

Soft-ionization mass spectrometric observation of isomeric effects occurring in the synthesis of bis-sulfonium salts from thiacyclanes/xylylene dibromides and collision induced dissociation of bis-sulfonium cations

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ABSTRACT

Micro-synthesis of bis-sulfonium salts from *ortho*-, *meta*- and *para*-xylylene dibromides and mono- and bicyclic sulfides was performed for their further investigation by tandem electrospray/ionization mass spectrometry (ESI-MS) with the use of collision-induced dissociation (CID). Reaction products were detected by ESI-MS (without chromatographic separation), combined high-performance liquid chromatography/ESI-MS and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). It was shown that only the reaction of *ortho*- and *para*-xylylene dibromides with cyclic sulfides gave rise to corresponding bis-sulfonium salts yielding products of elimination of protonated sulfide from doubly charged ions during ESI and MALDI ionization. Fragmentation pathways of bis-sulfonium even-electron dications generated in ESI conditions were examined for the first time. The mass spectra revealed peaks for only single charged fragments included thiacyclane hydrocarbon residues, benzene- and sulfur-containing ions. Drastic quantitative and qualitative differences between *ortho*- and *meta*(*para*)-isomers allowing their easy differentiation were observed and explained. They were manifested in the character of eliminated thiacyclane residue and in the peak intensity ratios of m/z 104 and 91 benzene-containing ions. Isomeric di-cations with regio-isomeric structures of monocyclic sulfides demonstrated strong differences in CID spectra.

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1. Introduction

The last three decades have been marked by the extensive use of “soft” ionization mass spectrometry (MS) methods for solving various analytical tasks. Among them, the methods of atmospheric pressure ionization [mainly electrospray/ionization (ESI)] and desorption/ionization [mainly matrix-assisted laser desorption/ionization (MALDI)] are particularly widely distributed and popular. They are distinguished by their ability to analyze semi-volatile, non-volatile, highly polar salt-like and other thermally unstable compounds. ESI-MS method is particularly efficient in combination with liquid chromatography [most frequently, high-performance liquid chromatography (HPLC)] and ESI-MS and MALDI-MS allow the analysis of high molecular-weight compounds with formally unlimited molecular masses [1]. Nevertheless, both

these MS methods are also widely applied to the investigation of small molecules [2,3].

It should be underlined that the main ionization processes of ESI and MALDI are due to protonation (cationization) or deprotonation that typically produce closed-shell ions permitting easy determination of molecular weights. However, ordinary ESI and MALDI mass spectra provide practically no structural information. Without additional techniques, both methods are not acceptable to the analysis of non-polar or low polarity molecules owing to low ionization efficiency or its absence at all [4]. Analysis of low-molecular-weight compounds by MALDI-MS meets another problem: one should avoid the evaporation of a sample during its introduction into the high-vacuum ionization region of a mass spectrometer.

To overcome many of the mentioned problems, preliminary chemical modification (derivatization) of analytes is frequently employed. Among such approaches, fixed-charge derivatization is particularly efficient in ESI-MS and MALDI-MS because prepared derivatives are salt-like products of low volatility and contain ready ion that can be easily desorbed or extracted and provides high

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ionization efficiency [4,5]. Such ions can be subjected to collision-induced dissociation (CID) with registration of MS/MS or higher order MSⁿ spectra to get structural information.

Recently we began the ESI and MALDI mass spectrometric study of low-polarity organic sulfides that are widespread in living organisms, oils, synthetic products. In these studies, organic cyclic sulfides (thiacyclanes) were preliminary converted into non-volatile sulfonium salts under action of various alkyl- or aralkyl halides [6]. CID mass spectra of corresponding sulfonium cations appeared to be very structurally informative and displayed drastic differences between regio-isomers [7]. It should be noted that the same derivatization methodology was recently applied to the investigation of petroleum benzthiophenes [8] and methionine-containing peptides [9].

Our further interests were directed toward the micro-preparation of bis-sulfonium salts on the basis of thiacyclanes and dihalides and the study of CID of the corresponding dicationic species generated under ESI conditions. We assumed that CID mass spectra of isomeric bis-sulfonium cations would show pronounced differences. This assumption was based on the known fact that multiply, and particularly, doubly charged species decompose easier than singly charged ions owing to Coulomb repulsion and CID spectra can be useful for differentiation of isomers [10]. In the literature, one can find a number of papers devoted to CID mass spectra of multiply charged poly-cations. The greatest attention is paid to multiply charged poly-protonated peptides and proteins, generated under ESI conditions, in terms of determining the structural features of biopolymers (see, for example, one of the earliest papers [11]). A number of papers were devoted to ESI mass spectrometric features of bisquaternary ammonium dicationic species of various origin (see, for example, [12–14]). However, there are practically no publications describing the fragmentation of similar bis-sulfonium dicationic species as well as bis-phosphonium dicationic species. Therefore, the main aim of the present work was to elucidate the features of decomposition of bis-sulfonium dicationic species generated under ESI conditions and the influence of thiacyclane and dihalide regio-isomerism on tandem mass spectra. For preparation of bis-sulfonium salts, we used various isomeric alkyl-substituted mono- and bicyclic sulfides and *ortho*-, *meta*- and *para*-xylylene dibromides (Fig. 1).

These xylylene dibromides are interesting in that they are the basis for the preparation of bis-sulfonium salts being very suitable precursors for the synthesis of poly(arylene vinylene)s – polymeric materials having unique electronic and optic properties. In all cases *para*-xylylene dihalides and related compounds were used for alkylation of various organic sulfides. The resulting bis-sulfonium salts underwent reversible reaction accompanied by elimination of protonated sulfide and reaction mixtures contained *para*-quinodimethane intermediates that are capable of polymerization to polyelectrolytes and abovementioned polymers [15,16]. It is to be noted that one of the earlier papers [17] presented preliminary data that *ortho*-xylylene dihalides can yield *ortho*-quinodimethane precursors in addition to bis-sulfonium salts as well. In this regard and in addition to mass spectrometric investigation of isomeric bis-sulfonium salts, we decided to apply ESI-MS, MALDI-MS and high-performance liquid chromatography-mass spectrometry (HPLC-MS) to the analysis of reaction mixtures.

2. Experimental

2.1. Starting compounds and reagents

Initial 2- and 4-methylthianes, isomeric 2- and 3-thiabicyclo[4.4.0]decanes, 7- and 8-thiabicyclo[4.3.0]nonanes, their methyl- and *n*-propyl-substituted analogs were synthesized and characterized earlier [6,18]. The purity of samples (according to the GC/MS data) was at least 90%. 1,2- and 1,3-Di(bromomethyl)-

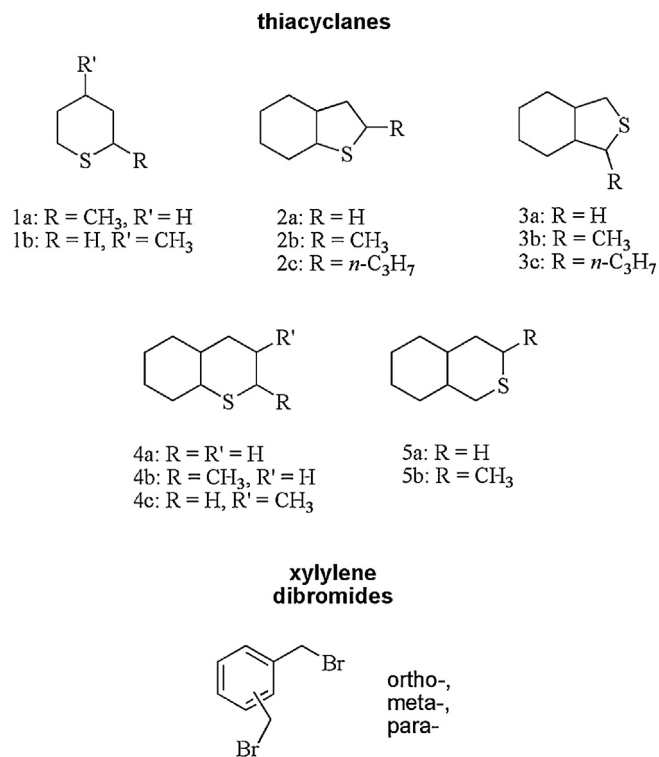


Fig. 1. Structures of cyclic sulfides and xylylene dibromides used for the synthesis of bis-sulfonium salts.

benzenes were purchased from Alfa Aesar (Lancashire, Great Britain) and 1,4-di(bromomethyl)-benzene – from Fluorochem (Derbyshire, Great Britain). The solvents (acetonitrile and tetrahydrofuran) as well as sodium perchlorate were of chemically pure grade and purchased from Khimmed (Russia). The matrix in MALDI experiments was 2,5-dihydroxyacetophenone purchased from Aldrich Chemical Co. (Belgium).

2.2. Micro-preparation of bis-sulfonium salts

A mixture of a cyclic sulfide (0.04 mmol), α,α' -xylylene dibromide (0.04 mmol), and sodium perchlorate (minimum amount) was vigorously stirred in acetonitrile (minimum amount) on a shaker for 24 h at 70 °C. Reaction mixture was further investigated by mass spectrometry without additional purification and fractionation.

For recording MALDI mass spectra, the resulting reaction mixture was stirred with a solution of the matrix (2,5-dihydroxyacetophenone) in tetrahydrofuran, applied onto a steel target, and dried.

2.3. Instruments and equipment

MALDI mass spectra were recorded on a Bruker autoflex speed mass spectrometer (Bruker Daltonics Inc., Germany) equipped with a solid-state UV laser ($\lambda = 355$ nm) and a reflectron in the positive ion detection mode. An MTP 384 ground steel target was used for MALDI experiments.

ESI mass spectra and tandem ESI mass spectra were recorded on a Shimadzu LCMS-8040 triple-quad mass spectrometer. A solution of a reaction mixture in dry acetonitrile was directly injected bypassing a liquid chromatographic column. In addition, reaction mixture was introduced into the mass spectrometer via liquid chromatography column with reversed phase Chromolith HighResolution RP-18 (50 mm \times 4.6 mm, micropore size 2 μ m, mesopore size 130 Å) from MilliporeSigma, Germany). Mixture of acetonitrile

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