

## CONVENIENT SYNTHESIS OF S-CONTAINING HETEROBICYCLES

Shiro Ikegami\*, Jun-ichi Ohishi, and Yasuo Shimizu

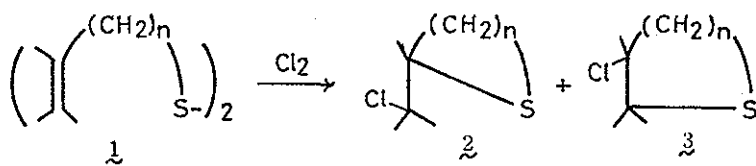
Division of Pharmaceutical Chemistry, National Institute of Radiological Sciences, Anagawa, Chiba-shi 280, Japan

6-exo-Chloro-2-thiabicyclo[2. 2. 1]heptane and its 1-methyl analog, and 4-exo-chloro-6-thiabicyclo[3. 2. 1]octane are synthesized by the intramolecular cyclization of sulfenyl chlorides formed in situ from the reaction of the corresponding cycloalkenyl disulfides with chlorine.

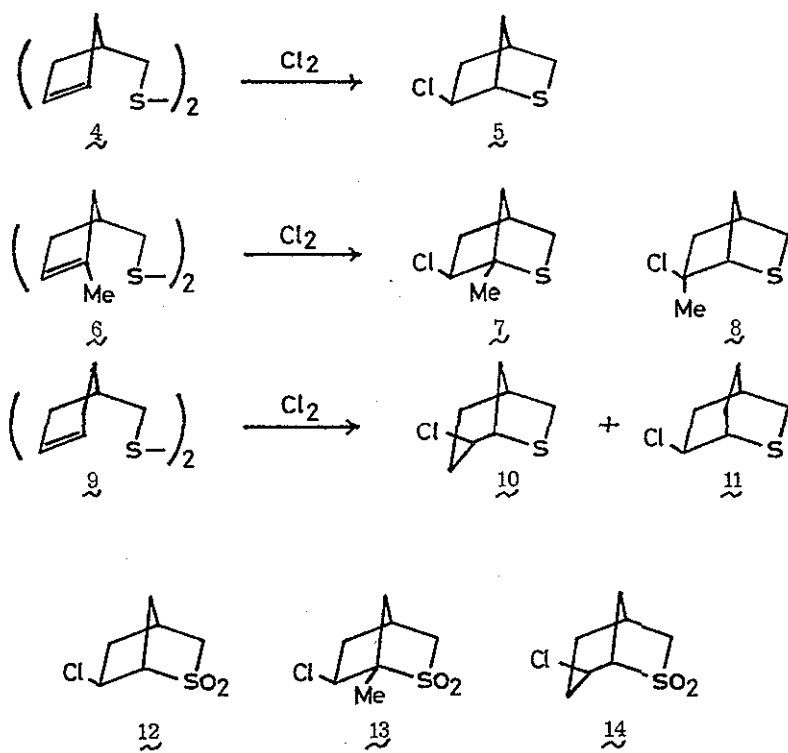
Rapid and stereospecific trans addition of sulfenyl halides to olefins<sup>1</sup> provide a powerful utilization to the synthesis of S-containing heterobicycles which usually require a long synthetic pathway. The intramolecular additions of sulfenyl chlorides (1) also proceeded smoothly and gave the corresponding cyclic  $\beta$ -chloro sulfides (2, 3) quantitatively (Scheme 1)<sup>2</sup>

The application of this reaction to the cyclic olefins (4, 6, 9) resulted in the quantitative formation of the corresponding bicyclic  $\beta$ -chloro derivatives (5, 7, 10) (Scheme 2). The procedure is very simple; e. g. the calculated volume of chlorine gas was introduced to a solution of disulfide in methylene dichloride or chloroform at -30~-50° by the aid of a hypodermic syringe. Careful evaporation of the solvent left the quantitative amount of the corresponding bicyclic chloride which was spectroscopically and gas chromatographically pure.

Scheme 1.



Scheme 2.



The disulfide (4) yielded a single product, which was identical with a compound prepared by another route.<sup>3</sup> Similarly, 6 gave a single isomer (7). No detection of 8 was observed. This result is extremely interesting because one may expect the major formation of 8. Probably, less stability of 8 than 7 may be due to strong repulsive interaction between 6-endo-methyl group and the lone pair electrons of the endo-side of the sulfur atom. The reaction of 9 with chlorine gave a mixture of 10 and 11 in a ratio of 69:31 as initial products.<sup>4</sup> However, rapid isomerization between both isomers trended toward a single isomer and only 10 was obtained.  $\beta$ -Chloro sulfide is usually so reactive that structural characterization was done as the corresponding  $\beta$ -chloro sulfone after oxidation with m-chloroperbenzoic acid: 12, mp. 99-99.5°; 13, mp. 141.5-142.5°; 14, mp. 183.5-184.5°; 14 (Cl = Br), mp. 131.5-132°.<sup>5</sup> Skeletal identification of 10, moreover, was confirmed by comparison of 14 (Cl = H), mp. 233.5-234.5° with that of reported value.<sup>6</sup>

The  $\beta$ -chloro sulfides (5, 7, 10) are important as synthetic intermediates because they can be directed to other derivatives easily; for example, hydrolysis (aqueous Na<sub>2</sub>CO<sub>3</sub>-acetone), methanolysis (MeOH), and acetolysis (AcOH-AcONa) gave the corresponding hydroxy, methoxy, and acetoxy derivatives in quantitative yields.

#### References and Footnotes

1. As a review: W. H. Mueller, Angew. Chem. Internat. Edit., **8**, 482 (1969).
2. S. Ikegami, J. Ohishi, and Y. Shimizu, Tetrahedron Letters, 3923 (1975).
3. 6-exo-Chloro-2-thianorbornane (5) was also prepared from HCl-addition

to 2-thia-5-norbornene which was synthesized by the cycloaddition of cyclopentadiene with thiophosgene followed by LAH-reduction of the resulting adduct. ( S. Ikegami, J. Ohishi, K. Tsuneoka, and S. Akaboshi, Unpublished results ).

4. The structure of 11 was determined on the basis of its chemical behavior and its pmr signal; that is, both compounds, 10 and 11, were mutually interconvertible and the proton of the  $\beta$ -position of 11 dioxides exhibited a signal at 4.86 ppm, multiplets of doublet,  $J = 9$  Hz.

5. Pmr data ( ppm from TMS in  $\text{CDCl}_3$  ) and elemental analyses of all  $\beta$ -chloro sulfones are indicated as follows: 12, pmr; 3.54 ( br. s.,  $\text{C}_1\text{-H}$  ), 4.74 ( d. d.,  $J_{5\text{en},6} = 6.5$  Hz,  $J_{5\text{ex},6} = 3$  Hz,  $\text{C}_6\text{-H}$  ). Anal. Calcd. for  $\text{C}_6\text{H}_9\text{O}_2\text{ClS}$ ; C, 39.89; H, 5.02; S, 17.75; Cl, 19.62. Found; C, 39.82; H, 5.11; S, 17.66; Cl, 19.51. 13, pmr; 4.74 ( d. d.,  $J_{5\text{en},6} = 6.5$  Hz,  $J_{5\text{ex},6} = 3$  Hz,  $\text{C}_6\text{-H}$  ). Anal. Calcd. for  $\text{C}_7\text{H}_{11}\text{O}_2\text{ClS}$ ; C, 43.19; H, 5.70; S, 16.47; Cl, 18.21. Found; C, 42.90; H, 5.80; S, 16.28; Cl, 18.22. 14, pmr; 4.61 ( m,  $\text{C}_4\text{-H}$  ). Anal. Calcd. for  $\text{C}_7\text{H}_{11}\text{O}_2\text{ClS}$ ; C, 43.19; H, 5.70; S, 16.47; Cl, 18.21. Found; C, 42.91; H, 5.80; S, 16.36; Cl, 18.39. 14 (  $\text{Cl} = \text{Br}$  ), pmr; 4.74 ( m,  $\text{C}_4\text{-H}$  ). Anal. Calcd. for  $\text{C}_7\text{H}_{11}\text{O}_2\text{BrS}$ ; C, 35.16; H, 4.64; S, 13.41; Br, 33.41. Found; C, 35.16; H, 4.71; S, 13.24; Br, 33.95.

6. S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead ( *J. Org. Chem.*, 22, 1590 (1957) ) report mp.  $236\text{-}237^\circ$  for 14 (  $\text{Cl} = \text{H}$  ) and mp.  $310^\circ$  for 11 dioxides (  $\text{Cl} = \text{H}$  ).

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