yield 99%) was filtered off. Then 0.40 ml (3.2 mmol) of antimony pentachloride in 3 ml of dichloromethane was added to the filtrate. In 30 min the temperature was raised to ambient, the separated precipitate was filtered off and washed with carbon tetrachloride ( $5 \times 5$  ml). We obtained 1.30 g of compound **XIV** (yield 94%), mp  $186\text{--}188^\circ\text{C}$  (decomp.) (publ.  $185^\circ\text{C}$  17].

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