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REVIEW

Chemistry of Halomethyl Thioketones

M. G. Voronkov, L. G. Shagun, and V. A. Shagun

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia

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Abstract—The review summarizes and systematizes the authors' data on the synthesis and reactivity of halomethyl thioketones. Reactions involving the title compounds as intermediates are also considered. Mechanisms of formation of halomethyl thioketones are discussed in terms of the results of quantum-chemical calculations.

I. INTRODUCTION

Synthesis, structure, reactivity, and many surprising chemical transformations of thiocarbonyl compounds have long attracted researchers' attention [1–15]. In 1960s, the chemistry of thioketones has started to extensively develop. Apart from stable thioketones, some labile compounds were synthesized and studied [2–13]. Aliphatic thioketones turned out to be especially unstable: they were converted *in statu nascendi* into cyclic trimers, 1,3,5-trithianes [1, 4, 12]. In 1996, Blansh and Mayer were the first to obtain dialkyl thioketones by the action of hydrogen sulfide on alcoholic solutions of the corresponding ketones in the presence of sulfuric acid [3, 4]. This procedure for the transformation of ketone carbonyl group into thiocarbonyl has become one of the simplest and most convenient and efficient methods.

The initial stage in the formation of dialkyl thioketones is protonation of the carbonyl oxygen atom with sulfiric acid. The subsequent thiolysis of the resulting carbenium ion with hydrogen sulfide yields thioketone (Scheme 1). The reaction output depends on a number of factors, including temperature, solvent nature, reaction time, stability of the product, and its ability to undergo enethiolization. A necessary condition for the process to be successful is optimal concentration of the catalyst (Brønsted acid). The reaction slows down when the catalyst concentration is both increased and reduced [16]. Syntheses of dialkyl thioketones were usually performed at –70°C in an alcoholic medium. At –40°C, the corresponding

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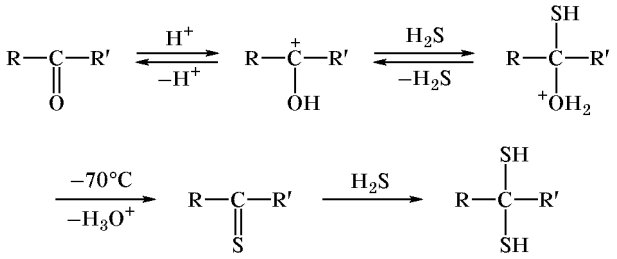
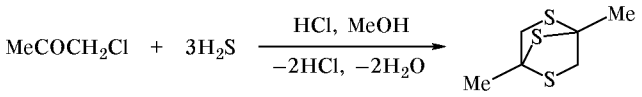
Scheme 1.



geminal dithiols were formed in addition to the desired thioketones.

Prior to our studies, α-halo thioketones of the general formula $RC(=S)CH_2X$ were not reported, though numerous attempts were made to synthesize quite reactive chlorothioacetone from chloroacetone [17–19]. Hydrothiolysis of chloroacetone in a solution of hydrogen chloride in methanol was first accomplished by Bohme, Pfeiffer, and Schneider as early as 1942 [17]. However, instead of the expected chlorothioacetone, the authors isolated trithianorbornane (2,5-dimethyl-*endo*-2,5-epithio-1,4-dithiane). In 1948, these studies were reproduced by Brintzinger and Ziegler who supposed bis(thioacetonyl) sulfide to be the product [18]. Bohme and Schneider reported soon that the product has in fact the structure of trithianorbornane [19]. At the same time, Hromatka and Engel [20] confirmed that the reaction of chloroacetone with hydrogen sulfide in a saturated alcoholic solution of hydrogen chloride yields 2,5-dimethyl-*endo*-2,5-epithio-1,4-dithiane (Scheme 2). Its structure was proved by X-ray analysis only in 1967 [21].

Scheme 2.



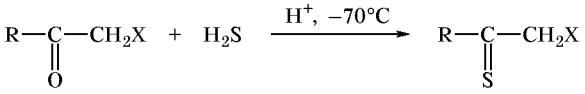
Although the above attempts to synthesize α-halo thioketones were unsuccessful, we hoped to obtain such compounds and examine their specific electronic structure and assumingly unique reactivity. The results of numerous preliminary experiments have justified our expectations, and the way to α-halo thioketones has been discovered.

II. SYNTHESIS OF α-HALO THIOKETONES

II.1. From Alkyl Halomethyl Ketones without a Solvent

While carrying out acid hydrothiolysis of chloroacetone in the absence of a solvent at –70°C, we succeeded for the first time in synthesizing chlorothioacetone; moreover, the product was obtained in quantitative yield [22]. Further on, following an analogous procedure, from the corresponding α-halo ketones we obtained α-bromo- and α-fluorothioacetones and also α-bromo- and α-fluoromethyl *tert*-butyl thioketones [23, 24] (Scheme 3).

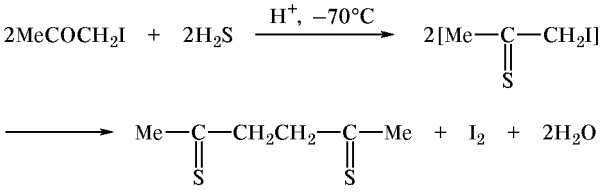
Scheme 3.



R = CH_3, $C(CH_3)_3$; X = F, Cl, Br.

An attempt to prepare in a similar way 1-iodo-2-propanethione from 1-iodo-2-propanone resulted in vigorous evolution of molecular iodine, and the product was 2,5-hexanedithione (Scheme 4) [25].

Scheme 4.

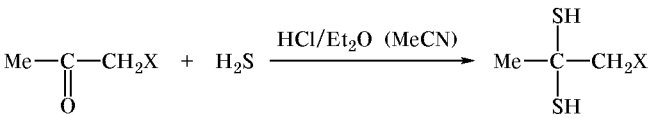


Obviously, unstable 1-iodo-2-propanethione is formed as intermediate. This reaction is a novel example of C–C bond formation.

II.2. From Haloacetones in Aprotic Solvents

Reactions of hydrogen sulfide with fluoro-, chloro-, and bromoacetones in a solution of hydrogen chloride in ether or acetonitrile at –70°C afforded the corresponding 1-halopropane-2,2-dithiols (yield 97%) instead of thioketones [26, 27].

Scheme 5.

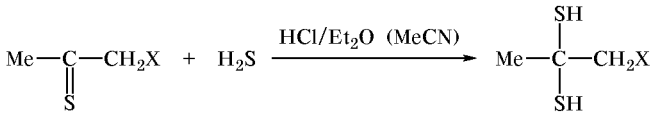


X = F, Cl, Br.

The corresponding halothioacetones are likely to be intermediates in the above transformation. In fact, halothioacetones are smoothly converted ino the cor-

responding geminal dithiols by the action of hydrogen sulfide in ether or acetonitrile at –50°C [24, 28] (Scheme 6).

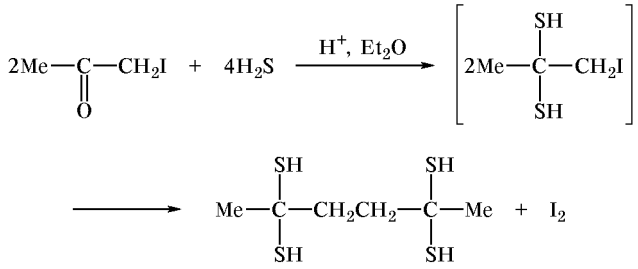
Scheme 6.



X = F, Cl, Br.

By contrast, hydrothiolysis of iodoacetone in the same solvents is accompanied by liberation of molecular iodine with formation of 2,2,5,5-hexanetetrathiol [25] (Scheme 7).

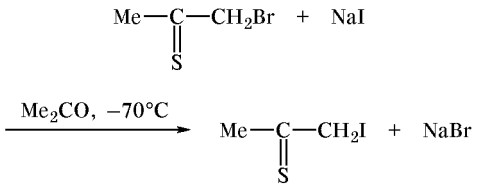
Scheme 7.



II.3. Halogen Exchange

However, we succeeded in synthesizing 1-iodo-2-propanethione by the action of NaI on bromothioacetone in Me_2CO at –70°C [29] (Scheme 8).

Scheme 8.

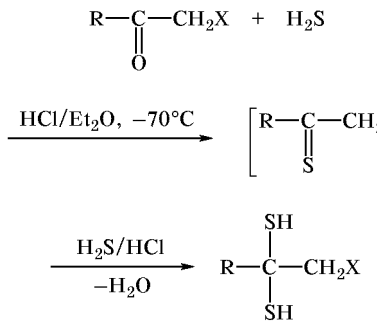


Analogous exchange reactions with chloro- and fluorothioacetones in acetone failed. Iodothioacetone is unstable: It gradually loses iodine even at –70°C, yielding 2,5-hexanedithione.

II.4. From Aryl and Heteryl Halomethyl Ketones

It was difficult to apply the conditions found for aliphatic analogs to the synthesis of aromatic and heteroaromatic α-halothioketones, for the initial ketones are solid substances. Treatment of α-haloacetophenones, 1-chloro-2-(1-naphthyl)ethan-2-one, and 2-acetyl-5-chlorothiophene with a mixture of hydrogen sulfide and hydrogen chloride in ether or acetonitrile at –50 to –70°C afforded the corresponding geminal dithiol in quantitative yield [26, 28] (Scheme 9).

Scheme 9.

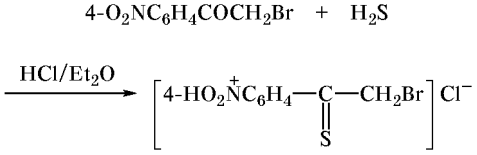


R = Ph, 4-MeC_6H_4, 5-chloro-2-thienyl, 1-naphthyl;
X = F, Cl, Br.

The isolation of geminal dithiols involves some difficulties while removing residual hydrogen chloride and hydrogen sulfide from the reaction mixture (after preliminary purging with nitrogen) by washing with water at 0 to 1°C; during this procedure, dithiols were converted into thioketones which underwent instantaneous trimerization in aqueous medium [30].

Intermediate formation of aromatic thioketones was inidicated by blue color of the reaction mixture, but our efforts to isolate them were unsuccessful. By contrast, the thionation of bromomethyl 4-nitrophenyl ketone in ether gave the corresponding thioketone hydrochloride [28] (Scheme 10).

Scheme 10.



The formation of that product is a rare example of hydrogen chloride coordination to a nitro group, which ensures a sufficient stability of the resulting thioketone.

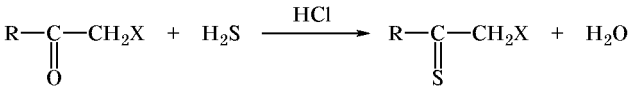
Thus, the results of acid-catalyzed hydrothiolysis of α-halo ketones depend on the solvent nature (if it is present), temperature, and isolation procedure. The product may be the corresponding thioketone, geminal dithiol, or trithianorbornane.

III. STRUCTURE AND REACTIVITY OF HALOMETHYL THIOKETONES

III.1. Mechanism of Reaction of Haloacetones with Hydrogen Sulfide

The most probable mechanism of formation of halothioacetones was established by studying the potential energy surface for the reaction of hydrogen sulfide with haloacetones in the presence of hydrogen chloride* (Scheme 11).

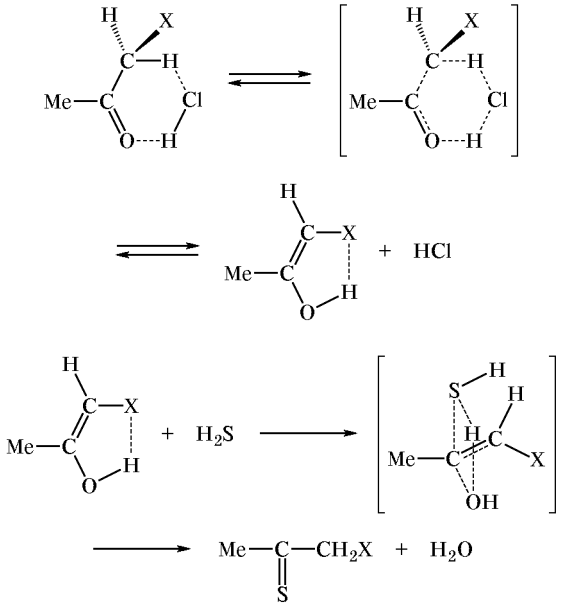
Scheme 11.



X = F, Cl, Br.

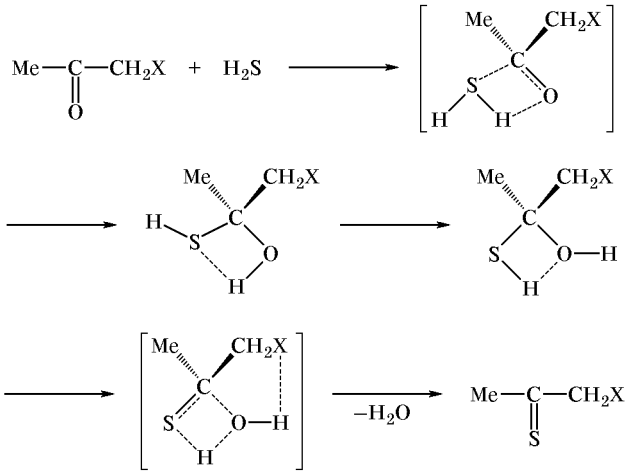
The first reaction stage is 1,3-prototropic rearrangement in haloacetone (enolization), where hydrogen chloride acts as mediator (Scheme 12). The result is that the activation barrier is considerably reduced, as compared to purely intramolecular 1,3-proton shift. For example, the energies of activation in the absence and in the presence of HCl are 183 and 93.9 kJ/mol, respectively (X = F). In the next stage, hydrogen sulfide reacts with the active enol form of haloacetone through a transition state shown below.

Scheme 12.



The energies of activation are 230.3, 232.5, 237.7, and 241.1 kJ/mol for X = F, Cl, Br, and I, respectively. The energy of dissociation of C–X bond for X = F, Cl, and Br is higher than the energy of activation for the reaction of hydrogen sulfide with the active enol form (459.8, 320.6, and 259.2 kJ/mol, respectively), while the energy of dissociation of C–I bond is lower (192.3 kJ/mol) [31]. Moreover, unlike fluoro-, chloro-, and bromoacetones, iodoacetone with HCl form associates in which the most favorable is coordination of hydrogen chloride to ionized iodine atom (intermolecular hydrogen bond). Therefore, the reaction of iodoacetone with hydrogen sulfide in the presence of HCl takes a pathway different from those typical of the other haloacetones [25]. The attack by hydrogen sulfide on haloacetone to give a four-membered transition state, followed by intramolecular autoprotonation and elimination of water (Scheme 13; an analogous mechanism was considered in [30]), is less favorable than the above path by 85–115 kJ/mol.

Scheme 13.

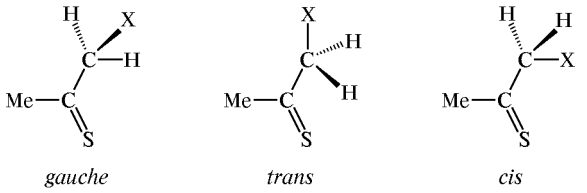


III.2. Conformations and Relative Stability of Halomethyl Thioketones

Thioketones in the gas phase give rise to three rotational conformers, *cis*, *trans*, and *gauche*, differing by mutual orientations of the heteroatoms. The activation barriers separating these states exceed 25 kJ/mol. Therefore, the conformers should be distinguishable by spectral methods provided that they exist in solution. An exception is fluorine-containing thioketone: the results of calculations performed for the gas phase predict only two rotamers, *cis* and *trans*.

The *gauche* conformer is the most stable. In keeping with the calculated dipole moments, its polarity increases as the atom number of the halogen rises

* For the sake of uniformity, given are the results of B3LYP quantum-chemical calculations with the LANL2DZ basis set.

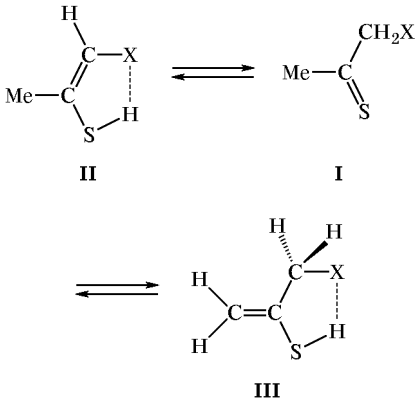


X = F, Cl, Br, I.

(μ = 0.7, 1.8, 2.3, and 2.6 D for X = F, Cl, Br, and I, respectively. The maximal orthogonality, or the angle characterizing deviation of the X heteroatom from the molecular plane, is observed for X = I (φ = 76°); this means that the interaction between lone electron pair of the iodine atom and π-orbital of the C=S bond is the strongest, as compared to the other halogens. The most planar structure (φ = 0) is typical of X = F. The *trans* confomers are second in stability; they are the least polar due to opposite orientation of the heteroatom dipoles. The difference in the relative stabilities of the respective *gauche* and *trans* conformers increases in the series F < Cl < Br < I (0, 10.3, 14.6, and 20.4 kJ/mol, respectively). Here, the order of variation of the polarity does not change (I > Br > Cl ≈ F), while the differences in this series considerably decrease (to 0.7–1.0 D). The *cis* conformers are the least stable (except for X = I) due to enhanced negative dipole–dipole interactions; the relative stabilities are 15.2, 16.0, 18.2, and 20.3 kJ/mol for X = F, Cl, Br, and I. The polarity of the *cis* conformers sharply increases, and the order of variation of their dipole moments is the reverse. The most polar is fluorothioacetone (μ = 4.49 D), and iodothioacetone is the least polar (μ = 3.72 D). The significant difference in the polarity of *gauche* and *trans* conformers, on the one hand, and *cis* structures, on the other, indicates that the latter could be stabilized in strongly polar solvents.

III.3. Intramolecular 1,3-Prototropic Rearrangements

Halothioacetones can exist as three prototropic tautomers whose stability decreases in the series **I** > **II** > **III**, regardless of the halogen nature. The transformation of **I** into **III** involves 1,3-prototropic shift as rate-determining stage (energy of activation 160–195 kJ/mol) with subsequent low-barrier (energy of activation 40–60 kJ/mol) rotational transition to a structure stabilized by formation of five-membered pseudochelate ring. Likewise, the rearrangement **I** → **II** includes 1,3-prototropic shift with an energy of activation of 145–170 kJ/mol, followed by low-barrier formation of pseudochelate heterocyclic structure which is additionally stabilized by the presence of an allyl fragment.



X = F, Cl, Br, I.

IV. PHYSICAL PROPERTIES OF α-HALOTHIOKETONES

Alkyl halomethyl thioketones $RC(=S)CH_2X$ are crimson–red unstable oils with a very unpleasant odor. They are soluble in common organic solvents. Alkyl halomethyl thioketones can be stored for a long time at –50 to –70°C. The ^1H NMR spectra of solutions of some alkyl halomethyl thioketones in $CDCl_3$ at –50°C are given in table.

V. CHEMICAL PROPERTIES OF α-HALO THIOKETONES

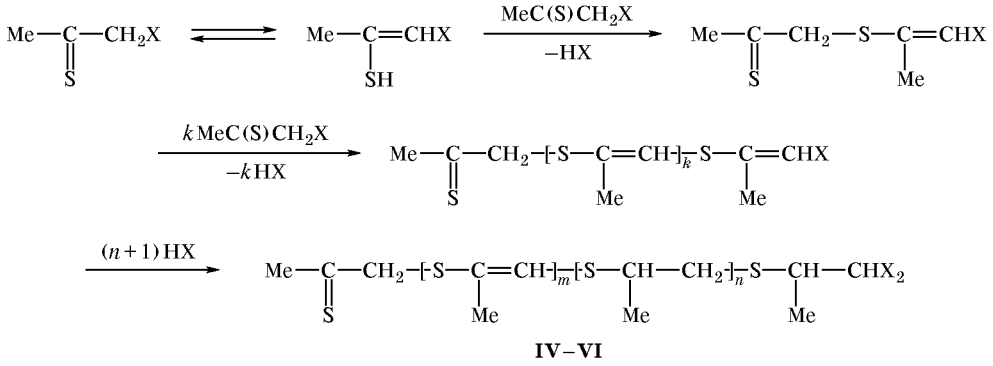
V.1. Homopolycondensation

α-Halothioacetones $MeC(=S)CH_2X$ at 20°C undergo spontaneous polymerization to give black linear polymers with a molecular weight of 1200 (X = I), 1400 (X = Br), or 1800 (X = Cl) [32]. Their structure was established by IR, UV, and ESR spectroscopy and polarography. The molecular weights

^1H NMR spectra (δ, ppm) of alkyl halomethyl thioketones $RC(=S)CH_2X$ in $CDCl_3$

R	X	CH_3	CH_2	References
Me	Br	2.01	3.88	[22]
Me	Cl	1.82	3.89	[22]
Me	F	2.37	4.89	[23]
Me	I	2.44	5.11	[29]
t-Bu	Br	1.22	4.19	[24]
t-Bu	F	1.65	5.08	[24]
4-$NO_2C_6H_4$	Br		4.67	[28]

Scheme 14.



IV–VI

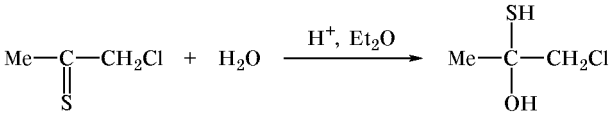
IV, X = Cl, *m* = 17, *n* = 4; **V**, X = Br, *m* = 14, *n* = 0; **VI**, X = I, *m* = 11, *n* = 0.

were determined by the isopiestic method, and their electric and photo conductivities were examined. Scheme 14 illustrates the way of formation of these polymers (structures **IV**–**VI**). Polymers **IV**–**VI** give rise to high-quality films on various supports (such as quartz, glass, or aluminum), which possess electric and photoconductivity. Such polymers can be used in the development of active materials for electrophotographic layers and solar energy transducers.

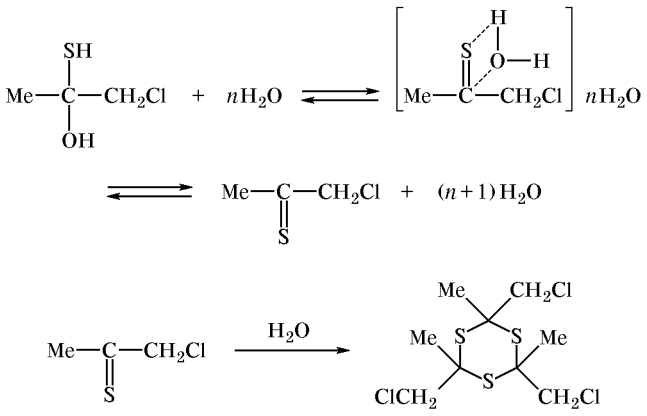
V.2. Reaction with Water

The reaction of 1-chloro-2-propanethione with an aqueous solution of hydrogen chloride at 0°C in diethyl ether gave 1-chloro-2-sulfanyl-2-propanol in quantitative yield [30] (Scheme 15).

Scheme 15.



Scheme 16.



The product is a new representative of organic compounds having geminal hydroxy and sulfanyl groups. This moiety exhibits unusual chemical properties. For example, treatment of 1-chloro-2-sulfanyl-2-propanol with water leads to dehydration with formation of chlorothioacetone which then undergoes trimerization (Scheme 16).

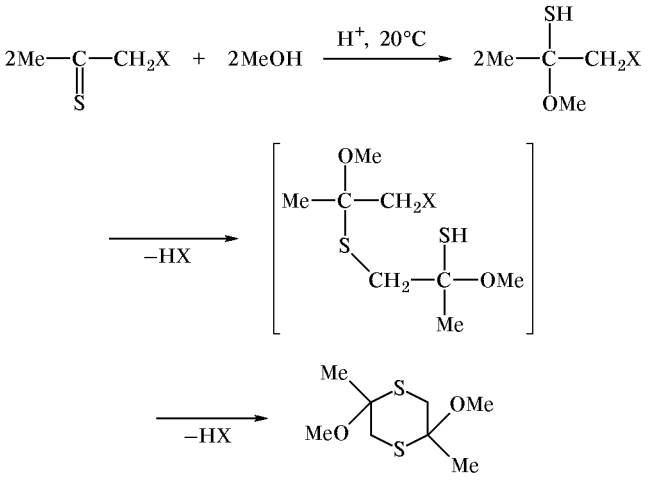
The preference of dehydration rather than hydrogen sulfide elimination in the >C(OH)SH moiety in aqueous medium was confirmed by quantum-chemical simulation [30]. Regardless of the calculation method, gas-phase decomposition of 1-chloro-2-sulfanyl-2-propanol with elimination of hydrogen sulfide was found to be more favorable than with elimination of water. The only mechanism implying preferential dehydration is 1,3-intramolecular prototropic rearrangement (autoprotonation) with subsequent elimination of water. However, the system under study does not conform to the main qualitative factors determining the height of the energy barrier; these factors are nearly optimal linear configuration of the three-center pseudohydrogen-bonded S–H···O bridge, relation between the acidity of the S–H bond and the basicity of the OH center, and quasiaromaticity of the H-chelate ring. Therefore, proton transfer and the subsequent dissociation require a high activation barrier to be overcome. Presumably, the conditions for dehydration of the hydroxy thiol are determined by the presence of a solvate (hydrate) shell which ensures preferential elimination of water rather than hydrogen sulfide or hydrogen chloride. According to the calculations, intermolecular cooperative 1,3-proton transfer is considerably facilitated in an associate formed by the geminal hydroxy thiol and two water molecules. The activation barrier is almost twice as low as that found for the isolated molecule. Thus, in the reaction under study, tautomerism promoted by

water molecules formally leads to internal autoprotonation which is responsible for the predominant dehydration process.

V.3. Alcoholysis

α-Halo thioketones turned out to be new promising initial compounds for the synthesis of 2,5-substituted 1,4-dithianes. They rapidly react with methanol at 20°C in the presence of hydrogen chloride, yielding *trans*-2,5-dimethoxy-2,5-dimethyl-1,4-dithiane [33]. The reaction begins with addition of methanol at the thiocarbonyl group and is completed by intermolecular condensation with liberation of hydrogen chloride (Scheme 17). The structure of the product was established by X-ray analysis, as well as by NMR and IR spectroscopy.

Scheme 17.



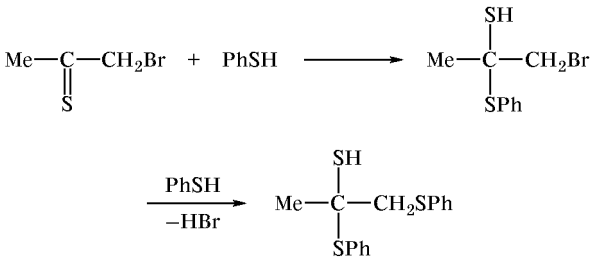
X = Br, Cl.

Unlike methanol, higher alcohols (such as ethanol, 2-propanol, and 1-butanol) react with α-halo thioketones very slowly.

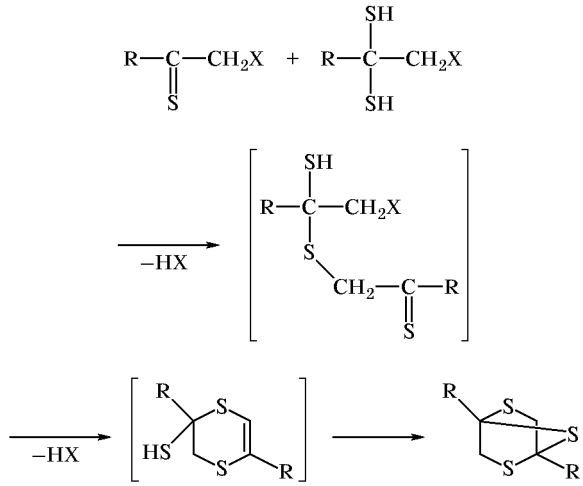
V.4. Reactions with Thiols

The reaction of α-halo thioketones with thiols was studied in detail using bromothioacetone and benzenethiol as reactants. In the first stage, benzenethiol adds at the thiocarbonyl group to give 1-bromo-2-phenylsulfanyl-2-propanethiol. In the presence of excess benzenethiol, the bromine atom is replaced by phenylsulfanyl group, affording 1,2-bis(phenylsulfanyl)-2-propanethiol (Scheme 18). α-Halo thioketones readily react with isostructural α-halogenated geminal dithiols, finally leading to the corresponding 2,5,7-trithianorbornanes [24, 33] (Scheme 19). This reaction can be regarded as a new general and convenient method for the synthesis of 2,5,7-trithianorbornane derivatives.

Scheme 18.



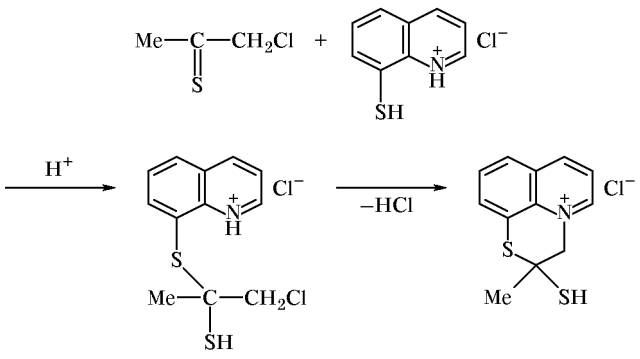
Scheme 19.



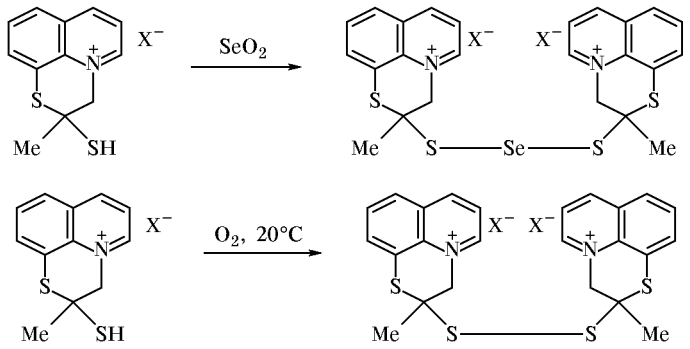
R = Me, *t*-Bu; X = F, Cl.

Chloro- or bromothioacetone reacts with 8-sulfanylquinoline hydrohalide in methanol or dimethylformamide, yielding 8-(1-chloromethyl-1-sulfanylethylsulfanyl)quinolinium salt. The subsequent intramolecular alkylation at the nitrogen atom gives

Scheme 20.



Scheme 21.



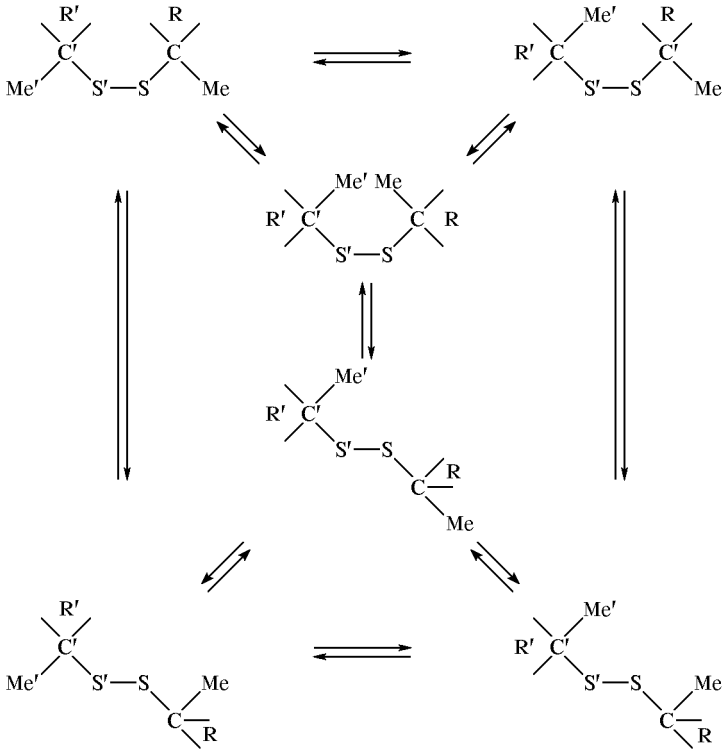
X = Br, Cl, ClO_4.

2-methyl-2-sulfanyl-2,3-dihydro[1,4]thiazino[2,3,4-*ij*]-quinolin-4-ium halide [34] (Scheme 20). We succeeded in isolating the intermediate product in 33% yield. Thiazinoquinolinium salts are readily oxidized with selenium dioxide and even with atmospheric oxygen (Scheme 21). The reaction with SeO_2 was effected at 20°C in methanol, and the corresponding selenides were obtained in quantitative yield. The oxidation with atmospheric oxygen afforded 2,2′-dithiobis-(2-methyl-2,3-dihydro[1,4]thiazino[2,3,4-*ij*]quinolin-4-ium) salts. The molecular structure of the product with X = Cl was established by X-ray analysis [35]. Unlike X-ray diffraction data, the ^1H and ^{13}C NMR spectra of the same compound in $CDCl_3$ showed the presence of several spectroscopically distinguishable conformers. The results of quantum-chemical calculations also predict the existence of at least six stable conformations [36] (Scheme 22).

V.5. Reaction with Diazomethane

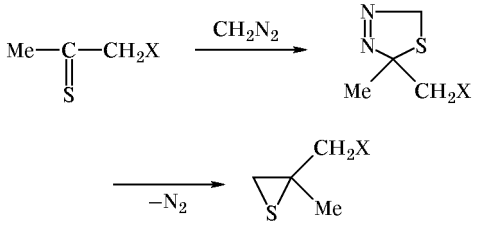
Halothioacetones readily react with diazomethane [22]. The reaction direction depends on the halogen nature. Treatment of bromothioacetone with diazo-

Scheme 22.



methane leads to 2-bromomethyl-2-methyl-2,5-dihydro-1,3,4-thiadiazole. On storage, this product is converted into 2-bromomethyl-2-methylthiirane. The reaction of chloroacetone with diazomethane directly yields 2-chloromethyl-2-methylthiirane (Scheme 23). Probably, the corresponding 1,3,4-thiadiazole is also formed as intermediate, but we failed to isolate it.

Scheme 23.



X = Br, Cl.

VI. CONCLUSION

Our systematic studies allowed us to develop a simple and efficient method for the synthesis of previously unknown halomethyl thioketones. The products can be obtained in high yields. The mechanism of formation and electronic structure of these compounds were studied by quantum-chemical methods. The reactivity and synthetic potential of halomethyl thioketones were examined, specifically, they were brought into hydrolysis [30], alcoholysis [33], thiolysis [24, 33], thiylation [24, 28], and methylation [22].

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