SYNTHETIC STUDIES ON SOME THIAMODIFIED ADAMANTANE SKELETONS

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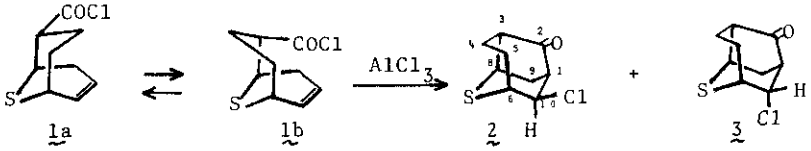
Although much attention has been paied recently to bridged polycycles, studies on heteroanalogs seem to be not extensive compared to the carbocyclic systems. This might be due to the lack of efficient synthetic routes to the heteroanalogs. In this view point, we have been exploring synthetic routes to 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 regiospecific and stereoselective intramolecular Friedel-Crafts reaction.

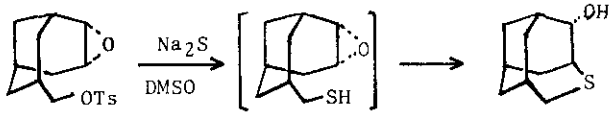
On heating under reflux in the presence of $AlCl_3$, 9-thiabicyclo[3.3.1]non-2-ene-6-carboxylic acid chloride (1) gave 10-eq-chloro- (2) and 10-ax-chloro-7-thiaprotoadamantan-2-one (3) as the cyclization products. 7-Thiaprotoadamantane and some related derivatives were prepared from 2 and 3.



1a 1b 2 3

(ii) Facile synthesis of 4-thiahomoadamantane skeleton and related derivatives via a C_9+C_1S 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.



4 5 6

Reference

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