

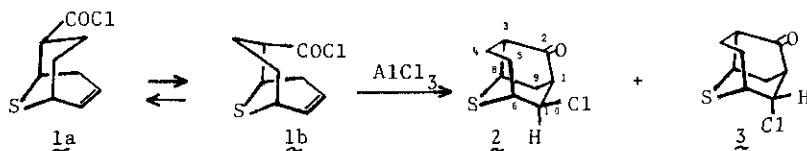
SYNTHETIC STUDIES ON SOME THIAMODIFIED ADAMANTANE SKELETONS

Tadashi Sasaki, Shoji Eguchi, Shinichi Yamada, and Hiroshi Ban
 Institute of Applied Organic Chemistry, Faculty of Engineering,
 Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Although much attention has been paid recently to bridged polycycles, studies on heteroanalogs seem to be not extensive compared to the carbocyclic systems. This might be due to the lack of efficient synthetic routes to the heteroanalogs. In this view point, we have been exploring synthetic routes to heteromodified adamantane skeletons as one of novel new-typed heterocycles.¹ We have now developed the following two routes to some thiamodified adamantane skeletons.

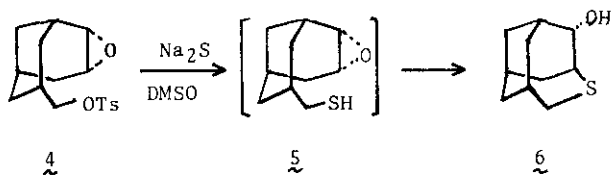
(i) Facile synthesis of 7-thiaprotoadamantane and related derivatives via a regio-specific and stereoselective intramolecular Friedel-Crafts reaction.

On heating under reflux in the presence of AlCl_3 , 9-thiabicyclo[3.3.1]non-2-ene-6-carboxylic acid chloride (1) gave 10-eq-chloro- (2) and 10-ax-chloro-7-thiaprotoadamantan-2-one (3) as the cyclization products. 7-Thiaprotoadamantane and some related derivatives were prepared from 2 and 3.



(ii) Facile synthesis of 4-thiahomoadamantane skeleton and related derivatives via a $\text{C}_9+\text{C}_1\text{S}$ type cyclization.

On treatment with Na_2S , 6,7-epoxybicyclo[3.3.1]nonan-3-endo-carbinyl tosylate (4) gave 2-anti-hydroxy-4-thiahomoadamantane (6) as an intramolecular cyclization product of 5. No regioisomer was produced, however, thiahomoprotoadamantane derivatives were produced by a novel skeletal rearrangement of 6 on PDC oxidation.



Reference

(1) Sasaki, T. *Heterocycles* 1979, 13, 531.