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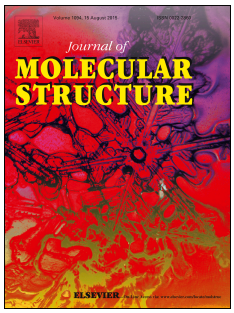

Synthesis and structural analysis of 1,1,2-trichloro-2-[2-chloro-2-(organylsulfanyl)ethenyl]cyclopropanes: NMR, X-ray diffraction and QTAIM approach

Valentina S. Nikonova, Ekaterina P. Levanova, Nikolai A. Korchevin, Igor A. Ushakov, Alexander V. Vashchenko, Igor B. Rozentsveig

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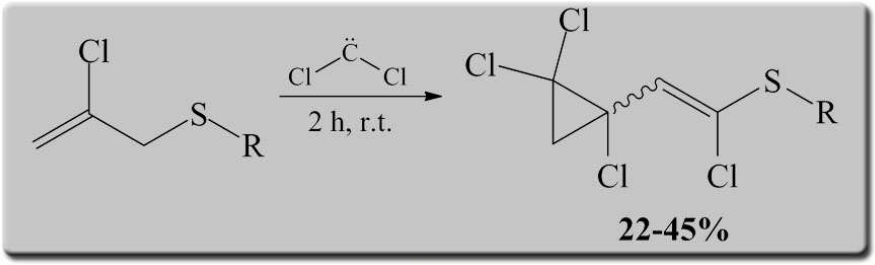
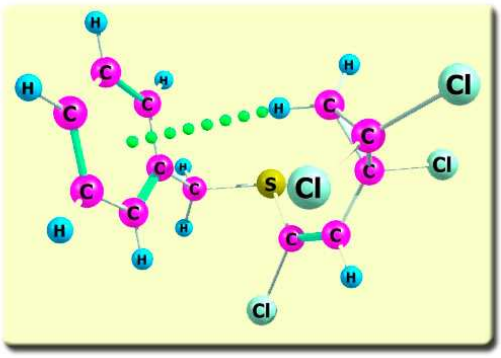
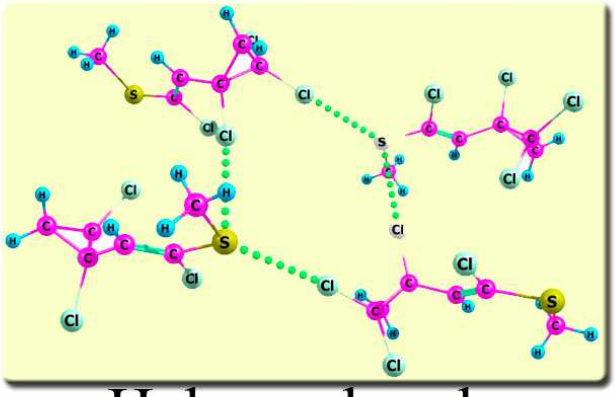




CH/π-interaction



Halogen bonds

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Synthesis and structural analysis of 1,1,2-trichloro-2-[2-chloro-2-(organylsulfanyl)ethenyl]cyclopropanes: NMR, X-ray diffraction and QTAIM approach.

Valentina S. Nikonova*, Ekaterina P. Levanova, Nikolai A. Korchevin, Igor A. Ushakov, Alexander V. Vashchenko, Igor B. Rozentsveig

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorskogo st. 664033, Irkutsk, Russia

Corresponding author e-mail: vachrina@irioch.irk.ru

ABSTRACT

A range of novel 1,1,2-trichloro-2-[2-chloro-2-(organylsulfanyl)ethenyl]cyclopropanes **2a-f** were synthesized by reaction of (2-chloroprop-1-en-3-yl)sulfides with dichlorocarbene generated from $CHCl_3$. The process apparently proceeds via carbenylation of sulfur atom followed by 2,3-sigmatropic rearrangement with subsequent dehydrochloration and cyclopropanation of the terminal double bond. The resulted trichlorocyclopropane derivatives were studied by ^{1}H and ^{13}C NMR spectroscopy as well as X-ray single-crystal analysis that revealed intramolecular CH-π interaction and the formation of intermolecular halogen bonds.

Keywords: Sulfides, cyclopropane, carbenylation, dichlorocarbene, X-ray, non-covalent interactions, halogen bond, AIM analysis

1. Introduction

Geminal dichlorocyclopropyl compounds containing pharmacophoric fragments [1-3] are key reagents allowing to obtain a wide range of carbocyclic and heterocyclic derivatives [1-6], functionalized monomers such as olefins, dienes, allenes [1] and polymers on their base [7-10], photographic materials [11], fungicides and insecticides [12,13]. Despite the numerous papers devoted to the synthesis and reactions of various substituted cyclopropanes [1-13] the information on dihalocyclopropanes containing both alkenyl and sulfanyl groups is lacking in the literature. At the same time, compounds having such reactive centers provide opportunities for further transformation to give different heteroatom derivatives. Thus, the development of efficient methods for the preparation of sulfur-containing alkenyl-functionalized cyclopropane compounds represents an urgent challenge.

Previously, a synthetic approach to (2-chloroprop-1-en-3-yl)sulfides based on the reaction of 2-chloropropen-1-yl-3-isothiuronium chloride with halo-organic compounds has been

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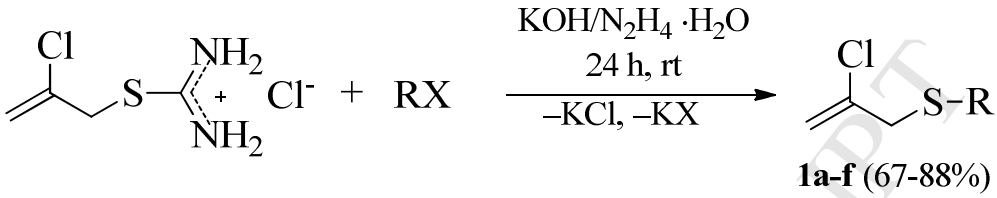
developed (Scheme 1) [14]. In the present paper, we report on a dichlorocarbenylation of (2-chloroprop-1-en-3-yl)sulfides **1a-f** in order to develop a method for obtaining of sulfides functionalized with halogenated alkenyl and cyclopropyl moieties. Dichlorocarbene is commonly generated by the reaction of chloroform with a base in the presence of a phase transfer catalyst [15-17].



1a-f (67-88%)

R = Me (**a**), Pr (**b**), n-Bu (**c**), Ph (**d**), $PhCH_2$ (**e**), CH_2CH_2Cl (**f**);
X = Cl, Br, I

Scheme 1.

2. Experimental

2.1. General

^1H and ^{13}C NMR spectra were registered in $CDCl_3$ solutions on a Bruker DPX-400 (400.13 and 100.62 MHz, respectively) instrument with TMS as an internal standard. CHNS analyzer Thermo scientific Flash 2000 was used to perform elemental analysis.

2.2. Synthesis and crystallization

The initial (2-chloroprop-1-en-3-yl)sulfides **1a-f** were synthesized as described previously [14]. All solvents were distilled prior to use. Phase-transfer catalyst benzyltriethylammonium chloride (TEBAC) was purified by recrystallization from ethanol. Column chromatography was performed using silica-gel 60 (230-400 mesh) with hexane as an eluent. Single crystals for XRD analysis was obtained by recrystallization from dichloromethane.

2.2.1. *1,1,2-Trichloro-2-[2-chloro-2-(methylsulfanyl)ethenyl]cyclopropane (**2a**).*

An aqueous solution of 50% KOH (15.5 g) was added dropwise to a vigorously stirring mixture of chloropropenylmethylsulfide **1a** (0.57 g, 4.6 mmol), TEBAC (0.006 g, 0.03 mmol) and 15 ml of chloroform. After stirred at room temperature for 2 h, the reaction mixture was diluted with 50 ml of water and washed with chloroform (3x30 ml). Separated organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give two isomers of **2a**.

2a-*E*: yield 0.24 g (21%), colorless liquid. ^1H NMR ($CDCl_3$, δ, ppm): 2.12, 2.15 (AB, 2H, ^2J 9.0 Hz, CH_2), 2.50 (s, 3H, CH_3), 6.30 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 15.93 (CH_3),

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36.54 (CH_2), 47.21 (CCl), 63.28 (CCl_2), 126.03 (=CH), 140.04 (=CCl). Anal. calcd. for $C_6H_6Cl_4S$: C, 28.60; H, 2.40; Cl, 56.28; S, 12.72. Found, %: C, 28.43; H, 2.48; Cl, 56.12; S, 12.95.

2a-*Z*: yield 0.11 g (10%), white solid. Mp: 319 K. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.12, 2.15 (AB, 2H, ^2J = 9.0 Hz, CH_2), 2.43 (s, 3H, CH_3), 6.10 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 17.10 (CH_3), 36.40 (CH_2), 47.31 (CCl), 62.87 (CCl_2), 120.92 (=CH), 140.57 (=CCl). Anal. calcd. for $C_6H_6Cl_4S$: C, 28.60; H, 2.40; Cl, 56.28; S, 12.72. Found, %: C, 28.55; H, 2.35; Cl, 56.04; S, 13.03.

2.2.2. *1,1,2-Trichloro-2-[2-chloro-2-(propylsulfanyl)ethenyl]cyclopropane (**2b**).*

Compound **2b** was synthesized by the following general procedure described for **2a** via the reaction of chloropropenylpropylsulfide **1b** (0.5 g, 3.3 mmol) in 10 ml of chloroform with 11.2 g of 50% KOH aqueous solution in the presence of TEBAC (0.004 g, 0.02 mmol). Two isomers of **2b** were obtained.

2b-*E*: yield 0.12 g (12%), colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.02 (t, 3H, CH_3), 1.66 (m, 2H, CH_2), 2.07, 2.11 (AB, 2H, ^2J 9.1 Hz, CH_2), 2.86, 2.97 (m, 2H, CH_2S), 6.28 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 13.27 (CH_3), 23.40 (CH_2), 35.45 (CH_2S), 37.21 (CH_2), 47.82 (CCl), 63.76 (CCl_2), 127.68 (=CH), 139.76 (=CCl). Anal. calcd. for $C_8H_{10}Cl_4S$: C, 34.31; H, 3.60; Cl, 50.64; S, 11.45. Found, %: C, 34.75; H, 3.34; Cl, 50.20; S, 11.70.

2b-*Z*: yield 0.09 g (10%), colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.00 (t, 3H, CH_3), 1.64 (m, 2H, CH_2), 2.07, 2.10 (AB, 2H, ^2J = 9.1 Hz, CH_2), 2.82 (m, 2H, CH_2S), 6.24 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 13.18 (CH_3), 22.32 (CH_2), 35.47 (CH_2S), 36.78 (CH_2), 47.80 (CCl), 63.26 (CCl_2), 124.76 (=CH), 139.88 (=CCl). Anal. calcd. for $C_8H_{10}Cl_4S$: C, 34.31; H, 3.60; Cl, 50.64; S, 11.45. Found, %: C, 34.28; H, 3.73; Cl, 50.44; S, 11.54.

2.2.3. *1,1,2-Trichloro-2-[2-chloro-2-(butylsulfanyl)ethenyl]cyclopropane (**2c**).*

Compound **2c** was synthesized by following general procedure described for **2a** via the reaction of chloropropenylbutylsulfide **1c** (0.85 g, 5.2 mmol) in 15 ml of chloroform with 17.3 g of 50% KOH aqueous solution in the presence of TEBAC (0.007 g, 0.03 mmol). Two isomers of **2c** were obtained.

2c-*E*: yield 0.31 g (20%), colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.95 (t, 3H, CH_3), 1.46 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 2.09, 2.13 (AB, 2H, ^2J = 9.2 Hz, CH_2), 2.90, 3.01 (m, 2H, CH_2S), 6.30 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 13.63 (CH_3), 21.81 (CH_2), 32.01 (CH_2), 33.21 (CH_2S), 37.22 (CH_2), 47.82 (CCl), 63.79 (CCl_2), 127.71 (=CH), 139.80 (=CCl). Anal.

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calcd. for $C_9H_{12}Cl_4S$: C, 36.76; H, 4.11; Cl, 48.22; S, 10.90. Found, %: C, 36.59; H, 4.10; Cl, 48.35; S, 10.96.

2c-*Z*: yield 0.39 g (25%), colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.94 (t, 3H, CH_3), 1.45 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 2.09, 2.13 (AB, 2H, ^2J = 9.0 Hz, CH_2), 2.87 (m, 2H, CH_2S), 6.26 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 13.00 (CH_3), 21.10 (CH_2), 30.22 (CH_2), 32.57 (CH_2S), 36.13 (CH_2), 47.16 (CCl), 62.63 (CCl_2), 123.94 (=CH), 139.29 (=CCl). Anal. calcd. for $C_9H_{12}Cl_4S$: C, 36.76; H, 4.11; Cl, 48.22; S, 10.90. Found, %: C, 36.55; H, 4.23; Cl, 48.10; S, 11.10.

2.2.4. *{[1-Chloro-2-(1,2,2-trichlorocyclopropyl)ethenyl]sulfanyl}benzene (**2d**).*

Compound **2d** was synthesized following the general procedure described for synthesis of **2a** by the reaction of chloropropenylphenylsulfide **1d** (1.00 g, 5.4 mmol) in 16 ml of chloroform with 18.0 g of 50% KOH water solution in the presence of TEBAC (0.007 g, 0.03 mmol). Two isomers of **2d** were obtained.

2d-*E*: yield 0.31 g (18%), white solid. Mp: 350 K. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.18, 2.24 (AB, 2H, ^2J = 9.2 Hz, CH_2), 6.49 (s, 1H, =CH), 7.39, 7.49 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 37.16 (CH_2), 47.85 (CCl), 63.66 (CCl_2), 128.84 (=CH), 130.06 (C_p), 129.40 (C_o), 132.50 (C_m), 130.76 (C_{ipso}), 139.55 (=CCl). Anal. calcd. for $C_{11}H_8Cl_4S$: C, 42.07; H, 2.57; Cl, 45.15; S, 10.21. Found, %: C, 42.10; H, 2.30; Cl, 45.27; S, 10.32.

2d-*Z*: yield 0.15 g (9%), white solid. Mp: 327 K. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.10, 2.16 (AB, 2H, ^2J = 9.2 Hz, CH_2), 6.25 (s, 1H, =CH), 7.39, 7.49 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 36.68 (CH_2), 47.69 (CCl), 63.23 (CCl_2), 126.02 (=CH), 129.35 (C_p), 129.67 (C_o), 133.15 (C_m), 130.86 (C_{ipso}), 138.38 (=CCl). Anal. calcd. for $C_{11}H_8Cl_4S$: C, 42.07; H, 2.57; Cl, 45.15; S, 10.21. Found, %: C, 41.83; H, 2.85; Cl, 45.17; S, 10.10.

2.2.5. *({[1-Chloro-2-(1,2,2-trichlorocyclopropyl)ethenyl]sulfanyl}methyl)benzene (**2e**).*

Compound **2e** was synthesized following the general procedure described for synthesis of **2a** by the reaction of chloropropenylbenzylsulfide **1e** (2.00 g, 10.1 mmol) in 30 ml of chloroform with 34.0 g of 50% KOH water solution in the presence of TEBAC (0.014 g, 0.06 mmol). Two isomers of **2e** were obtained.

2e-*E*: yield 0.65 g (20%), white solid. Mp: 331 K. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.37, 1.87 (AB, 2H, ^2J = 9.2 Hz, CH_2), 3.99, 4.27 (AB, 2H, ^2J = 13.5 Hz, CH_2S), 6.40 (s, 1H, =CH), 7.29 (m, 1H, CH_p), 7.30 (m, 2H, CH_m), 7.30 (m, 2H, CH_o). ^{13}C NMR ($CDCl_3$, δ, ppm): 37.07 (CH_2), 37.90 (CH_2S), 47.57 (CCl), 63.64 (CCl_2), 127.93 (=CH), 128.91 (C_p), 129.00 (C_o), 131.06 (C_m),

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137.31 (C_{ipso}), 138.81 (=CCl). Anal. calcd. for $C_{12}H_{10}Cl_4S$: C, 43.94; H, 3.07; Cl, 43.22; S, 9.77. Found, %: C, 44.03; H, 2.95; Cl, 42.97; S, 10.03.

2e-*Z*: yield 0.34 g (10%), colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.02, 2.07 (AB, 2H, ^2J = 9.1 Hz, CH_2), 4.08, 4.11 (AB, 2H, ^2J = 15.4 Hz, CH_2S), 6.23 (s, 1H, =CH), 7.30 (m, 1H, CH_p), 7.31 (m, 2H, CH_m), 7.31 (m, 2H, CH_o). ^{13}C NMR ($CDCl_3$, δ, ppm): 36.65 (CH_2), 38.19 (CH_2S), 47.52 (CCl), 63.03 (CCl_2), 127.52 (=CH), 127.71 (C_p), 128.75 (C_o), 128.97 (C_m), 136.00 (C_{ipso}), 138.9 (=CCl). Anal. calcd. for $C_{12}H_{10}Cl_4$: C, 43.94; H, 3.07; Cl, 43.22; S, 9.77. Found, %: C, 43.75; H, 3.13; Cl, 43.10; S, 9.96.

2.2.6. *1,1,2-Trichloro-2-[2-chloro-2-[(2-chloroethyl)sulfanyl]ethenyl]cyclopropane (**2f**).*

Compound **2f** was synthesized following the general procedure described for synthesis of **2a** by the reaction of chloropropenylbutylsulfide **1f** (0.70 g, 4.1 mmol) in 15 ml of chloroform with 14.0 g of 50% KOH water solution in the presence of and TEBAC (0.007 g, 0.03 mmol). Two isomers of **2f** were obtained.

2f-*E*: yield 0.143 g (12%), colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.07, 2.10 (AB, 2H, ^2J = 9.3 Hz, CH_2), 3.19 (m, 2H, CH_2S), 3.62 (m, 2H, CH_2Cl), 6.41 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 34.75 (CH_2S), 36.50 (CH_2), 41.87 (CH_2Cl), 47.34 (CCl), 62.94 (CCl_2), 127.94 (=CH), 137.49 (=CCl). Anal. calcd. for $C_7H_7Cl_5S$: C, 27.98; H, 2.35; Cl, 59.00; S, 10.67. Found, %: C, 28.02; H, 2.31; Cl, 59.15; S, 10.50.

2f-*Z*: yield 0.169 g (14%), colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.08, 2.15 (AB, 2H, ^2J = 9.1 Hz, CH_2), 3.18 (m, 2H, CH_2S), 3.62 (m, 2H, CH_2Cl), 6.33 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 34.80 (CH_2S), 36.96 (CH_2), 42.45 (CH_2Cl), 47.34 (CCl), 63.49 (CCl_2), 129.29 (=CH), 137.49 (=CCl). Anal. calcd. for $C_7H_7Cl_5S$: C, 27.98; H, 2.35; Cl, 59.00; S, 10.67. Found, %: C, 28.13; H, 2.37; Cl, 58.77; S, 10.72.

2.3. X-ray study

Crystal data was collected on a Bruker D8 VENTURE PHOTON 100 CMOS diffractometer with MoK_α radiation (λ = 0.71073) at 100.0(2) K using the ω- and φ-scan techniques. The absorption correction was carried out with SADABS. The structure was solved and refined using the Bruker SHELXTL Software Package [18]. The H atoms were determined from a difference Fourier synthesis.

Crystal data, data collection and structure refinements details for compounds **2a-*Z*** and **2e-*E*** are summarized in Table 1 and deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table1. Experimental data and precise structures of compounds **2a**-*Z* and **2e**-*E*.

Compound	**2a**-*Z*	**2e**-*E*
Formula	$C_6H_6Cl_4S$	$C_{12}H_{10}Cl_4S$
Spice dimensions, mm	0.041 x 0.247 x 0.368	0.103 x 0.348 x 0.541
CCDC #	1538904	1538905
Temperature, K	100.0(2)	100.0(2)
Crystal system	Monoclinic	Monoclinic
Space group	*P2₁/n*	*P2₁/n*
θ_{max},	30.08	30.03
a, Å b, Å c, Å β, ˚	5.7355(7) 16.3492(18) 10.3356(11) 93.793(4)	15.1384(19) 6.0126(7) 16.0171(19) 108.704(4)
V, $Å^3$	967.05(19)	1380.9(3)
Z	4	4
D_{calc}, g/cm^3	1.731	1.578
F (000), e^-	504	664
Transmission coefficients (range)	0.6320-0.9460	0.6190-0.9060
Reflections collected	23014	50226
Independent reflections	2829	4039
Number of ref.param.	101	154
Final R_1 , %	3.79	2.85
Rw (all data)	0.0701	0.0672
Goodness-of-fit on F^2	1.033	1.050
$(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$, $e/Å^3$	0.540 and -0.310	0.460 and -0.290

2.4. Quantum chemical calculatios

Calculations were performed by the M062X/6-311+G(d,p) method using the Gaussian09 program package [19]. Calculated wave functions for geometries taken from X-ray analysis were

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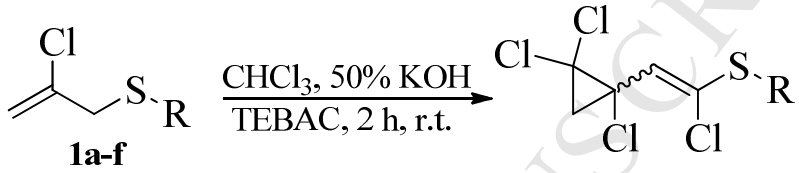
used to perform QTAIM analysis with AIMAll software in order to evaluate the nature and energies of non-covalent bonds in **2a**-*Z* and **2e**-*E* [20].

3. Results and discussion

3.1 Synthesis

The (2-Chloroprop-1-en-3-yl)sulfides **1a-f** reacts readily with dichlorocarbene generated *in situ* from chloroform to give previously unknown 1,1,2-trichloro-2-[2-chloro-2-(organylsulfanyl)ethenyl]cyclopropanes **2a-f** (Scheme 2) as a mixture of E- and Z-isomers (1:1 ratio), which in some cases can be separated and isolated by column chromatography.



1a-f **2a-f** (22-45%)

R = Me (**a**), Pr (**b**), n-Bu (**c**), Ph (**d**), $PhCH_2$ (**e**), CH_2CH_2Cl (**f**).

Scheme 2.

Optimization of the reaction conditions reveals that total conversion of the initial sulfides **1a-f** is reached in 2 hours at room temperature. Upon further increasing of the reaction time, the addition of dichlorocarbene to the internal chlorovinyl group does not occur. The decrease of temperature slows down the reaction but does not change the product yields or reaction direction.

A tentative mechanism of this reaction is presented on Scheme 3. At the first step a molecule of dichlorocarbene attacks the sulfide to generate ylide **A** followed by 2,3-sigmatropic rearrangement with subsequent dehydrochloration to give dichlorodiene sulfide **B**. Then second dichlorocarbene molecule attacks the terminal double bond of sulfide **B**. Apparently, the selectivity of this step is caused by steric effects. Further carbenylation of the sulfanyl group in **2a-f** is not observed that can be explained by deactivation of sulfur atom conjugated to the chlorovinyl fragment.

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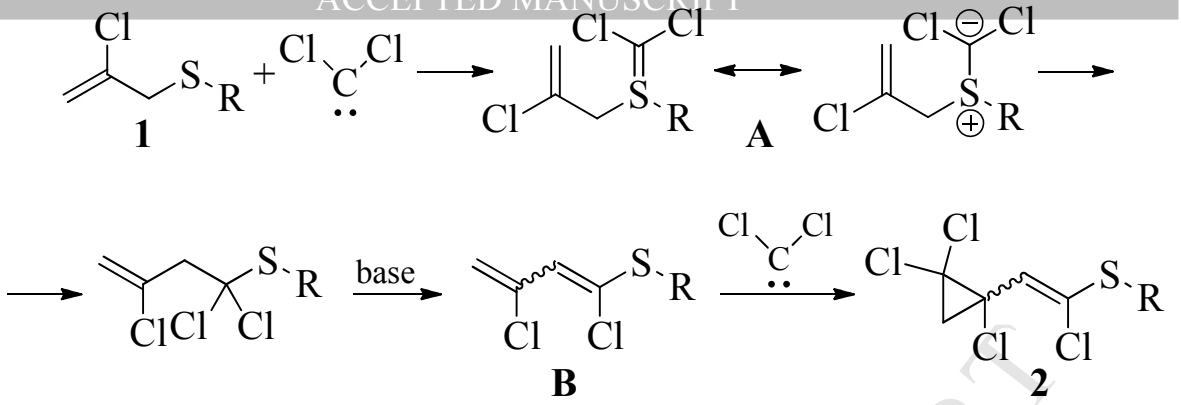

Scheme 3.

It is known that 2,3-sigmatropic rearrangement of allyl-substituted sulfur ylides is an efficient regio- and stereoselective approach to $Csp^3 – Csp^3$ or $S – Csp^3$ bonds formation [21-24] but such reactions involving chloropropenyl-substituted sulfides have not been yet studied.

3.2 NMR and X-ray study

The structure of compounds **2a-f** was proved by ^1H and ^{13}C NMR studies. The assignment of *E*- and *Z*-isomers of **2e** was made by XRD analysis and the experimental values of the chemical shifts of vinyl group protons. According to ^1H NMR spectra, signals of the vinyl protons in *E*-isomer are shifted downfield in comparison with those in *Z*-isomer by about 0.2-0.3 ppm. It can be assumed that such tendency is valid for the rest of *E*- and *Z*-isomers of **2a-f**.

The unit cell of **2a**-*Z* is presented by 2 enantiomers: ((Z)-1-chloro-2-[(1R)-1,2,2-trichlorocyclopropyl]ethenyl methyl sulfide and (Z)-1-chloro-2-[(1S)-1,2,2-trichlorocyclopropyl]ethenyl methyl sulfide) (Fig. 1a). Ratio of R:S is 50:50 %. The same situation is observed in solid **2e**-*E* (Fig. 1b).

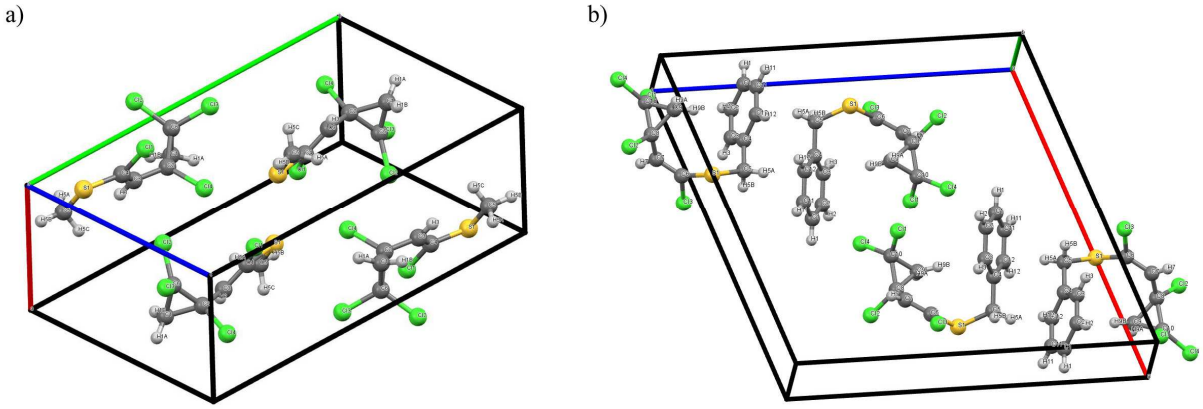

Fig.1. Unit cells of **2a**-*Z* (a) and **2e**-*E* (b)

An interesting feature of **2e** *E*-isomer is the significant upfield shift of CH_2 proton peaks in the cyclopropyl moiety in comparison to those in **2e** *Z*-isomer (1.37, 1.87 ppm for *E*-isomer

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and 2.02, 2.15 ppm for Z-isomer, respectively) and cyclopropyl protons of **2a-d,f**. This phenomenon can be explained by participation of CH_2 protons in CH/π-interaction with π-system of the phenyl ring. Analysis of sp^2-CH/π interactions in 11579 compounds shows that medium D_{pln} value (the CH/π plane distance) is equal to 2.73±0.13 Å and medium C-H-π-plane angle is ~ 154±13° (Fig. 2a) [25]. According to XRD analysis, for **2e**-*E* these values equal 2.914 Å and 170°, respectively (Fig. 2b). The higher values for **2e**-*E* are due to high electron-withdrawing effect of three chlorine atoms in the cyclopropyl fragment. In addition, Plevin *et al* have studied the CH/π interactions in a database of 183 three-dimensional protein structure and shown that the average length of C-π distance *d* (Fig. 2a) equal 4.2 Å [26], while for *E*-isomer of **2e** this value is 4.14 Å (Fig. 2b).

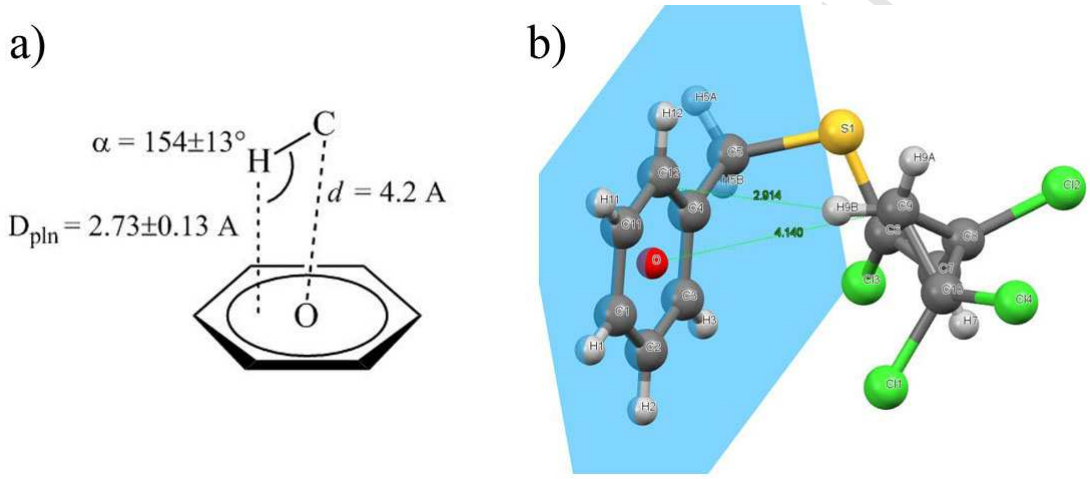

Fig.2. CH/π interactions in literature data and *E*-isomer of **2e**

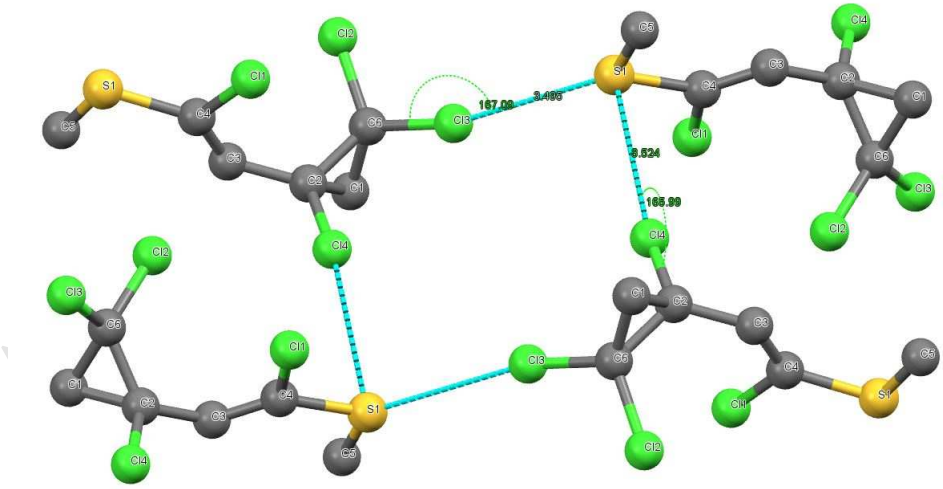

Fig.3. Halogen bonds in *Z*-isomer of **2a**

Another situation is observed in solid **2a**-*Z*. According to XRD data, chlorine atoms in the cyclopropyl fragment are involved in the intermolecular halogen bonding with sulfur atom of the neighboring molecules forming cyclic associates (Fig. 3). Each lone pair of sulfur atom

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interacts with chlorine atom of another molecule via weak halogen bonds with lengths of 3.495 Å and 3.524 Å respectively. The C-Cl···S angles areequal to 167.09° and 165.99°, respectively that correspond to mean values for such interactions described in literature [27,28]. Thus, molecules of **2a**-*Z* are bonded into layers, while molecules of **2e**-*E* do not form chain-like structures in the crystals (Fig. 4).

a) b)

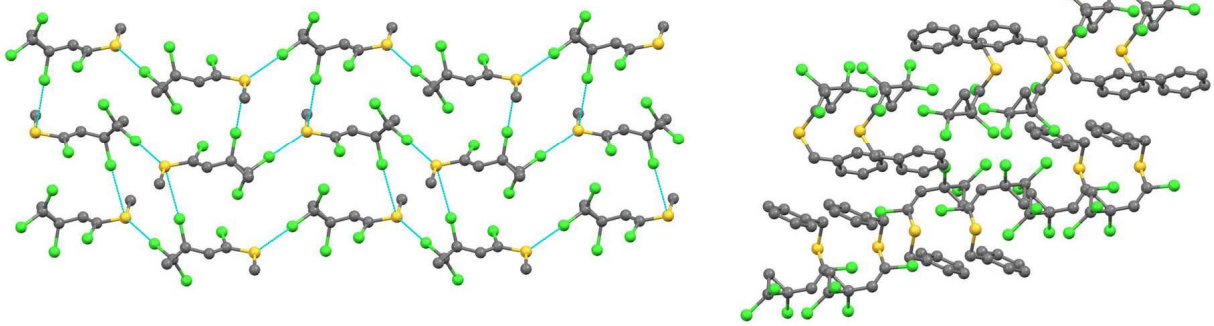

Fig.4. Packing in crystals of **2a**-*Z* (a) and **2e**-*E* (b), hydrogen atoms omitted for clarity

3.3 Theoretical calculations

To evaluate the energies of non-covalent bonds in crystals of **2a**-*Z* and **2e**-*E* a QTAIM analysis was performed. Bond critical points (BCPs) in the molecules were found and their topological properties were determined: the electron density ρ(r), the Laplacian of electron density $\nabla^2\rho(r)$, and the total energy densities *H*(r). The energies of interaction (E) were calculated by the equation $E_{bond} \approx -1/2V^e(r)$, where $2V^e(r)$ is potential energy density in the corresponding BCP [29]. The obtained data (Table 2) show that the CH/π-interaction in **2e**-*E* is characterized by a very weak bond with $E_{bond} \approx 0.7$ kcal/mol, while energy value of intermolecular halogen bonds in **2a**-*Z* is ~1.2 kcal/mol.

Table 2. Bond lengths (*l*, Å), and calculated BCP Properties (ρ(r), $\nabla^2\rho(r)$, *H*(r), V^e; au) and Energies (E_{bond}, kcal/mol) of intra- and intermolecular non-covalent bonds in **2a**-*Z* and **2e**-*E*[a)]

Compound	Bond	*l*	ρ(r)	$\nabla^2\rho(r)$	*H*(r)	V^e	E_{bond}
2a-*Z*	S···Cl(1)	3.495	0.006395	0.024966	-0.001336	-0.003569	1.12
	S···Cl(2)	3.524	0.007228	0.025240	-0.001215	-0.003879	1.21
2e-*E*	C-H··π	2.914[b)]	0.004824	0.012372	-0.000433	-0.002227	0.70

[a)]all calculations were performed for geometry in solid phase obtained by XRD; [b)]measured CH/π-plane distance

4. Conclusion

Carbenylation of (2-chloroprop-1-en-3-yl)sulfides **1a-f** with dichlorocarbene generated from chloroform allows one to obtain a range of novel 1,1,2-trichloro-2-[2-chloro-2-

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(organylsulfanyl)ethenyl]cyclopropanes **2a-f** which are promising reagents for organic synthesis. X-ray study has revealed the existence of weak CH/π interaction in *Z*-isomer of 1,1,2-trichloro-2-[2-chloro-2-(methylsulfanyl)ethenyl]cyclopropane (**2a**-*Z*) resulting in downfield shift of the CH_2-group protons in the ^{1}H NMR spectra. It is also shown that molecules of *E*-isomer of ({[1-chloro-2-(1,2,2-trichlorocyclopropyl)ethenyl]sulfanyl}methyl)benzene (**2e**-*E*) are involved in the C-Cl···S halogen bonding that forms layered structure in crystals of this compound.

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Highlights

- The range of novel 1,1,2-trichloro-2-[2-chloro-2-(organylsulfanyl)ethenyl]cyclopropanes were synthesized via carbenylation of corresponding (2-chloroprop-1-en-3-yl)sulfides
- New compounds were fully characterized
- The structures of resulted compounds were studied employing NMR, X-ray diffraction and QTAIM methods that revealed intramolecular CH-π interaction and the formation of intermolecular halogen bonds.

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