# Ring Expansion or Spirocyclisation of (Phenylthiomethylene)cycloalkanes with Aluminium Chloride *via* β-Thio Carbocations

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The title reactions can be explained by Wagner–Meerwein rearrangement of α-thio carbocations (thionium ions) to β-thio carbocations; this unusual reactivity may be due to superelectrophilic activation by aluminium chloride.

(Phenylthiomethylene)cycloalkanes **1** are readily available from cycloalkanones.[1] During unrelated studies on the chemistry of these phenyl vinyl sulfides **1**, we discovered[2,3] their cyclisation either to ring-expanded annelated benzotetrahydrothiophenes **2**, or to their spiro-isomers **3** upon treatment with excess aluminium chloride in dichloromethane at room temperature (Scheme 1).†

These benzotetrahydrothiophene products **2** and **3** are presumably formed by an intramolecular alkylation of the benzene ring by a β-thio carbocation. Scheme 2 shows a possible mechanism.

The small amount of hydrogen chloride present in the AlCl₃ could add to the double bond of the vinyl sulfide, giving the α-chlorosulfide **4**. This would be reversibly ionised to the
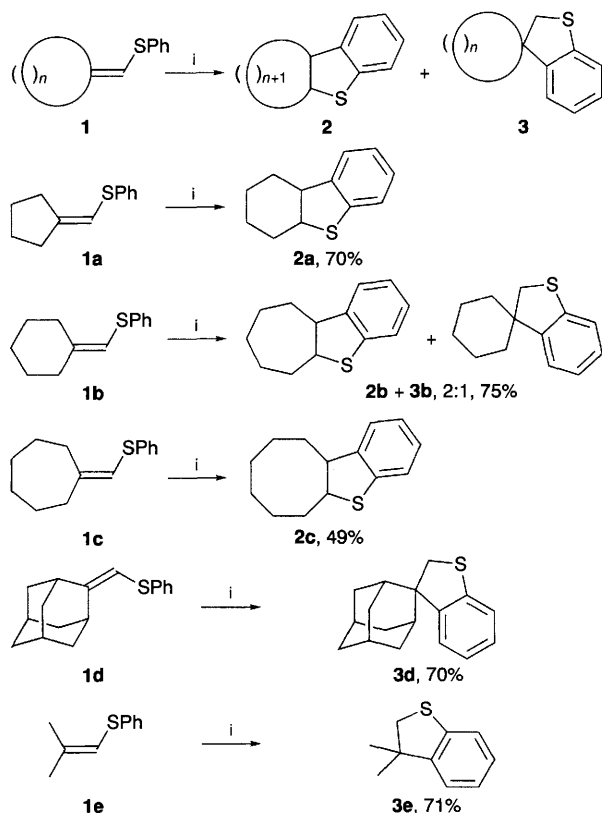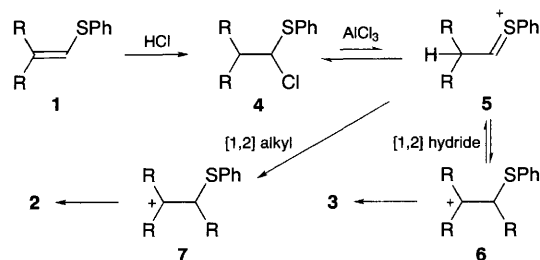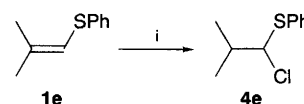
thionium[4] ion **5**, which could undergo a Wagner–Meerwein rearrangement, with migration either of hydride to give the tertiary cation **6**, or of alkyl to give the less stable secondary ion **7**. Both these cations could be in equilibrium with the corresponding chlorides (not shown). Cyclisation would then lead to the observed products, **2** or **3**. It seems likely that this cyclisation would be much slower for the more stable and more hindered cation **6**, thus enabling an equilibrium to be established with the thionium ion **5**. The ease of migration of an alkyl group in **5** would depend upon the nature of the R groups. For example, starting with the alkenes **1b** and **1d**, alkyl migration would involve unfavourable ring expansion of a cyclohexane or adamantane ring system, respectively. This would seem to explain the rather different selectivities observed from the different substrates.

In order to check this mechanism, we have carried out the following experiments. Firstly, we have shown that hydrochloric acid does add to the double bond of the vinyl sulfide **1e** to give **4e**, even in the absence of aluminium chloride as a catalyst (Scheme 3). In addition, we have synthesised‡ several α-chlorosulfides **4**, and treated them with excess AlCl₃ at low temperature. Quantitative conversion to the β-chlorosulfides **8** is observed (Scheme 4).§ The corresponding neopentyl-type chlorosulfide **4f** undergoes methyl migration under similar conditions to give the β-chlorosulfide **9**. At room temperature, cyclisation occurs to give the same products **2** and **3** as above (Scheme 1). This proves that hydrogen migration occurs reversibly between ions **5** and **6** (Scheme 2), with slower alkyl migration competing with cyclisation.

One particular feature of our mechanistic scheme is unusual: the Wagner–Meerwein migration of hydrogen or alkyl towards a thionium ion centre. Both *ab initio* calculations and experimental results show[5] that thionium ions are stabilised about as much as the corresponding α-alkoxy ions (oxonium ions). The gas phase stabilisation energy[5] of MeS⁺=CH₂ **10** (relative to



**Scheme 1** *Reagents and conditions*: i, CH₂Cl₂, 3 mol. equiv. AlCl₃, room temp., 20 h



**Scheme 2**



**Scheme 3** *Reagents and conditions*: i, CH₂Cl₂, HCl, room temp., 20 h, 50% conversion
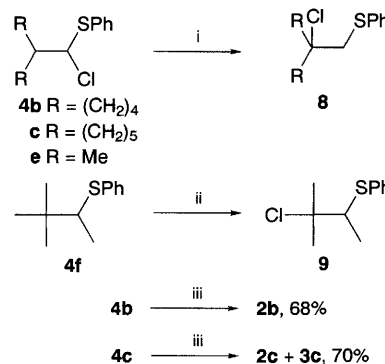


**Scheme 4** *Reagents and conditions*: i, CH₂Cl₂, 3 mol. equiv. AlCl₃, −78 °C, 2 h, quantitative conversion; ii, as i, −78 to 0 °C, 2 h, quantitative conversion; iii, as i, −78 °C to room temp., 20 h

Me$^+$) is 74 kcal mol$^{-1}$ (1 cal = 4.184 J), intermediate between those[6] of the isopropyl cation (61 kcal mol$^{-1}$) and of the *tert*-butyl cation (80 kcal mol$^{-1}$). These gas-phase data generally agree extremely well with experimental data in solution.[7] The thionium ions **5** have an additional stabilising alkyl group, and their stability can be estimated from that of MeS$^+$=CH$_2$ **10**, and from the difference[7] in stability between CH$_2$=O$^+$H and MeCH=O$^+$H (22 kcal mol$^{-1}$) as being *ca.* 90–95 kcal mol$^{-1}$, *i.e.* well above that of a tertiary carbocation such as **6**. In conclusion, the Wagner–Meerwein migrations shown in Scheme 2 should be too unfavourable to occur.

This is in agreement with most experimental results. Thionium ions only undergo migration when the resulting cation is stabilised by a β-trimethylsilyl group,[8] or by an α-hydroxy group.[9] In these cases, the reactivity of the thionium ions is roughly comparable to that of the corresponding oxonium ions, the main difference being the rate of formation of the onium species. For other thionium ions with structural features which should favour rearrangement, no migration has been observed.[10] The reverse reaction, migration of an alkyl group towards a neighbouring carbocationic centre, with formation of a stabilised oxonium or thionium[11] ion, is much more common.

In the cases discussed here thionium ions **5** isomerise to less stable tertiary cations **6** or to much less stable secondary cations **7**. These abnormal and highly unfavourable steps could be driven by the formation of stable cyclised products **2** or **3**, but it is more likely that they are owing to the aluminium chloride.¶

Most of the sulfides in Scheme 2 would be expected to exist in equilibrium with their aluminium chloride complexes in the presence of an excess of this strong Lewis acid. Hydrogen chloride should add with normal regioselectivity to *uncomplexed* **1** to give α-chlorosulfide **4**. However, the key intermediate for rearrangement is presumably the doubly activated species **12** obtained by ionisation of the *complexed* α-chlorosulfide **11** (Scheme 5). Doubly activated intermediates like **12**, known as superelectrophiles,[12] have been shown to arise during several reactions, in particular the methylthiomethylation of aromatics[13] with a 1:2 mixture of MeSCH$_2$Cl and AlCl$_3$.

By complexing the sulfur atom, aluminium chloride reverses the order of stability of α- and β-thio carbocations,‖ and therefore provides the driving force for the rearrangement of **5** to **6** or **7**. This formal *umpolung* of the phenyl vinyl sulfides **1** explains how they can lead to unexpected β-thio carbocations, thereby opening a new synthetic route to spiro or annelated benzothiopyrans **2** and **3**.
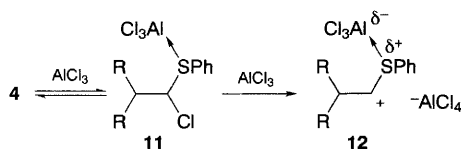
**Scheme 5**

## Footnotes

† *Selected analytical data*: **2a** $v_{max}$ (film)/cm$^{-1}$, 3057, 2951, 2944, 2865, 1473, 1438, 1251, 1071; δ$_H$ (CDCl$_3$, 200 MHz) 1.4–1.8 (m, 4H), 1.9–2.2 (m, 2H), 2.4–2.8 (m, 2H), 3.1 (m, 2H), 7.2–7.8 (m, 4H); δ$_C$ (CDCl$_3$, 50 MHz) 23.3, 31.2, 32.1, 35.3, 38.1, 42.9, 124.6, 125.5, 127.6, 130.3, 136.1, 138.4; *m/z* 190 (M$^+$), 147, 77; **3d** (Found: C, 79.7; H, 8.1. C$_{17}$H$_{20}$S requires C, 79.63; H, 7.86%), mp 94 °C, $v_{max}$(KBr)/cm$^{-1}$, 2979, 2945, 2862, 2843, 1470, 1456, 1450, 1435, 1423, 1097, 1064; δ$_H$ (CDCl$_3$, 200 MHz) 1.93 (m, 12H), 2.37 (s, 1H), 2.44 (s, 1H), 3.42 (s, 2H), 7.0–7.3 (m, 3H), 7.79 (m, 1H); δ$_C$ (CDCl$_3$, 50 MHz) 27.4, 27.6, 33.1, 34.0, 35.3, 39.6, 43.8, 56.3, 123.3 (2 Cs), 126.9, 127.5, 142.2, 146.3; *m/z* 256 (M$^+$), 147, 134, 91; the spectra of **3e** were identical to those reported in the literature.[14]

‡ By chlorination (*N*-chlorosuccinimide–CCl$_4$) of the corresponding sulfides, derived from thiophenol and the corresponding alkyl halide, or the toluene-*p*-sulfonyl ester of the cycloalkylmethyl alcohol. See ref. 4 for similar experimental procedures.

§ The β-chlorosulfides **8** and **9** were identical to the major, Markovnikov, adducts obtained from phenyl sulfenyl chloride and from the corresponding di- or tri-substituted alkene.[15]

¶ The reactions of Schemes 1 and 3 were unsuccessful with the weaker Lewis acids SnCl$_4$ and TiCl$_4$. Aluminium chloride in dichloromethane is a known oxidant;[16] however, radical cation species do not seem to be involved in the reactions discussed here.

‖ A β-thiocarbocation such as **6** is usually stabilised by nucleophilic attack of a sulfur lone pair, forming an episulfonium ion, which might well be more stable than a thionium ion, even in the absence of AlCl$_3$. However, this stabilisation is geometrically impossible in the transition state for rearrangement of **5** to **6**.

## References

1 W. Adam and L. A. A. Encarnacion, *Chem. Ber.*, 1982, **115**, 2592.

2 Compound **3e** was obtained in low yield by heating **1e** at 200 °C on acidic alumina, see: T. Abdin, T. A. Danilova, E. A. Viktorova, G. Dzhamalova and S. Khushvaktova, *Vestn. Mosk. Univ. Khim.*, 1973, **14**, 491, (*Chem. Abstr.*, 1973, **79**, 125998u).

3 Vinyl sulfides can be oxidatively photocyclised to give benzothiophenes. See, for example: S. H. Groen, R. M. Kellogg, J. Buter and H. Wynberg, *J. Org. Chem.*, 1968, **33**, 780.

4 For chemistry of thionium ions, see: C. Schmitz, J. N. Harvey and H. G. Viehe, *Bull. Soc. Chim. Belg.*, 1994, **104**, 105, and references therein.

5 Y. Apeloig and M. Karni, *J. Chem. Soc., Perkin Trans. 2*, 1988, 625, and references therein.

6 From data tabulated in F. P. Lossing and John L. Holmes, *J. Am. Chem. Soc.*, 1984, **106**, 6917.

7 E. M. Arnett and T. C. Hofelich, *J. Am. Chem. Soc.*, 1983, **105**, 2889.

8 K. Tanino, K. Sato and I. Kuwajima, *Tetrahedron Lett.*, 1989, **30**, 6551.

9 B. M. Trost and G. K. Mikhail, *J. Am. Chem. Soc.*, 1987, **109**, 4124; L. A. Paquette, U. Dullweber and B. M. Branan, *Heterocycles*, 1994, 187.

10 See, for example: W. E. Parham and L. D. Edwards, *J. Org. Chem.*, 1968, **33**, 4150; I. Paterson and I. Fleming, *Tetrahedron Lett.*, 1979, 2179; W. Engel, I. Fleming and R. H. Smithers, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1637.

11 M. Hannaby and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3007.

12 G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 767. See also: S. Saito, Y. Sato, T. Ohwada and K. Shudo, *J. Am. Chem. Soc.*, 1994, **116**, 2312.

13 G. A. Olah, Qi Wang and G. Neyer, *Synthesis*, 1994, 276.

14 L. W. Spruce, J. B. Gale, K. D. Berlin, A. K. Verma, T. R. Breitman, Xinhua Ji and D. van der Helm, *J. Med. Chem.*, 1991, **34**, 430.

15 B. Giese and P. Mazumdar, *Chem. Ber.*, 1981, **114**, 2850; Y. Masaki, K. Hashimoto and K. Kaji, *Tetrahedron*, 1984, **40**, 3481.

16 H. Bock, W. Kaim, M. Kira, L. Réné and H. G. Viehe, *Z. Naturforsch., Teil B*, 1984, **39**, 763.