4. Yu. P. Kitaev, I. M. Skrebkova, V. V. Zvervev, and L. I. Maslova, Izv. Akad. Nauk SSSR, Ser. Khim., 28 (1971).
5. Yu. M. Kargin, V. Z. Kondranina, and N. I. Semakhina, Izv. Akad. Nauk SSSR, Ser. Khim., 278 (1971).
6. A. V. Il'yasov, Yu. M. Kargin, N. N. Sotnikova, et al, Izv. Akad. Nauk SSSR, Ser. Khim., 932 (1971).
7. T. V. Troepel'skaya, E. N. Munin, Z. S. Titova, and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Ser. Khim., 899 (1978).
8. V. Z. Latypova, M. Yu. Kitaeva, and Yu. M. Kargin, Zh. Obshch. Khim., 54, 2426 (1984).
9. Yu. M. Kargin and V. Z. Latipova, Summaries in Science and Technology. Physical Chemistry, Electrochemistry [in Russian], Vol. 7, VINITI, Moscow (1981), p. 210.
10. Yu. M. Kargin, V. Z. Latipova, R. Kh. Fassakhov, et al, Zh. Obsch. Khim., 49, 2139 (1979).

ELECTRONIC STRUCTURE OF ORGANYLTHIOCHLOROACETYLENES AND THEIR REACTIONS WITH O-CONTAINING NUCLEOPHILES

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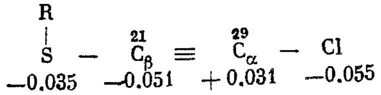
UDC 543.422.25:530.145:541.6:
547.379'131:547.562.4'133

We previously showed that the ^{13}C NMR spectra of organylthiochloroacetylenes exhibit two acetylenic carbon signals [1]. In the ^{13}C NMR spectra of alkylthiochloroacetylenes obtained without proton decoupling the upfield C_{sp} signal splits into a triplet with a coupling constant of 6.1 Hz. The signal of the second acetylenic C atom does not split, which allows its assignment to the C_{sp} bearing the Cl atom (C_α). Since the ^{13}C chemical shift is an adequate measure of the total charge density on the resonating C nucleus [2], the analysis of the ^{13}C NMR of organylthiochloroacetylenes suggests the C_α atom contains the lesser electron density.

By the PPDP/2 method with the original parametrization (spd-basis) [3] the distribution of electron density in organylthiochloroacetylenes was calculated. The effective nucleus of the R substituent and the linear $-S-C{=}C-Cl$ chain are situated in the same plane.* Geometric parameters were taken from [4]



$$\begin{array}{ccccccc} R & & & & & & \\ | & & 21 & & 29 & & \\ S & - & C_\beta & \equiv & C_\alpha & - & Cl \\ -0.035 & & -0.051 & & +0.031 & & -0.055 \end{array}$$

The figures under the atoms indicate the effective charge on the atom, the figures above indicate the contribution of the AO to the HCMO (in %). Data are shown for compounds with $R = C_6H_5$. The data for $R = C_2H_5$ are not significantly different. From analysis of the molecular diagram it follows that for organylthiochloroacetylenes nucleophilic substitution by both "hard" and "soft" nucleophiles should occur on C_α. However the possibility of attack by hard nucleophiles on C_β is not excluded, since in calculation of the direction of nucleophilic substitution in charge-controlled reactions, the dominating terms in the general equation of perturbation theory [5] are those with maximum orbital populations. Nucleophilic substitution at a multiple bond prcceeding in a plane orthogonal to the plane of the molecular skeleton (with charges on the p-orbitals orthogonal to the molecular skeleton of $q_{p_z}^{C_\beta} = -0.017$ and $q_{p_z}^{C_\alpha} = +0.052$) leads to inversion of the hard center and hard nucleophiles attack the center C_β.

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*Orthogonal distribution of the R substituent framework and the $-S-C{\equiv}CCl$ chain is less favorable by 0.15 and 0.26 eV for $R = C_2H_5$ and C_6H_5; respectively.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya No. 3, pp. 612-616, March, 1988. Original article submitted July 25, 1986.

0568-5230/88/3703-0514$12.50

TABLE 1. Physicochemical Constants, Yields, and Elemental Analytical Data of the Synthesized Compounds (R'O)CCl=CHSR (I)-(VIII)

Compound	R	R'	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found, %			Molecular formula	Calculated, %		
							Br	Cl	S		Br	Cl	S
(I)	C_3H_7	C_6H_5	40	125(1)	1,5660	1,2658	–	15,57	14,05	$C_{11}H_{13}ClOS$	–	15,52	14,02
(II)	C_3H_7	p-BrC_6H_4	30	172(1)	1,5890	1,4081	25,34	11,22	12,09	$C_{11}H_{12}BrClOS$	25,76	11,5	12,10
(III)	C_3H_7	p-ClC_6H_4	53	130(1)	1,5720	1,2356	–	26,54	12,02	$C_{11}H_{12}Cl_2OS$	–	26,91	12,18
(IV)	C_3H_7	p-FC_6H_4	41	107(1)	1,5525	1,2096	–	14,27	12,78	$C_{11}H_{12}FClOS$	–	14,37	12,09
(V)	C_4H_9	C_6H_5	50	127(1)	1,5550	1,1295	–	14,31	13,10	$C_{12}H_{15}ClOS$	–	14,16	13,29
(VI)	C_4H_9	p-ClC_6H_4	44	150(1)	1,5640	1,2050	–	25,60	11,85	$C_{12}H_{14}Cl_2OS$	–	25,58	11,56
(VII)	C_4H_9	m-$CH_3C_6H_4$	33	122(1)	1,5534	1,1064	–	13,98	12,62	$C_{13}H_{17}ClOS$	–	13,81	12,48
(VIII)	C_6H_5	C_6H_5	21	179(1)	1,6210	1,1818	–	12,90	12,31	$C_{14}H_{11}ClOS$	–	13,49	12,22

TABLE 2. Physicochemical Constants, Yields, and Elemental Analytical Data of the Synthesized Compounds (R'O)CH=CSR(OR') (IX)-(XIII), RS(R'O)C=CHCl (XIX), (XXII), and $RSCH_2$-COOR' (XVIII), (XXIII)

Compound	R	R'	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found, %				Molecular formula	Calculated, %			
							C	H	Cl	S		C	H	Cl	S
(IX)	C_3H_7	C_6H_5	32	172(1)	1,5762	1,1148	70,53	6,38		11,60	$C_{17}H_{18}O_2S$	71,30	6,33		11,19
(X)	C_3H_7	p-ClC_6H_4	24	206(1)	1,5895	1,2394			19,09	9,54	$C_{17}H_{16}Cl_2O_2S$			19,95	9,03
(XI)	C_4H_9	C_6H_5	30	160(1)	1,5720	1,0951	71,28	6,75		10,50	$C_{18}H_{20}O_2S$	71,96	6,71		10,67
(XII)	C_4H_9	p-ClC_6H_4	40	222(1)	1,5870	1,2245			17,90	9,07	$C_{18}H_{20}Cl_2O_2S$			19,20	8,68
(XIII)	C_4H_9	m-$CH_3C_6H_4$	40	175(1)	1,5620	1,0809	73,15	7,42		9,91	$C_{20}H_{24}O_2S$	73,31	7,36		9,76
(XVIII)	C_3H_7	C_3H_7	14	–	1,4615	–	62,81	7,64		18,40	$C_{11}H_{16}O_2S$	62,26	7,54		18,18
(XIX)	C_3H_7	C_3H_7	20	–	1,4960	–	49,08	7,52	18,49	17,95	$C_8H_{15}ClOS$	49,35	7,71	18,20	
(XXII)	C_2H_5	C_2H_5	30	–	1,5063	–	46,28	7,00	19,05	17,95	$C_7H_{13}ClOS$	46,54	7,20	19,67	17,72
(XXIII)	C_2H_5	C_2H_5	24	–	1,4885	–	61,00	7,15		16,35	$C_{10}H_{14}O_2S$	60,60	7,07		16,16

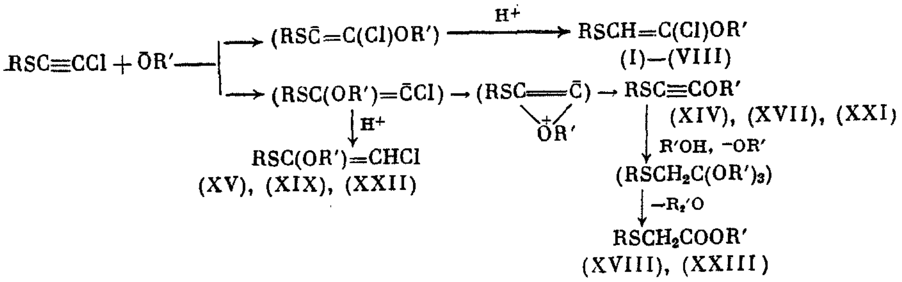
TABLE 3. PMR Spectral Parameters for Products of Reaction of Organylthiochloroacetylenes with O-Containing Nucleophiles

Compound	δ, ppm, CCl_4					Type and ratio of isomers
	CH_3	CH_2	CH_2S	OAr, OCH_2	=CH	
(I)	0,95 t	1,59 m	2,73 t	7,05	5,50 s 6,03 s	$E:Z=1:1$
(II)	0,92 t	1,49 m	2,60 t	7,10 m	5,70 s	E
(III)	0,95	1,64 m	2,59 t	6,96 m	5,71 s	E
(IV)	0,92 t	1,56 m	2,56 t	7,01 m	5,56 s	E
(V)	0,90 t	1,48 m	2,60 t	7,06 m	5,68 s, 6,00 s	$E:Z=1:1$
(VI)	0,90 t	1,47 m	2,60 t	7,04 m	5,71 s	E
(VII)	0,87 t	1,38 m	2,56 t	6,95 m	5,64 s	E
(VIII)				6,92 m 7,46 m (SC_6H_5)	5,95	E
(IX)	0,93 t	1,57 m	2,48 t	7,10 m	5,10 s	E
(X)	0,95 t	1,63 m	3,55 t	7,06 m	5,21 s	$E:Z=5:1$
(XI)	0,87 t	1,80 m	2,54	7,06 m	5,21 s 5,74 s	E
(XII)	0,88 t	1,50 m	2,57 t	7,16 m	5,20 s	E
(XIII)	0,89 t	1,49 m	2,54 t	6,78 m	5,03 s	E
(XVI)	0,92 t	1,54 m	2,54 m	7,10 m	5,25 H^1, 6,31 H^2 J_{HH} = 5 Hz	–
(XVIII) *	0,97 t	1,60 m	2,56 m	3,97 m	–	–
(XIX)	0,97 m	1,60 m	2,55 m	3,92 m	5,17 s	Z
(XXII)	1,02 m		2,49 m	3,80 m	5,18 s	Z
(XXIII) *	1,05 m		2,60 m	3,92 m	–	

*δ CH_2CO = 3.04 ppm.

Continuing our study of the reactivity of organylthiochloroacetylenes, we reacted them with oxygen-containing nucleophiles. Upon reaction of organylthiochloroacetylene with phenols in the presence of their Na-derivatives a mixture of two products is formed: 1-chloro-1-aroxy-2-alkylthioethenes (I)-(VIII) and 1,2-diaroxy-2-alkylthioethenes (IX)-(XIII) (Scheme). Reaction proceeds with nucleophilic substitution on the C_α atom, which indicates formation of chloroethenes (I)-(VIII). However, unlike the reactions of organylthiochloroacetylenes with S-, N-, and P-containing nucleophiles studied earlier [1, 6, 7], products of substitution on Cl, RSC≡CX (XIV), were not isolated. At the same time formation of 1,2-diaroxyethenes (IX)-(XIII) indicates possible substitution of Cl by an aroxy group followed by addition of phenol to (XIV). β-Adducts, 1-chloro-2-aroxy-2-alkylthioethenes (XV), are not formed in this reaction, therefore attack of phenolate anion on the C_β atom of organylthiochloroacetylene does not occur or it plays an insignificant role.

Scheme



$$\underset{(IX)-(XIII),\ (XX),\ (XXIV)}{RSC{\equiv}COR' + R'OH \rightarrow RSC(OR'){=}CH(OR')}$$

R′ = Ar (I)–(XV); R′ = Alk (XVII)–(XXIV) (Tables 1 and 2)

In the IR spectra of compounds (I)-(VIII) an intense double bond absorption band is present at 1590 cm^{-1}. The physicochemical constants and yields of the synthesized compounds are shown in Tables 1 and 2. In the PMR spectra of compounds (I) and (V) together with the alkylthio group and benzene ring signals two olefinic proton signals are present at 5.5 and 6.0 ppm. In the PMR spectra of products (II)-(IV) and (VI)-(VIII) only a vinylic proton signal at 5.7 ppm is found. Apparently in this case formation of the E-isomer is preferable (Table 3). The structure of (III) was confirmed by its dipole moment (μ_{found} = 2.00 D, μ_{calc} = 1.99 D) and by reduction with $LiAlH_4$, which resulted in 1-(p-chlorophenoxy)-2-(propylthio)-ethene (XVI)

$$p\text{-}ClC_6H_4OC(Cl){=}CHSC_3H_7 \xrightarrow{LiAlH_4} p\text{-}ClC_6H_4OCH{=}CHSC_3H_7 \quad (XVI)$$

The chemical shifts for the vinyl protons in the PMR spectrum of (XVI) are characteristic of a structure with a cis-arrangement of H atoms.

Tha IR spectra of compounds (IX)-(XIII) have double bond absorption bands at 1640 cm^{-1}. Comparison of chemical shifts for vinyl protons calculated by the additive scheme [8] with those found experimentally for compounds (IX)-(XIII) suggests preferable formation of E-isomers with geminal aroxy groups. The presence of a δCH signal of 5.47 ppm in the PMR spectrum of (X) indicates the presence of a second isomer (Z).

Upon reaction of organylthiochloroacetylenes with hard anionic nucleophiles, particularly with alcohols in the presence of their sodium derivatives in diethyl ether, 1-organylthio-1-alkoxy-2-chloroethenes (XIX) and (XXII) were obtained. Their formation can be explained by the attack of alcoholate anions on the Cβ atom, which is in qualitative conformity with the results of quantum chemical calculations. Moreover, the reaction mixture contains acetylenic esters (XVII), (XXI), and products of their nucleophilic attack by alcohols (XVIII), (XX), (XXIII), and (XXIV) (see scheme). We have not succeeded in separating the reaction mixture and only the compounds (XVIII), (XIX), (XXII), and (XXIII) were isolated pure by column chromatography. The presence of other products in the reaction mixture was proven by IR and PMR spectroscopy. The IR spectrum of the reaction mixture has an intense absorption band at 2170 cm^{-1}, not characteristic of starting acetylene. Therefore it can be attributed to the νC≡C bond in the substitution product of (XVII) and (XXI). An intense absorption band at 1600-1610 cm^{-1} corresponds to the double bond vibrations in (XIX), (XX), (XXII) and (XXIV). In the IR spectra of compounds (XVII) and (XXIII) an intense ester group absorption band at 1740 cm^{-1} is present. The PMR spectra contain signals of the CH_2CO group protons at ~ 3 ppm and signals of protons on the substituents at the S and O atoms. Formation of ester is caused probably by nucleophilic substitution of the Cl atom in the chloroacetylene by the alkoxy group followed by addition of alcohol to the acetylenic product in the alkaline medium, and decomposition of the orthoester formed. The same process of ester formation is found in [9] upon reaction of phenylhaloacetylenes with alcoholates in alcohol.

EXPERIMENTAL

IR spectra were taken on a IKS-22 spectrometer in the region of 600-4000 cm^{-1} on microlayers. PMR spectra were obtained on a Tesla BS-487 instrument, 80 and 60 MHz, with HMDS as internal standard. GLC analyses of the compounds and the reaction mixtures were carried out on a LKhM-8MD chromatograph with a 2m ×3 mm column with 15% silicon DS-550 on chromaton NAW (0.200-0.250 mm). The column temperature was 80-250°C, flow of He was 25-40 ml/min, and a katharometer was used as detector. Dipole moments were measured in benzene solution at 250°C at 1 MHz. Calculations were made with the Gedestrand formula. Quantum chemical calculations were carried out on a BESM-6 computer. Preparative separation of the compounds was done by column chromatography on Al_2O_3 (activity grade II), with hexane as eluent.

Reaction of Propylthiochloroacetylene with Sodium Propylate. 2.3 g (0.1 mole) of Na was was dissolved with heating in 6.5 g (0.1 mole) of abs. propanol in 50 ml abs. ether. At 20°C, 13.4 g (0.1 mole) of propylthiochloroacetylene was added dropwise. The mixture was stirred for 10 h, filterd, and the ether was distilled off. IR spectrum of the reaction mixture (ν, cm^{-1}): 2170-2175 (C=C, 1600-1610 (C=C), 1740 (C=O). By fractional distillation a fraction with bp 82-115°C was isolated. According to GLC data it consisted of 42% of (XIX) and 42% of (XVIII), and 16% of two unidentified products. Compounds (XVIII) and (XIX) were isolated individually by column chromatography. Reaction of ethylthiochloroacetylene with MeONa in ether proceeded analogously.

Reaction of n-Butylthiochloroacetylene with Sodium Phenolate. To 9.4 g (0.1 mole) of phenol 4 g (0.1 mole) of NaOH in 5 ml water was added. After 2 h water was distilled off under vacuum. The residue was dissolved in DMSO and to the solution 14.8 g of n-butylthiochloroacetylene was added dropwise. The reaction mixture was stirred for 2 h at 20-22°C and filtered. By vacuum distillation 12.4 g of (V) and 9.1 g of (II) were isolated. Compounds (I)-(IV), (VI)-(X), (XII), and (XIII) were obtained in the same way.

1-p-Chlorophenoxy-2-propylthioethene (XVI). To a solution of 22.8 g (I) in ether a suspension of 3.8 g $LiAlH_4$ in ether was added. The reaction mixture was refluxed for 5 and filtered. By distillation 7.72 g of (XVI) was isolated.

CONCLUSIONS

Reactivity of organylthiochloroacetylenes toward O-containing nucleophiles was studied. It was established that phenolate anions attack the acetylenic C atom bound to the Cl atom and alcoholate anions attack the carbon atom bound to the S atom, which corresponds with the data of quantum chemical calculations.

LITERATURE CITED

1. A. N. Mirskova, S. F. Seredkina, I. D. Kalikhman, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., 2818 (1985).
2. B. I. Ionin, B. A. Ershov, and A. I. Kol'tsov, NMR Spectroscopy in Organic Chemistry [in Russian], Khimiya, Leningrad (1983), p. 22.
3. D. P. Santri and G. A. Segal, J. Chem. Phys., 158 (1967).
4. Tables of Intratomic Distances and Configuration in Molecules and Ions, London (1958), p. 147.
5. G. Klopman, ed., Chemical Reactivity and Reaction Paths, Wiley, New York (1974).
6. S. G. Seredkina and A. N. Mirskova, Reports of the Conference on Chemistry and Technology of Organosulfur Compounds and Petroleum Sulfur Compounds, Riga (1984), p. 129.
7. S. G. Seredkina, V. E. Kolbina, V. G. Rozinov, et al., Zh. Org. Khim., 52, 2694 (1982).
8. M. U. Matter, C. Pasqual, E. Pretsch, et al., Tetrahedron, 25, 693 (1969).
9. Rynihi Tanaka, M. Rodgers, R. Simonatis, and S. I. Miller, Tetrahedron, 27, 2651 (1971).

REACTIONS OF ALKYLTHIOCHLOROACETYLENES WITH O,N- AND S,N-CONTAINING BIFUNCTIONAL NUCLEOPHILES

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UDC 543.422.25:530.145:541.6:
547.379'131:547.435.21

Reaction of organylthiochloroacetylenes with bifunctional nucleophiles makes possible the synthesis of various S-, N-, and O-containing acetylenic and heterocyclic compounds. Thus, organylthiochloroacetylenes easily react with tertiary (2-hydroxyethyl)amines and 2-mercaptoethanol with formation of 2-(organylthiomethylene)-3,3-dialkyl-1,3-oxazolidine chlorides and 2-(organylthiomethylene)-1,3-oxathiolanes respectively [1, 2].

In continuation of these investigations we have studied the reaction of alkylthiochloroacetylenes (ATCA) with N-methyl-2-hydroxyethylamine, 2-hydroxyethylamine, and 2-mercaptoethylamine.

Reaction of ATCA with N-methyl-2-hydroxyethylamine was carried out at a molar ratio of 1:2 [excess amine was used to bind HCl to N-methyl-N-(2-chloroethyl)amine]. The reaction apparently proceeds via enamine formation (see [3])

$$\mathrm{RSC{\equiv}CCl} \xrightarrow[-\mathrm{HCl}]{\mathrm{CH_3NHC_2H_4OH}} [\mathrm{RSC{\equiv}CN(CH_3)C_2H_4OH}] \xrightarrow[+\mathrm{HCl}]{\mathrm{CH_3NHC_2H_4OH}}$$

$$\to \underset{(\mathrm{Ia\text{-}c})}{\mathrm{RSCH_2{-}C(O){-}N(CH_3)C_2H_4OH}} + \mathrm{CH_3NHC_2H_4Cl}$$

$\mathrm{R} = \mathrm{C_3H_7}(\text{Б}),\ \mathrm{C_2H_5}(\mathrm{a}),\ \mathrm{C_4H_9}(\mathrm{c}).$

Yields and characteristics of compounds (I) are shown in Tables 1 and 2. Unlike reaction of organylthiochloroacetylenes with tertiary (2-hydroxyethyl)amines, in the reaction of ATCA with secondary (2-hydroxyethyl)amines the presence of hydrogen chloride in the reaction mixture insures predominant hydration of the intermediate enamine over its intramolecular cyclization.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 616-619, March, 1988. Original article submitted July 1, 1986.

0568-5230/88/3703-0518$12.50