

3-Thio-Claisen Rearrangement of the Allyl Vinyl Sulfonium Ion

Jeremy N. Harvey and Heinz G. Viehe*

Laboratoire de Chimie Organique, Université Catholique de Louvain, Lavoisier, Place L. Pasteur, B-1348 Louvain-la-Neuve, Belgium

Generated *in situ*, the parent allyl vinyl sulfonium ion rapidly undergoes the title rearrangement to give a γ,δ -unsaturated thionium ion; a similar process appears to be involved in the reaction of phenyl vinyl sulfoxide with isobutene.

The aliphatic Claisen rearrangement of allyl vinyl ethers is a reaction of synthetic importance. Many analogous processes have been described, in particular the thio-Claisen rearrangement leading to γ,δ -unsaturated thiocarbonyl compounds.¹

This reaction is not very convenient with ordinary vinyl sulfides, because the product is either an unstable thioaldehyde, which must be hydrolysed *in situ* during the reaction,² or a thioketone which can only occasionally be isolated.³ More commonly used are *S*-allylated ketene O,S; N,S; or S,S acetals which can easily be generated by *S*-allylation of the corresponding thioenolate. The rearrangement then leads to stable thioesters, thionoesters or thioamides.⁴ These products are often obtained with high diastereospecificity, due to the chair-like transition state during the Claisen rearrangement.

A positive charge on the 3-atom in a hexa-1-5-diene system can greatly accelerate [3,3]-sigmatropic rearrangement.⁵ A few results in the literature confirm that this is true in 3-thio derivatives. Thus, thio-Claisen rearrangements of indolyl allyl sulfonium ions have been reported to be fast at room temperature,⁶ whereas the corresponding reaction of the sulfide only occurs in refluxing toluene.^{4a} The zwitterionic species obtained by reaction of allyl sulfides with dichloroketene rearrange diastereoselectively to yield thioesters.⁷ Allyl vinyl sulfoxides, bearing a partial positive charge on sulfur, rearrange about two orders of magnitude faster than the corresponding sulfide.⁸ It should also be mentioned that the very fast and much used [2,3]-rearrangement of *S*-allyl sulfonium ylides to give homoallylic sulfides is isoelectronic with the thio-Claisen rearrangement discussed here.⁹

As yet, however, the chemistry of simple aliphatic allyl vinyl sulfonium ions has not, to our knowledge, been described.

We chose to generate the allyl vinyl sulfonium ions **1** by base-promoted elimination from a sulfonium ion **2** bearing a β leaving group. This elimination had already been used to give isolated dialkyl vinyl sulfonium ions.¹⁰

The β -chloro sulfide **3** could readily be alkylated with allyl methanesulfonate **4**, leading to the β -chloro sulfonium ion **5**. When a methanol solution of sodium methanolate was slowly added to this salt at 0 °C, the expected hemithioacetal **6** was observed in *ca.* 70% yield. Presumably, elimination to form the vinyl sulfonium ion **7** is followed by rearrangement to the thionium ion **8** which then recombines with excess methanolate.

It is known¹⁰ that nucleophiles add very rapidly to vinyl sulfonium ions such as **7**. Conceivably, the conditions of our reaction could have involved an equilibrium between the ion **7** and the β -methoxy sulfonium ion **9**, *via* the sulfonium ylide **10**. We synthesised the sulfonium ion **9**, and under the same conditions as above, it did not react.

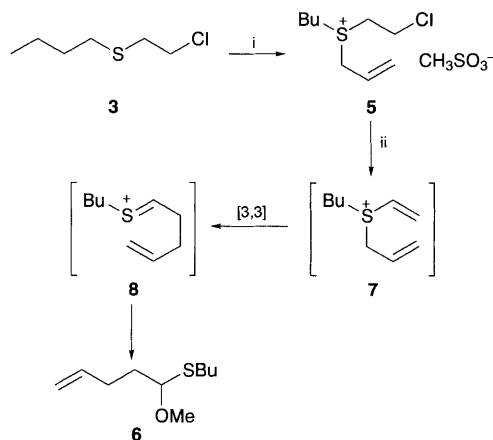
An interesting result was obtained by reversing the order of mixing used in our first experiments: when the sulfonium salt **5** was added to a solution of base, the β -methoxy sulfide **11** was

formed by [2,3]-rearrangement of the ylide **10** (Scheme 3). This approach to allyl sulfonium ylides does not appear to have been described before.

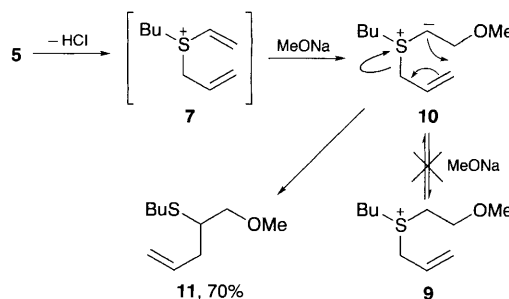
NMR analysis of the crude product of the experiments described in Schemes 2 and 3 underlines the contrast between the two procedures: when hemithioacetal **6** was obtained, no trace of compound **11** could be observed, and *vice-versa*. This gives some interesting insights into the chemistry of the ion **7**. Thus, the first two steps in the 'normal' reaction (Scheme 2), *i.e.* the elimination to form **7**, and the rearrangement to give the thionium ion **8**, must both occur at a faster rate than the introduction of the sodium methanolate solution from the addition funnel. The slowest of these two steps must therefore have a half-life smaller than about 1 min. If either step was slower, the concentration of methanolate ion would build up, leading to competitive addition to ion **7** as in Scheme 3.

Allyl vinyl sulfide itself is reported to be stable at room temperature,^{2c} so its thio-Claisen rearrangement must be many orders of magnitude slower than the rearrangement of the charged derivative **7**.

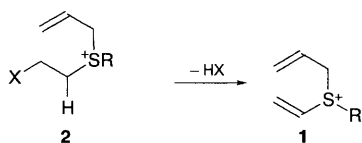
The use of β -chlorosulfides such as **3** as precursor for vinyl sulfonium ions is unsuitable for various reasons, including the high toxicity of β -chlorosulfides. Also, the hemithioacetal **6** formed in this way contained several impurities which we could not remove. This was perhaps due to competing alkylation of sulfide **3** by itself during reaction with allyl mesylate **4**. Upon



Scheme 2 Reagents and conditions: i, $\text{CH}_2=\text{CHCH}_2\text{O}_3\text{SMe}$ **4**, 60 °C, neat, 12 h; ii, MeONa, MeOH, room temp. 10 min



Scheme 3 Non reactivity of sulfonium salt **9**. Unexpected [2,3] rearrangement to form **11** upon reversal of the order of addition of reagents.



Scheme 1

using the β -pivalyloxy sulfide **12** as precursor, the crude product **6** after basic treatment contained much less impurities, and could be easily obtained in pure form.† β -Thioalcohols can be easily converted to esters such as **12**, and can in turn be made by a variety of procedures.

This work originated in our study of the mechanisms of the intriguing reactions of phenyl vinyl sulfoxide **13** with simple alkenes below room temperature upon activation with trifluoroacetic anhydride (TFAA).¹¹ With mono- or 1,2-di-substituted alkenes, we have suggested^{11b} that the mechanism involves ene-type reaction of an α -thiocarbocation, or thionium ion,¹² followed by selective isomerisation, driven by the electronegativity difference between oxygen and sulfur, of the resulting β -phenylthioalkyl trifluoroacetate.¹³

The reaction of sulfoxide **13** with isobutene **14** has a different mechanism, leading to the bis-alkylated product **15** (Scheme 5). We showed^{11b} that this product could be formed by ene-type reaction of the thionium ion **17** with isobutene **14**. The formation of the key intermediate **17** was tentatively explained by an addition of the rather nucleophilic¹⁴ alkene **14** to the activated intermediate **16**, as shown in Scheme 5.

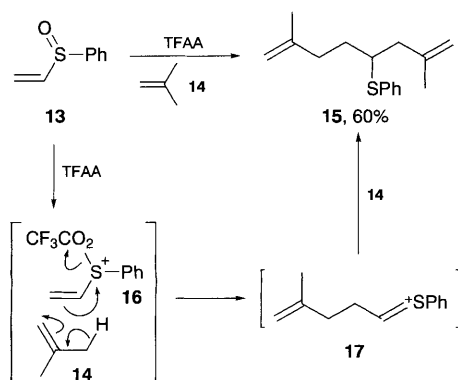
We now suggest instead that the alkene **14** reacts with the electrophilic sulfur atom of intermediate **16**, giving, after loss of trifluoroacetate anion and a proton, the sulfonium ion **18**. Thio-Claisen rearrangement of this ion then gives the thionium ion **17** which reacts as above.‡

Both steps of this scheme are supported by literature precedents. Thus, Me₂SO or methyl phenyl sulfoxide react with di- or tri-substituted alkenes upon activation with trifluoroacetic anhydride (TFAA) to give isolated allyl sulfonium salts.¹⁵ This process is an interrupted Pummerer reaction, also involved in the Swern–Moffat type oxidations of alcohols by Me₂SO. Similar reactions are known involving various R₂S⁺X ions¹⁶ (X = Hal, RCO₂, or NR₂) and carbon nucleophiles such as enols, enol ethers, electron-rich aromatics or enamines.¹⁷

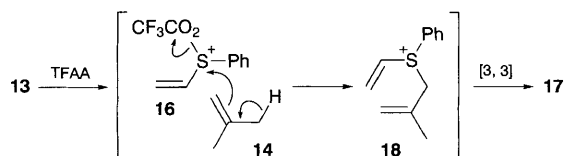
Our new interpretation not only provides a more convincing mechanism for the reaction of phenyl vinyl sulfoxide, it also suggests the existence of very rapid thio-Claisen rearrangements in allyl vinyl sulfonium ions. As a first investigation of



Scheme 4 Reagents and conditions: i, **4**, CF₃CH₂OH, room temp. 44 h; ii, MeONa, MeOH, room temp. 30 min



Scheme 5 Previous mechanism suggested for formation of bis-isobutene adduct **15**



Scheme 6 New suggested mechanism for reaction of Scheme 5

this promising line of research, we have shown here that the parent allyl vinyl sulfonium ion **7**, independently generated, does indeed undergo fast rearrangement.

We thank the SPPS for financial support.

Received, 29th August 1995; Com. 5/05693D

Footnotes

† Selected spectroscopic data for **6**: C₁₀H₂₀OS. ν_{\max} (film)/cm⁻¹ 3000–2800 and 1640; δ_{H} (200 MHz, CDCl₃, TMS) 0.92 (3 H, t, $J = 7.2$ Hz), 1.3–1.7 and 1.8–2.1 (6 H, m), 2.20 (2 H, m), 3.36 (3 H, s), 4.40 (1 H, dd, $J = 7.1$ and 6.0 Hz), 4.9–5.1 (3 H, m), and 5.81 (1 H, ddt, $J = 17.1$, 10.2 and 6.6 Hz); δ_{C} (50 MHz, CDCl₃) 13.6, 22.1, 27.8, 30.5, 32.3, 34.9, 54.4, 86.7, 115.0 and 137.6; m/z (EI), 188 (M⁺, 0.3%), 157, 156, 99, 85, 67 and 57 (100%).

‡ We suggest that the reactions of vinyl sulfoxides with allyl magnesium bromide (C. Iwata, N. Maezaki, T. Kurumada, H. Fukuyama, K. Sugiyama and T. Imanishi, *J. Chem. Soc., Chem. Commun.*, 1991, 1408; N. Maezaki, H. Fukuyama, S. Yagi, T. Tanaka and C. Iwata, *J. Chem. Soc., Chem. Commun.*, 1994, 1835) probably involve a very similar mechanism: nucleophilic attack at sulfur, thio-Claisen rearrangement, then deprotonation or reaction with a second equivalent of Grignard reagent).

References

- For a review, see P. Metzner, *Synthesis*, 1992, 1185.
- (a) E. J. Corey and J. I. Shulman, *J. Am. Chem. Soc.*, 1970, **92**, 5522; (b) L. Dalgaard and S.-O. Lawesson, *Tetrahedron*, 1972, **28**, 2051; (c) K. Oshima, H. Takahashi, H. Yamamoto and H. Nozaki, *J. Am. Chem. Soc.*, 1973, **95**, 2693.
- I. Ojima and K. Kondo, *Bull. Chem. Soc. Jap.*, 1973, **46**, 1539.
- (a) B. W. Bycroft and W. Landon, *J. Chem. Soc., Chem. Commun.*, 1970, 168; (b) Y. Tamaru, T. Harada and Z.-I. Yoshida, *J. Am. Chem. Soc.*, 1980, **102**, 2392; (c) P. N. Devine and A. I. Meyers, *J. Am. Chem. Soc.*, 1994, **116**, 2633.
- R. P. Lutz, *Chem. Rev.*, 1984, **84**, 205.
- (a) B. W. Bycroft and W. Landon, *J. Chem. Soc., Chem. Commun.*, 1970, 967; (b) K. Tomita, A. Terada and R. Tachikawa, *Heterocycles*, 1976, **4**, 733.
- U. Nubbemeyer, R. Öhrlein, J. Gonda, B. Ernst and D. Belluš, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1465 and references cited therein.
- Jih Ru Hwu and D. A. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3199.
- I. E. Markó, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, vol. 3, Pergamon, 1991, p. 913; see also Yun-Dong Wu and K. N. Houk, *J. Org. Chem.*, 1991, **56**, 5657; R. A. Moss, Guo-Jie Ho and C. Sierakowski, *J. Am. Chem. Soc.*, 1992, **114**, 3128.
- W. von E. Doering and K. C. Schreiber, *J. Am. Chem. Soc.*, 1955, **77**, 514; E. Kelstrup, A. Kjaer, S. Abrahamsson and B. Dahlén, *J. Chem. Soc., Chem. Commun.*, 1975, 629; Yuan L. Chow, B. H. Bakker and K. Iwai, *J. Chem. Soc., Chem. Commun.*, 1980, 521.
- (a) M.-H. Brichard, Z. Janousek, R. Merényi and H. G. Viehe, *Tetrahedron Lett.*, 1992, **33**, 2511; (b) J. Harvey, M.-H. Brichard and H. G. Viehe, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2275.
- For other ene-type reactions of thionium ions and leading references on thionium ions, see C. Schmitz, J. N. Harvey and H. G. Viehe, *Bull. Soc. Chim. Belg.*, 1994, **103**, 105.
- For this electronegativity effect, see J. N. Harvey and H. G. Viehe, *J. Prakt. Chem.*, 1995, **337**, 253.
- H. Mayr and M. Patz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 938.
- V. V. Veselovsky, V. A. Dragan and A. M. Moiseenkov, *Tetrahedron Lett.*, 1988, **29**, 6637; A. M. Moiseenkov, V. A. Dragan and V. V. Veselovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, **2**, 365. See also D. L. Schmidt, J. P. Heesch, T. C. Klingler and L. P. McCarty, *J. Org. Chem.*, 1985, **50**, 2840; F. Bellesia, M. Boni, F. Gelfi, U. M. Pagnoni and A. Pinetti, *Synth. Commun.*, 1992, **22**, 1101.
- For a review on such species, see G. Edwin Wilson Jr., *Tetrahedron*, 1982, **38**, 2597.
- Some leading references: reactions with enols, R. Neidlein and B. Stackebrandt, *Lieb. Ann. Chem.*, 1977, 914; with enol ethers, S. Jain, K. Shukla, A. Mukhopadhyay, S. N. Suryawanshi and D. S. Bhakuni, *Synth. Commun.*, 1990, **20**, 1315; with aromatics, see ref. 6(b); S. R. Akhtar, J. V. Crivello and J. L. Lee, *J. Org. Chem.*, 1990, **55**, 4222; K. Hartke and D. Strangemann, *Heterocycles*, 1986, **24**, 2399; D. K. Bates and K. A. Tafel, *J. Org. Chem.*, 1994, **59**, 8076; S. G. Pyne and A. R. Hajipour, *Tetrahedron*, 1994, **50**, 13 501; with enamines, see E. Vilsmeier and W. Tröger, *Synthesis*, 1980, 463.