



α -Thio Carbocations (Thionium Ions) as Intermediates in Brønsted Acid-Catalyzed Reactions of Enone-Derived 1,3-Dithianes and 1,3-Dithiolanes

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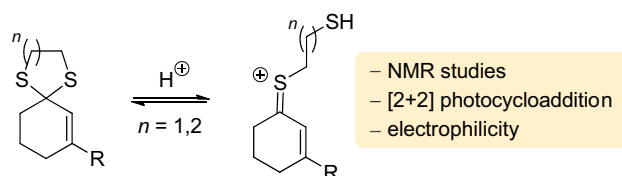
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Abstract

Evidence was collected for the intermediate formation of thionium ions in Brønsted acid-catalyzed [2 + 2] photocycloaddition and electrophilic addition reactions to enone dithianes and dithiolanes. Low-temperature NMR studies helped to elucidate the structure and configuration of the thionium ions and thus support previous and current results obtained by UV/Vis spectroscopy.

Graphical Abstract



Keywords Acid catalysis · Carbocations · Cyclisation · Dithianes · Photocycloaddition · Sulfonium ions

1 Introduction

The protonation of thiols and thioethers (sulfides) leads to primary and secondary sulfonium ions [1]. Pioneering NMR studies in super acid solution were performed by Olah et al. as early as 1967 [2]. The protonation of 1,3-dithiane was studied by Lambert et al. and a monoprotonated species was detected by ¹H-NMR and ¹³C-NMR spectroscopy [3]. A second species was identified to which the authors assigned an open chain form with a cationic sulfur atom [4]. A related

intermediate called a “carbonium–sulfonium ion” had earlier been observed upon protonation of 1,3-oxathiolane [5, 6]. Similar α -sulfur-substituted carbocations (α -thio carbocations, thionium ions) were invoked in the hydrolysis of *S,O*-acetals [7] and 2-substituted 1,3-dithianes [8]. We became interested in this chemistry when searching for UV/Vis transparent compounds which could be converted by Brønsted acid catalysis into potential chromophores. Based on previous work [9–12] it was conceived that 1,3-dithianes such as **1**, which showed no UV/Vis absorption above $\lambda > 250$ nm, would form colored thionium ions which could be photochemically excited at long wavelength. Indeed, the concept turned out to be valid and reactions such as **1** \rightarrow **2** (Fig. 1) could be promoted with visible light ($\lambda = 398$ nm) upon catalysis with strong Brønsted acids, such as HOTf or Tf₂NH (Tf = trifluoromethanesulfonyl) [13].

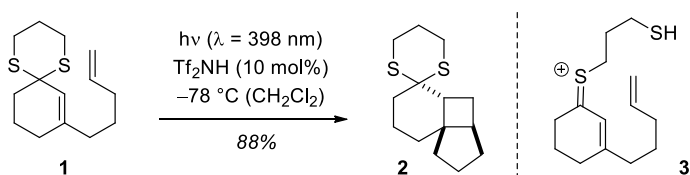
The existence of intermediate **3** was supported by its absorption spectrum but was not further substantiated. Its relative configuration has not yet been elucidated. In this paper, we disclose our results on the reaction of a

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Fig. 1 Previously reported Brønsted acid-catalyzed [2+2] photocycloaddition of 1,3-dithiane to product **2** and structure of the putative intermediate **3**



1,3-dithiolane related to **1** and on UV/Vis experiments with 1,3-dithiolanes and 1,3-dithianes in the presence of Tf_2NH . NMR spectroscopic evidence for the formation of cation **3** is provided and it was shown that conjugated thionium ions can also undergo a Michael-type addition reaction with a suitable intramolecular nucleophile.

2 Experimental

2.1 General Methods

All moisture and air sensitive reactions were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk techniques. Commercially available chemicals were used without further purification. For moisture sensitive reactions tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purified using a MBSPS 800 MBraun solvent purification system. Dichloromethane for photochemical reactions and Brønsted acid-catalyzed cyclization reactions was additionally dried over activated molecular sieves (4 Å). Dry methanol was obtained from Acros Organics. For NMR studies, Deutero dichloromethane- d_2 (99.6 at. % D) was employed, which was dried by filtration through a pad of activated basic aluminium oxide under argon atmosphere and was stored over molecular sieves (4 Å).

Photochemical experiments at $\lambda = 366 \text{ nm}$ were carried out in Duran tubes ($\varnothing = 1.0 \text{ cm}$) in an RPR-100 photochemical reactor (Southern New England Ultra Violet Company, Branford, CT, USA) equipped with 16 fluorescence lamps (Philips Lighting, Black Light Blue, 8 W, $\lambda = 366 \text{ nm}$). For low temperature irradiation, the reaction vessel was placed in the photoreactor for 20 min prior to irradiation. Flash column chromatography was performed on silica 60 (Merck, 230–400 mesh) with the indicated eluent mixture. All solvents for chromatography were distilled prior to use. TLC was performed on silica coated glass plates (Merck, silica 60 F254) with detection by UV-light ($\lambda = 254 \text{ nm}$) and/or by staining with a potassium permanganate solution [KMnO_4] followed by heat treatment.

2.2 Analytical Methods

NMR spectra were recorded at room temperature either on a Bruker AVHD-300, AVHD-400, AVHD-500 or an AV-500 cryo. For low temperature measurements ($-70 \text{ }^\circ\text{C}$)

a Bruker DRX400 was used. ^1H -NMR spectra were referenced to the residual solvent signal of chloroform- d_1 (CHCl_3 , $\delta = 7.26 \text{ ppm}$), benzene- d_6 (C_6HD_5 , $\delta = 7.16 \text{ ppm}$) or dichloromethane- d_2 (CH_2Cl_2 , $\delta = 5.32 \text{ ppm}$). ^{13}C -NMR spectra were referenced to the ^{13}C -D triplet of CDCl_3 ($\delta = 77.2 \text{ ppm}$) and C_6D_6 ($\delta = 128.1 \text{ ppm}$), or to the ^{13}C -D₂ quintet of CD_2Cl_2 ($\delta = 54.0 \text{ ppm}$). Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). The following abbreviations for individual multiplicities were used: *br*-broad, *s*-singlet, *d*-doublet, *t*-triplet, *q*-quartet, *quint.*-quintet. Assignments and the multiplicity of the ^{13}C -NMR signals were determined by two-dimensional NMR experiments (COSY, HSQC, HMBC, NOESY). Infrared spectra were recorded by the attenuated total reflection (ATR) technique using a JASCO IR-4100 spectrometer or a Perkin Elmer Frontier IR-FTR spectrometer. The signal intensities are assigned using the following abbreviations: *s* (strong), *m* (medium), *w* (weak). IR signals are reported as wave numbers $\tilde{\nu}$ (cm^{-1}). Mass spectra were carried out on a Agilent MS5977A MSD spectrometer coupled to a Agilent 7890 B gas chromatograph using a HP-5MS UI column (30 m, 0.25 mm, 0.25 μm , 5% diphenyl–95% dimethylpolysiloxane). HRMS data were determined at a Thermo Scientific DFS-HRMS spectrometer. UV/Vis Spectroscopy was performed on a Perkin Elmer Lambda 35 UV/Vis spectrometer. Spectra were recorded using a Hellma precision cell made of quartz SUPRASIL® with a pathway of 1 mm in dry CH_2Cl_2 . Concentrations are given for each spectrum.

2.3 Synthetic Protocols

Octahydro-6H-spiro[cyclopenta[1,4]cyclobuta[1,2]-benzene-5,2'-[1,3]dithiolane] (**5**): 7-(Pent-4-en-1-yl)-1,4-dithiaspiro[4.5]dec-6-ene (**4**, 23.4 mg, 97.3 μmol , 1.00 equiv) was dissolved in 9.7 mL CH_2Cl_2 ($c = 10 \text{ mM}$) in a Duran tube and the solution was cooled to $-40 \text{ }^\circ\text{C}$. After addition of Tf_2NH (5.71 mg 19.6 μmol , 0.20 equiv), the solution was irradiated at $\lambda = 366 \text{ nm}$ (128 W) for 13.5 h. Irradiation was stopped and NEt_3 (13.5 μL , 97.3 mmol, 1.00 equiv) was added. The solution was warmed to room temperature and solvent was removed in vacuo. After column chromatography (SiO_2 , $\text{P/Et}_2\text{O} = 99/1$), the title compound was obtained as a colourless oil (18.0 mg, 74.8 μmol , 77%). TLC: $R_f = 0.32$ ($\text{P/Et}_2\text{O} = 99/1$) [KMnO_4]; IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2925 ($\text{sp}^3\text{-CH}$), 2848 (*m*, $\text{sp}^3\text{-CH}$),

1448 (w, $\text{sp}^3\text{-CH}$), 635 (w, CSC); MS (EI, 70 eV): m/z (%) = 240 (88) $[\text{M}]^+$, 212 (99) $[\text{M}-\text{C}_2\text{H}_4]^+$, 179 (100) $[\text{C}_{11}\text{H}_{15}\text{S}]^+$, 171 (31), 131 (74) $[\text{C}_5\text{H}_7\text{S}_2]$, 91 (41), 79 (34); $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 298 K): δ (ppm) = 1.19 (*virt. td*, $^2J \cong ^3J = 12.3$ Hz, $^3J = 6.9$ Hz, 1H, H-1), 1.37–1.43 (m, 1H, H-8), 1.48–1.53 (m, 1H, H-3), 1.55–1.62 (m, 2H, H-3, H-4), 1.65 (*virt. td*, $^2J \cong ^3J = 13.0$ Hz, $^3J = 6.6$ Hz, 1H, H-1), 1.72–1.81 (m, 2H, H-2, H-7), 1.82–1.92 (m, 3H, H-2, H-7, H-8), 1.97 (ddd, $^2J = 12.9$ Hz, $^3J = 9.5$ Hz, $^3J = 7.5$ Hz, 1H, H-4), 2.08–2.14 (m, 1H, H-6), 2.21 (*virt. tt*, $^2J \cong ^3J = 9.0$ Hz, $^3J \cong 4.9$ Hz, 1H, H-3a), 2.33–2.41 (m, 2H, H-4a, H-6), 3.16–3.36 (m, 4H, $\text{SCH}_2\text{CH}_2\text{S}$); $^{13}\text{C-NMR}$ (126 MHz, CDCl_3 , 300 K): δ (ppm) = 20.5 (t, C-7), 25.6 (t, C-2), 27.8 (t, C-4), 29.3 (t, C-8), 32.6 (t, C-3), 34.6 (t, C-6), 38.0 (d, C-3a), 38.1 (t, $\text{SCH}_2\text{CH}_2\text{S}$), 39.8 (t, $\text{SCH}_2\text{CH}_2\text{S}$), 40.8 (t, C-1), 48.7 (d, C-4a), 49.3 (s, C8a), 70.3 (s, C-5); HRMS (EI, 70 eV): calculated: $(\text{C}_{13}\text{H}_{20}\text{S}_2)$: 240.1001; found: 240.1000.

10-Methyl-1,5-dithiadispiro[5.1.5⁸.3⁶]hexadec-10-ene (**12**): 8-(4-Methylpent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**11**, 23.0 mg, 85.7 μmol , 1.00 equiv) was dissolved in dry CH_2Cl_2 (8.6 mL) and the resulting mixture was cooled to -78 °C. Following the addition of 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**13**, 1.88 mg 6.43 μmol , 0.10 equiv) the solution was stirred for 5.5 h at -78 °C in the dark. After which the reaction was quenched via the addition of NEt_3 (11.9 μL , 84.7 μmol , 1.00 equiv). The solution was allowed to warm to room temperature and the solvent was removed in vacuo. After column chromatography (SiO_2 , $\text{P/Et}_2\text{O} = 99.5/0.5 \rightarrow 99/1$), the title compound was obtained as a colourless oil (20.1 mg, 73.7 μmol , 87%). TLC: $R_f = 0.35$ ($\text{P/Et}_2\text{O} = 98/2$) [KMnO_4]; IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2926 (s, $\text{sp}^3\text{-CH}$), 1444 (m, $\text{sp}^3\text{-CH}$), 1275 (w), 795 (w, $\text{sp}^3\text{-CH}$); MS (EI, 70 eV): m/z (%) = 268 (100) $[\text{M}]^+$, 200 (52) $[\text{M}-\text{C}_5\text{H}_8]^+$, 159 (60), 118 (62), 105 (58), 91 (32); $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 298 K): δ (ppm) = 1.28 (ddd, $^2J = 13.1$ Hz, $^3J = 9.3$ Hz, $^3J = 3.7$ Hz, 1H, H-14), 1.36–1.46 (m, 2H, H-13, H14), 1.53–1.58 (m, 1H, H-13), 1.62 (*br s*, 3H, CH_3), 1.60–1.73 (m, 2H, H-15, H-15), 1.78 (d, $^2J = 14.4$ Hz, 1H, H-9), 1.82–1.95 (m, 3H, H-3, H-9, H-12), 1.96–2.09 (m, 5H, H-3, H-7, H-7, H-12, H-16), 2.17 (ddd, $^2J = 13.0$ Hz, $^3J = 6.9$ Hz, $^3J = 3.3$ Hz, 1H, H-16), 2.68–2.79 (m, 2H, H-2, H-4), 2.89–2.99 (m, 2H, H-2, H-4), 5.32 (*virt. tq*, $^3J \cong 3.2$ Hz, $^4J = 1.6$ Hz, 1H, H-11); $^{13}\text{C-NMR}$ (126 MHz, CDCl_3 , 300 K): δ (ppm) = 19.1 (t, C-15), 22.7 (t, C-7), 24.2 (q, CH_3), 25.8 (t, C-3), 26.7 (t, C-2), 26.8 (t, C-4), 33.6 (s, C-8), 35.1 (t, C-13), 36.9 (t, C-14), 38.6 (t, C-16), 42.9 (t, C-12), 47.3 (t, C-9), 49.9 (s, C-6), 119.7 (d, C-11), 132.5 (s, C-10); HRMS (EI, 70 eV): calculated: $(\text{C}_{15}\text{H}_{24}^{32}\text{S}_2)$: 268.1314; found: 268.1309, calculated: $(\text{C}_{14}^{13}\text{CH}_{24}^{32}\text{S}_2)$: 269.1348; found: 269.1343.

2.4 Low-Temperature NMR Studies

Under an argon atmosphere Tf_2NH (43.9 mg, 156 μmol , 6.25 equiv) was filled into an NMR tube in a glovebox and was cooled to -78 °C outside the glovebox. Under argon atmosphere, the acid was dissolved in 0.7 mL dry CD_2Cl_2 and 8-methyl-1,5-dithiaspiro[5.5]undec-7-ene (**9**, 5.00 mg, 25.0 μmol , 1.00 equiv) was added. After mixing, the orange-yellow solution was warmed to 203 K (-70 °C) in a Bruker DRX400 spectrometer and spectra were recorded at 203 K. For $^{13}\text{C-NMR}$ and 2D experiments dithiane **9** (20.0 mg, 100 μmol , 1.00 equiv) and Tf_2NH (175 mg, 624 μmol , 6.25 equiv) were dissolved in 0.6 mL dry CD_2Cl_2 .

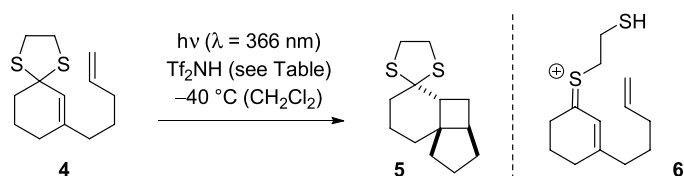
3 Results and Discussion

3.1 Photochemistry

Attempts to induce an intramolecular [2+2] photocycloaddition of 1,3-dithiolane **4** were unsuccessful if the irradiation was performed at $\lambda = 398$ nm. Gratifyingly, we found that the reaction was feasible once a short-wavelength light source was employed. At $\lambda = 366$ nm, a complete conversion to the desired cyclobutane **5** was observed after six hours in the presence of either 10 or one equivalent (equiv) of Brønsted acid (Table 1, entries 1, 2). At a lower catalyst loading of only 0.1 equiv the reactions remained incomplete and starting material could be recovered (entries 3, 4). A good compromise was a catalyst loading of 20 mol% (0.2 equiv) which allowed for full conversion after 13.5 h and resulted in a yield of 77%. The reason for the diminished reactivity of dithiolane **4** was found to be its somewhat lower basicity and/or lower tendency to form a thionium ion. If treated with the Brønsted acid Tf_2NH the UV/Vis absorption ($c = 0.5$ mM in CH_2Cl_2 solution) did not reach saturation even upon addition of 20 equivalents of the acid (Fig. 2). The absorbance at $\lambda = 353$ nm for putative intermediate **6** was only 0.2335 (path length of the cuvette $l = 0.1$ cm). In stark contrast, thionium ion **3** had shown saturation under otherwise identical condition already with 12.5 equiv of Tf_2NH and had produced an absorbance of 1.195 [13]. At $\lambda = 356$ nm a molar absorption coefficient of $\epsilon = 23,900 \text{ M}^{-1} \text{ cm}^{-1}$ was thus calculated according to the Lambert–Beer law.

3.2 UV/Vis Spectra

We further explored the structural parameters which favor the formation of thionium ions. While Satchell and co-workers had already observed colored intermediates if treating 2,2-diaryl-1,3-dithianes with perchloric acid [12], the 1,3-dithiane **7** ($c = 1.0$ mM) derived from acetophenone could not be converted into a species with a more intense

Table 1 Intermolecular [2 + 2] photocycloaddition of 1,3-dithiolane **4** to product **5** via putative intermediate **6**

Entry ^a	Tf ₂ NH (equiv)	<i>t</i> (h)	Yield (4) (%)	Yield (5) (%)
1	10	6	– ^b	79
2	1.0	6	– ^b	92
3	0.1	10	27	49
4	0.1	20	14	71
5	0.2	13.5	– ^b	77

^aAll reactions were performed on a scale of 0.1 mmol (*c* = 10 mM) with 16 fluorescence lamps as light sources

^bThe reaction went to full completion and no starting material could be re-isolated

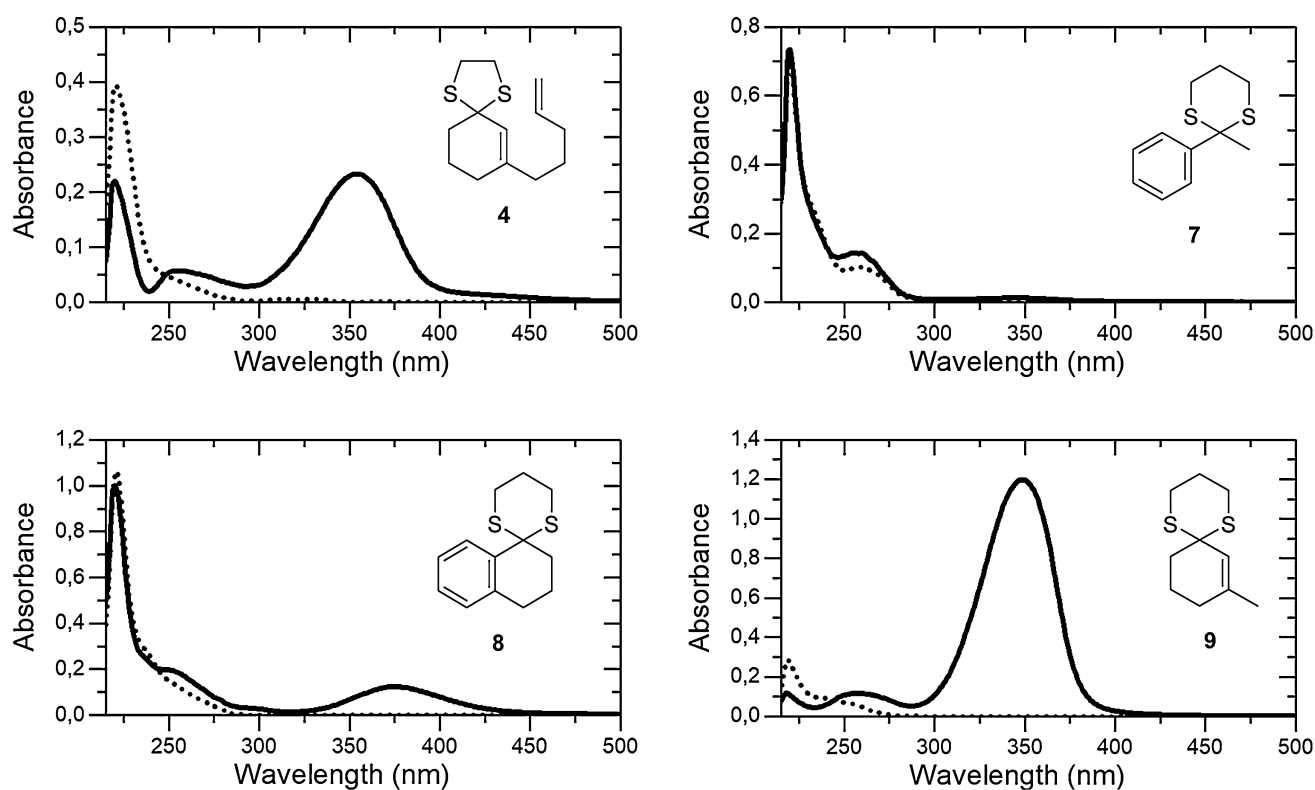
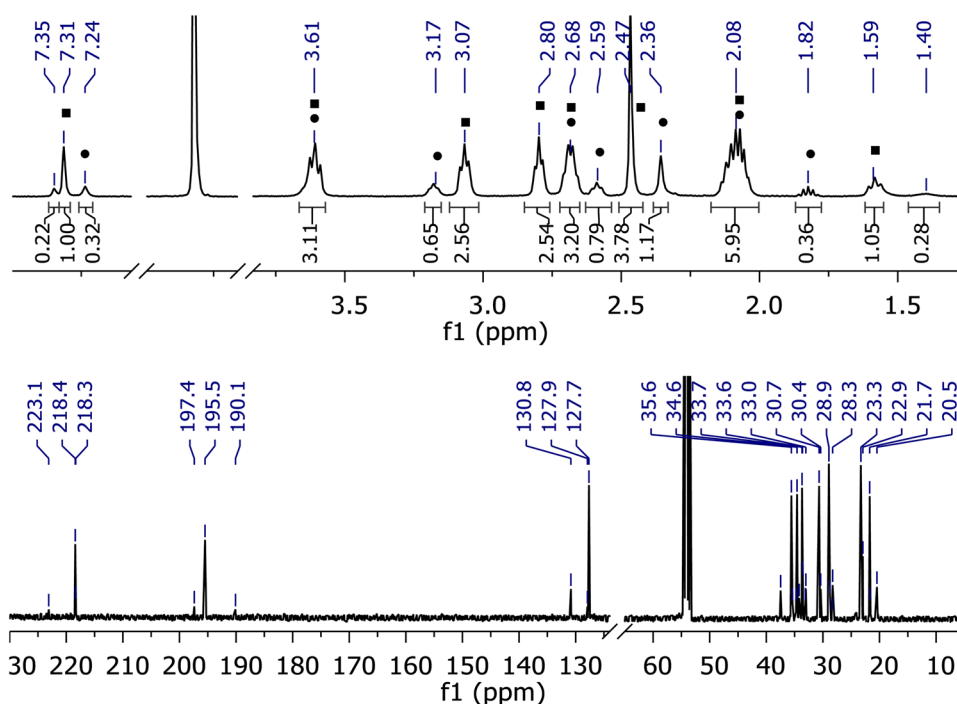


Fig. 2 UV/Vis absorption spectra of compounds **4**, **7–9** in CH₂Cl₂ solution without (.....) and with added Brønsted acid (Tf₂NH, see narrative)

chromophore (20 equiv Tf₂NH) and it is thus likely that there is no thionium ion being formed or that its concentration is very low at best. The more rigid 1,3-dithiane **8** (*c* = 1.0 mM) derived from α -tetralone exhibited a detectable absorption upon acid treatment (20 equiv Tf₂NH) although the measured absorbance was not very high (*A* = 0.1238). Still, it is evident that the rigid ring system facilitates formation of

the respective thionium ion by placing the conjugated arene π -system in proper conjugation with the cationic π -system of the cation. Similarly, the 1,3-dithiane **9** (*c* = 0.5 mM) derived from 2-methyl-2-cyclohexenone is stabilized by the olefinic π -system and the formation of a thionium ion seems to be facile. Indeed, the compound behaved similar to dithiane **1** and produced quantitatively the respective cation upon

Fig. 3 ^1H - and ^{13}C -NMR spectra of compound **9** in CD_2Cl_2 solution at -70°C upon addition of 6.25 equivalents of Tf_2NH



addition of 12.5 equiv of Tf_2NH . The calculated absorption coefficient at $\lambda = 349\text{ nm}$ was $\epsilon = 23,940\text{ M}^{-1}\text{ cm}^{-1}$. By comparison with the 1,3-dithiane derived from 2-pentyl-2-cyclohexenone (see Supporting Information) it was shown that the slightly hypsochromic absorption shift as compared with **1** (vide supra) is due to the length of the different alkyl chain but not due to the absence of the olefinic double bond.

3.3 Low-Temperature NMR Studies

Given the apparently clean formation of a thionium ion from **9** and given the less complex structure of **9** compared to **1**, it was attempted to substantiate the formation of the cation by low-temperature NMR studies. Upon addition of 6.25 equivalents of Tf_2NH at -70°C , a solution of compound **9** in CD_2Cl_2 produced a ^1H -NMR spectrum (Fig. 3) in which there were no signals of compound **9** detectable. Rather two new species had formed in a ratio of about 3/1. The respective signals are marked as ■ (major) and ● (minor) in the spectrum. A third species was identified based on its signals at high ($\delta = 1.40\text{ ppm}$) and low field ($\delta = 7.35\text{ ppm}$). All other signals of this species overlap with the signals of the major isomer and they cannot be distinguished at higher concentration which are necessary for a sufficient signal-to-noise ratio in 2D NMR experiments. Upon addition of acid, the structure of 1,3-dithiane **9** changes, indicated by the fact that the two enantiopic

hydrogen atoms in 5-position of the 1,3-dithiane ring are no longer split into two signals ($\delta = 1.68$ and 1.91 ppm). Rather they appear in a single broad peak centered at $\delta = 2.08\text{ ppm}$ overlapping with signals from other methylene protons.

The resonance of the olefinic hydrogen atom of **9** is shifted by 1.92 – 2.03 ppm from $\delta = 5.32\text{ ppm}$ to $\delta = 7.35$, 7.31 , and 7.24 ppm for each species. The strong downfield shift can be explained by an electron withdrawing atom or group, generated by the acid. The chemical shift at $\delta = 3.61\text{ ppm}$ is attributed to a methylene group next to a thionium ion, as already observed by Lambert et al. [3]. In the upfield region, three signals of possible HS- groups ($\delta = 1.82$, 1.58 , and 1.40 ppm) are visible indicating a ring opening of the dithiane. The signals in the ^{13}C -NMR spectrum at $\delta = 23.3$ and 20.5 ppm also indicate the presence of a thiol bound to an alkyl chain [14]. The ^{13}C -NMR spectrum further exhibits downfield shifted signals between 190.1 and 197.4 ppm which are

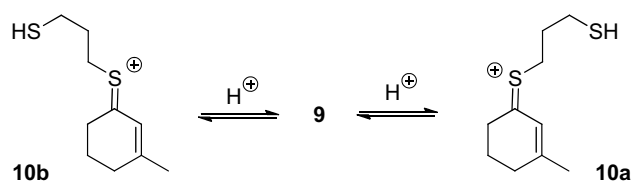
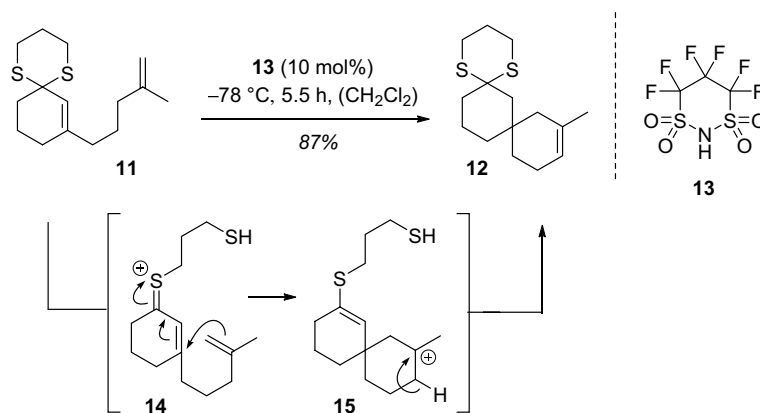


Fig. 4 Formation of thionium ions **10** as mixture of two diastereoisomers **10a** (^1H -NMR signals in Fig. 3: filled square) and **10b** (^1H -NMR signals in Fig. 3: filled circle)

Fig. 5 Brønsted acid-catalyzed cyclization of enone 1,3-dithiane **11** to spiro compound **12** via putative intermediates **14** and **15**



assigned to the olefinic quaternary carbon atoms in conjugation to the carbocation center. The cation center itself resonates at 218.3–223.1 ppm in the three species mentioned above. The ^{13}C -NMR signals of the sp^2 hybridized carbon atoms of all three species appear in three groups of three signals each ($\delta = 218.3\text{--}223.1$, $190.1\text{--}197.4$ and $127.7\text{--}130.8$ ppm), suggesting a structural similarity of all three species. In a NOESY experiment cross peaks between the signals of the methyl groups ($\delta = 2.47$ and 2.36 ppm), the olefinic hydrogen atoms ($\delta = 7.31$ and 7.24 ppm) and the endocyclic methylene group in β position to the positive charged sulfur atom ($\delta = 3.07$ and 3.17 ppm) were observed for the major and minor species.¹ The cross peaks are in phase with the diagonal resonance due to chemical exchange by interconversion of both species into one another on the ^1H -NMR timescale [15]. A chemical exchange is also indicated between two signals of the major species ($\delta = 3.61$ and 2.68 ppm), which can be assigned to the exocyclic methylene groups next to the sulfur atoms. Additionally, the olefinic hydrogen atom of the major species ($\delta = 7.31$ ppm) shows cross peaks with its methyl group ($\delta = 2.47$ ppm) and with both exocyclic methylene groups next to the sulfur atoms ($\delta = 3.07$ and 2.68 ppm), which are in opposite phase with the diagonal peaks due to an intramolecular NOE. The latter NOE indicates a spatial proximity of the olefinic hydrogen atom and the exocyclic methylene groups. In the minor species, the resonances of the methyl ($\delta = 2.47$ ppm) group and the olefinic hydrogen atom ($\delta = 7.24$ ppm) are shifted upfield ($\Delta\delta = -0.07$ and -0.09 ppm) compared to the major species. Additionally, the signal of the endocyclic methylene group in β position to the positive charged sulfur atom ($\delta = 3.17$ ppm) is shifted downfield ($\Delta\delta = +0.07$ ppm) compared to the major species. This observation suggests

that the major and the minor species are configurational isomers. Based on the NMR data, structure **10a** was assigned to the major (*Z*)-diastereoisomer of the thionium ions and structure **10b** was assigned to the (*E*)-diastereoisomer (Fig. 4). The structure of the minor component remains unclear. It is conceivable that the intermediate is a rotamer of compound **10a** as its NMR data are very similar to **10a**.

3.4 Thermal Acid-Catalyzed Cyclization

In order to collect further evidence for a cationic intermediate formed from enone 1,3-dithianes, we attempted to trap the thionium ion by a suitable nucleophile (Fig. 5). Indeed, when compound **11** was treated with acid **13** [16, 17] there was a reaction in the absence of light and product **12** was isolated in high yield [18, 19]. Cation **14**² seems to be sufficiently electrophilic to attack the nucleophilic 1,1-disubstituted alkene intramolecularly with concomitant formation of tertiary carbocation **15**. Product formation occurs subsequently upon proton elimination and re-cyclization of the thiol to the 1,3-dithiane.

4 Conclusion

In summary, it was shown that thionium ions are useful transient intermediates which can be generated upon treatment of enone 1,3-dithianes or 1,3-dithiolanes with a suitable Brønsted acid. The most characteristic feature of these ions is their strong absorption at long wavelength which allows for photochemical reactions to be performed under acidic

¹ The signal assignment of the major species, NOESY spectra and ^1H spectra of **9**, for comparison, are shown in the supporting information.

² A reviewer has pointed out that the olefin moiety (but not the dithiane) might be protonated to generate a persistent tertiary carbocation that undergoes the reaction. This hypothesis cannot be ruled out but requires an additional assumption. Thionium ion formation is indicated for the reaction **11** \rightarrow **12** by the yellow color of the reaction mixture and by the fact that compounds **9** and **11** are closely related.

catalysis. Apart from [2 + 2] photocycloaddition reactions other transformations seem feasible and research along these lines is ongoing in our laboratories.

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References

1. Olah GA, Prakash GKS, Sommer J (1985) *Superacids*. Wiley, New York, pp 188–191
2. Olah GA, Brien DH, Pittman CU Jr (1967) *J Am Chem Soc* 89:2996–3001
3. Lambert JB, Vulgaris E, Feathermann SI, Majchrzak M (1978) *J Am Chem Soc* 100:3269–3274
4. Lambert JB, Majchrzak M, Stec D III (1978) *J Org Chem* 44:4689–4695
5. Guinot F, Lamaty G, Munsch H (1971) *Bull Soc Chim Fr* 541–546
6. Guinot F, Lamaty G (1972) *Tetrahedron Lett* 13:2569–2572
7. Modena G, Scorrano G, Venturello P (1979) *J Chem Soc Perkin Trans* 2:1–6
8. Satchell DP, Satchell RS (1990) *Chem Soc Rev* 19:55–81
9. Föhlisch B, Haug E (1971) *Chem Ber* 104:2324–2337
10. Fabian J, Hartmann H (1973) *Tetrahedron* 29:2597–2608
11. Carlsen L, Holm A (1976) *Acta Chem Scand B* 30:277–279
12. Ali M, Satchell DPN, Le VT (1993) *J Chem Soc Perkin Trans* 2:917–922
13. Brenninger C, Pöthig A, Bach T (2017) *Angew Chem In Ed* 56:4337–4341
14. Freeman F, Angeletakis CN (1983) *Org Magn Reson* 21:86–93
15. Davis DG, Bax A (1985) *J Magn Reson* 64:533–535
16. Kütt A, Rodima T, Saame J, Raamat E, Mäemets V, Kaljurand I, Koppel IA, Garlyauskayte RY, Yagupolskii YL, Yagupolskii LM, Bernhardt E, Willner H, Leito I (2011) *J Org Chem* 76:391–395
17. Zhang M, Sonoda T, Mishima M, Honda T, Leito I, Koppel IA, Bonrath W, Netscher T (2014) *J Phys Org Chem* 27:676–679
18. Hosomi A, Sakurai H (1977) *J Am Chem Soc* 99:1673–1675
19. Mayr H, Henninger J, Siegmund T (1996) *Res Chem Intermed* 22:821–838