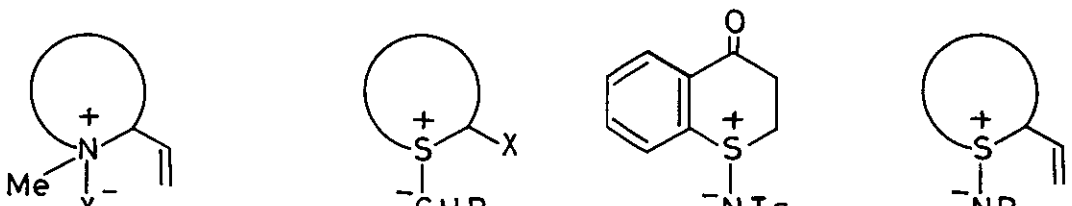
THERMAL RING EXPANSION OF 2-VINYLTHIACYCLOALKANE N-IMIDES BY [2,3]-SIGMATROPIC REARRANGEMENT

Haruki Sashida and Takashi Tsuchiya*

School of Pharmacy, Hokuriku University,
Kanagawa-machi, Kanazawa 920-11, Japan

Abstract —— The thermolysis of the 2-vinylthiacyclo-pentane, -hexane, and -heptane N-(p-toluenesulfonyl)imides (7) resulted in the [2,3]-sigmatropic rearrangement to give the corresponding ring expansion products (8).

The thermal sigmatropic rearrangements of cyclic allyl amine ylides (1) have been well studied in connection with those of related open chain compounds.[1] The amine N-ylides (1a)[2] and N-imides (1b)[3] are known to undergo [2,3]-sigmatropic rearrangement to give the corresponding ring expansion products, in contrast, the thermolysis of the amine N-oxides (1c)[4] results in a Stevens-type [1,2] rearrangement predominantly. The thiacycloalkane S-ylides (2a)[2,5] and (2b)[6] also undergo thermal [2,3] rearrangement. As regards to sulfonium imides, Tamura et al.[7] have reported that treatment of the thiochroman-4-one S-imides (3) with base gives tetrahydro-1,2-benzothiazepin-5-ones by a novel rearrangement via Hofmann



(1a) X=CHR
(1b) X=NCOR
(1c) X=O

(2a) X=
(2b) X=

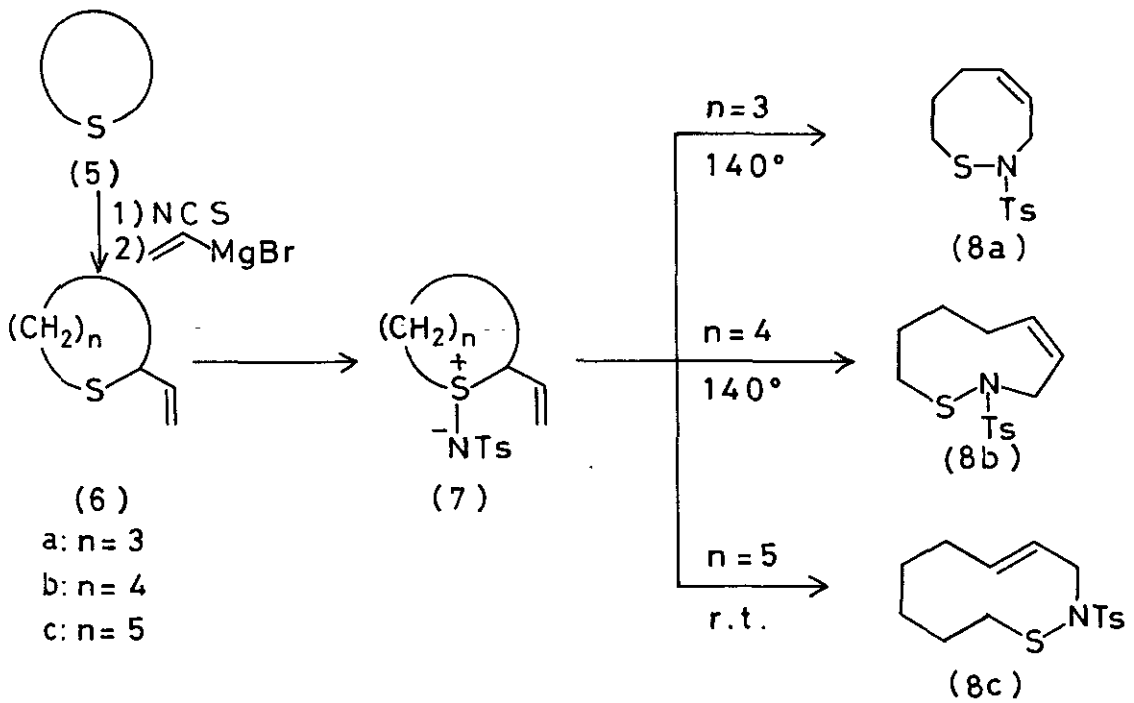
(3)

(4)

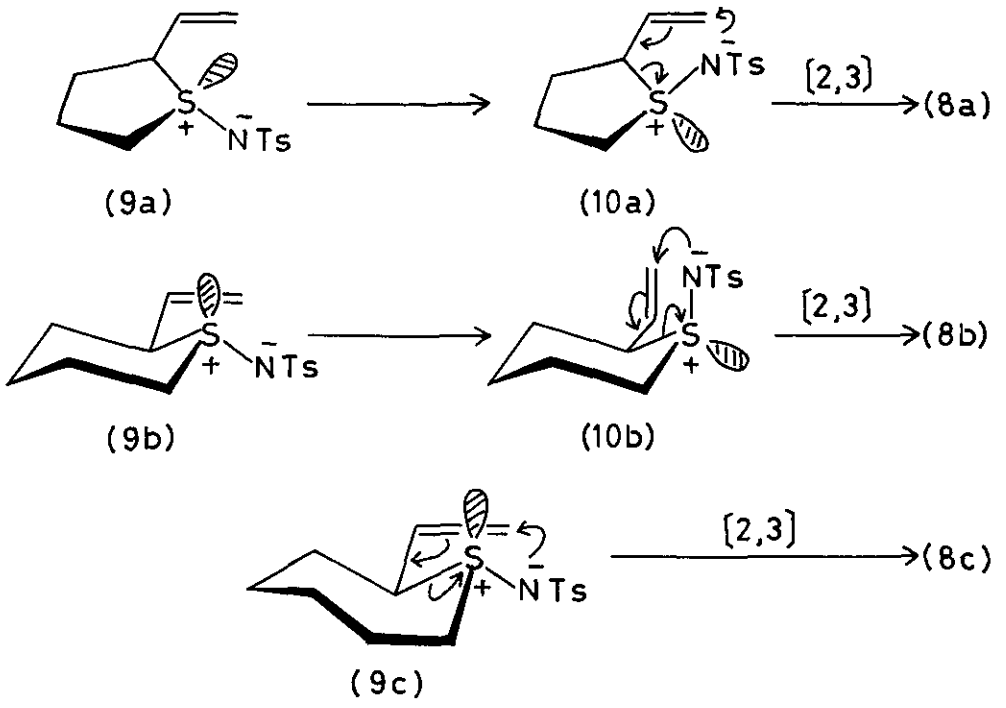
Scheme 1

elimination followed by cyclization. However, sigmatropic rearrangement have not been reported for cyclic sulfonium imides, although open-chain allyl sulfonium imides are known to undergo a [2,3]-sigmatropic rearrangement.[8] Therefore, we examined the thermal behavior of the cyclic sulfonium imides (4).

The 2-vinylthiacycloalkanes (6) were prepared from the corresponding five- (5a), six- (5b), and seven-membered (5c) thiacycloalkanes by successive treatment with N-chlorosuccimide (NCS) and vinylmagnesium bromide according to the reported method.[9] Treatment of the 2-vinylthiacyclo-pentane (6a) and -hexane (6b) with chloramine T[7] in methanol at room temperature gave the corresponding p-toluene-sulfonylimides (7a: mp 113 – 115 °C; 7b: mp 91 – 93 °C) in 60 – 70% yields as the sole diastereomers, respectively. Thermolysis of the S-imides (7a,b) in refluxing xylene for 4 h gave the ring expansion products (8a: mp 68 – 69 °C; 8b: viscous oil) in ca. 60% yields. The geometry of the double bond in the products (8a,b) was proved to be cis by the vicinal coupling constant (J = 10 Hz) in the ^{1}H-NMR spectra. On the other hand, treatment of the seven-membered thiacycloalkane (6c) with chloramine T at room temperature resulted in the formation



Scheme 2



Scheme 3

of the ring expansion products (8c: m.p. 123 – 124 °C, J = 15 Hz, trans) directly in 66% yield and the S-imide (7c) could not be isolated. This result indicates that the rearrangement of the seven-membered ring imide (7c) occurs readily below room temperature.

This ring expansion reaction may clearly proceed via [2,3]-sigmatropic rearrangement, analogous to the cases of the amine N-ylides (1a,b)[2,3] and the thiane S-ylides (2).[5] The cyclic thiane alkylation is known to occur by apparent equatorial attack on the most stable chair conformer,[10] so the stereochemistry of the imides (7) isolated seems to be trans as shown in the structures (9), although specific evidence on this point is not available. In the case of the five-membered ring imide (9a), the thermolysis may proceed by initial pyramidal inversion to the cis-diastereomer (10a), which then undergo rearrangement to give the product (8a) having a cis double bond, analogous to the thiacyclopentane S-ylide.[5] The six-membered ring imide (9b) also rearranges via 10b to give the cis-product (8b), contrast to the thiacyclohexane S-ylide whose trans-diasteromer rearranges without inversion to give the product having a trans double bond.[2]

In the case of the seven-membered ring imide, the trans-diastereomer (9c) can undergo rearrangement, thus the reaction occurs at a low temperature and the ring expansion product has a trans geometry.

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