Desilylative Pummerer-like Rearrangement of α-Trimethylsilyl-substituted Sulphoxides and Sulphides: Formation of α-Acyloxy and α-Halogeno Sulphides

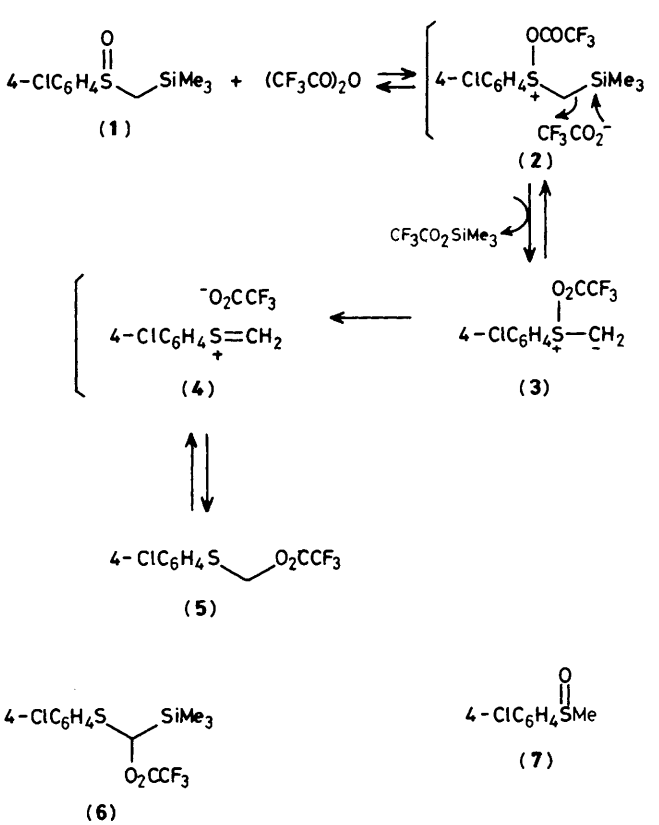
Hiroyuki Ishibashi,* Hiroshi Nakatani, Kazumi Maruyama, Kenjiro Minami, and Masazumi Ikeda
Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 607, Japan

α-Trimethylsilyl-substituted sulphoxides and sulphides undergo rearrangement with loss of the silyl group when treated respectively with trifluoroacetic anhydride and with *N*-halogenosuccinimide in the presence of trifluoroacetic acid, giving α-acyloxy sulphides and α-halogeno sulphides.

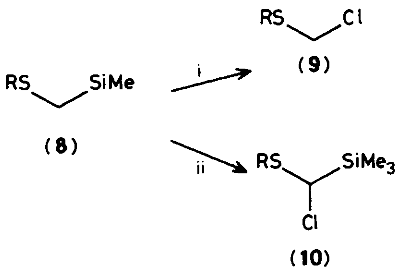
We report here a hitherto unknown desilylative Pummerer-like rearrangement of α-trimethylsilyl-substituted sulphoxides and sulphides which leads to the formation of α-acyloxy and α-halogeno sulphides.

Treatment of the α-silyl sulphoxide (**1**)[1] with trifluoroacetic anhydride (TFAA) in CH_2Cl_2 or trifluoroacetic acid (TFA) at 0 °C gave quantitatively the α-trifluoroacetoxy sulphide (**5**) [δ 5.53 (2 H, s) and 7.32 (4 H, s)] instead of the expected Pummerer rearrangement product (**6**). The product (**5**) was identical with that prepared from 4-chlorophenyl methyl sulphoxide (**7**) and TFAA.[2]

A mechanistic rationalisation of the formation of (**5**)



Scheme 1



Scheme 2. *Reagents:* i, *N*-chlorosuccinimide, CF_3CO_2H, CCl_4; ii, *N*-chlorosuccinimide, CCl_4.

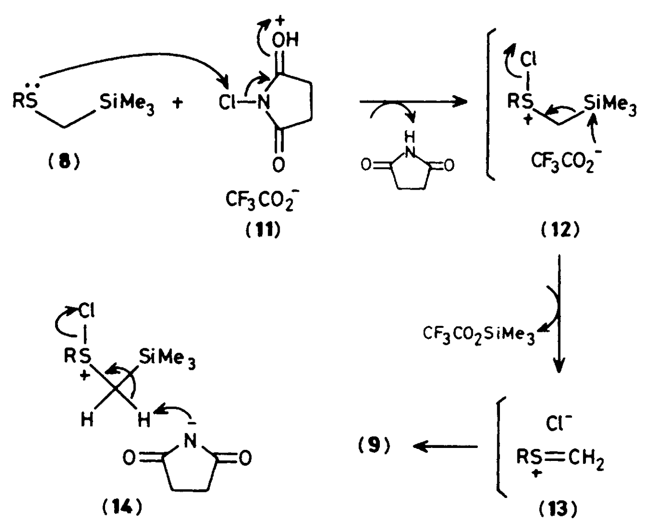
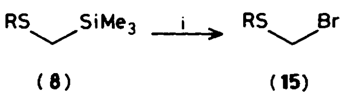


Table 1. Preparation of the α-halogeno sulphides (**9**) and (**15**).

R	α-Chloro sulphide (**9**) % yield[a]	α-Bromo sulphide (**15**) % yield[a]
$4\text{-}ClC_6H_4$	92	74
$3,4\text{-}Cl_2C_6H_3$	98	74
$2,6\text{-}Cl_2C_6H_3$	78[b]	63[b]
$4\text{-}MeC_6H_4$	87	43
Ph	77	45
Bu	78	[c]

[a] Yields after removal of insoluble materials into CCl_4 and n-hexane. [b] Isolated yield after chromatography on silica gel. [c] Complex mixture of products.



Scheme 3. *Reagents:* i, *N*-bromosuccinimide, CF_3SO_3H, CCl_4.

involves an attack of the trifluoroacetate ion on the trimethylsilyl group of the initially formed acyloxysulphonium salt (**2**) to give the ylide intermediate (**3**). This is followed by collapse to the ion pair (**4**), which then recombines to yield the acetate (**5**). An experiment using deuteriotrifluoroacetic acid as solvent showed no incorporation of deuterium in the product (**5**), excluding the possibility that (**5**) is formed *via* the 'deprotonative' Pummerer rearrangement product (**6**).

In an extension of this rearrangement, we next examined the reaction of α-silyl sulphides with *N*-halogenosuccinimides in the hope that a new route to α-halogeno sulphides might result. Thus, treatment of the α-silyl sulphide (**8**; R = $4\text{-}ClC_6H_4$) with *N*-chlorosuccinimide in CCl_4 in the presence of TFA (3 equiv.) at 0 °C afforded the α-chloro sulphide (**9**; R = $4\text{-}ClC_6H_4$) in 92% yield.† The use of acetic acid in place of TFA gave only the silyl-substituted chloride (**10**; R = $4\text{-}ClC_6H_4$). This compound remained unchanged when treated with TFA in CCl_4. Consequently, the mechanism for the formation of (**9**) from (**8**) may be interpreted as follows. In the presence of TFA, *N*-chlorosuccinimide would first give the protonated species (**11**),‡ which is attacked by the sulphur atom of (**8**) to form succinimide and the sulphonium salt (**12**). Trifluoroacetate ion thus produced, the conjugate base of stronger acid, attacks the silyl group instead of the proton α to the sulphur atom to give the ion pair (**13**), which recombines to afford the observed product (**9**). On the other hand, in the absence of TFA or in the weaker acetic acid, protonated species such as (**11**) are probably absent, and accordingly the sulphide (**8**) might react directly with *N*-chlorosuccinimide. The resulting succinimide anion (or possibly acetate ion), the conjugate base of the weaker acid, abstracts a proton α to the sulphur atom of the sulphonium salt (**14**), thereby leading to the silyl-substituted chloride (**10**). Other examples of the formation of the α-chloro sulphides (**9**) from (**8**) are summarised in Table 1.

Similarly, the α-silyl sulphides (**8**) yielded the α-bromo

---

† Treatment of (**8**) with *N*-chlorosuccinimide in the absence of TFA gave the α-chloro α-silyl sulphide (**10**; R = $4\text{-}ClC_6H_4$).[3]

‡ Indeed, formation of (**9**; R = $4\text{-}ClC_6H_4$) by reaction of 4-chlorothioanisole with *N*-chlorosuccinimide was greatly accelerated by TFA. We thank a referee for this suggestion.

sulphides (**15**) when treated with *N*-bromosuccinimide in CCl_4 in the presence of TFA.§ In these cases, the use of trifluoromethanesulphonic acid (1.1 equiv.) gave more satisfactory results, which are summarised in Table 1.

Received, 5th May 1987; Com. 610

---

§ Treatment of 4-chlorothioanisole with *N*-bromosuccinimide in CCl_4 gave no α-bromo sulphide (**15**; R = 4-ClC_6H_4) at room temperature.

References

1 Thermal rearrangement of α-silyl sulphoxides to α-silyloxy sulphides (silyl-Pummerer rearrangement) has been well documented: see W. P. Weber, 'Silicon Reagents for Organic Synthesis,' Springer-Verlag, Berlin, 1983, p. 346.
2 H. Ishibashi, H. Komatsu, K. Maruyama, and M. Ikeda, *Tetrahedron Lett.*, 1985, 5791.
3 H. Ishibashi, H. Nakatani, Y. Umei, W. Yamamoto, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, 1987, 589.