RING EXPANSION OF 2-ETHYNYLTHIACYCLOALKANES VIA SULFONIUM YLIDES
BY [2,3]-SIGMATROPIC REARRANGEMENT

Haruki Sashida and Takashi Tsuchiya

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

Abstract — Treatment of the O-ethynyl cyclic sulfonium salts (8) with DBU gave the corresponding ring-expansion products (11), presumably via the allenic intermediates (10) derived from the initially formed S-ylides (9) by [2,3]-sigmatropic rearrangement.

Ylides have been used as reactive intermediates in organic syntheses, particularly in reactions involving either thermal1 or photochemical2 intramolecular rearrangements. The thermal sigmatropic rearrangements of the cyclic allyl sulfonium ylides (1) have been well investigated,3,4 as have those of the cyclic amine N-ylides (2a),5 N-imides (2b),6 and N-oxides (2c).7 On the other hand, the open-chain propargylic S-ylides (3a)8 and N-oxides (3b)9 are known to undergo [2,3]-sigmatropic rearrangement to give allenic compounds.

Scheme 1
Therefore, we were interested in examining the thermal behavior of ethynyl cyclic ylides and have already reported the ring-conversion of 2-ethynylpyridine N-imides (4) into 3-azaindolizines\textsuperscript{10} and that of 6-ethynyl-1,2,5,6-tetrahydropyridine N-imides (5) into dihydrodiazonines.\textsuperscript{11} In connection with these results, we studied the thermolysis of cyclic sulfonium ylides having an ethynyl group in the 0\textsuperscript{1} position in the ring and now report our new results.

The ethynyl thiacycloalkanes (7Aa-d, 7Ba-c, and 7Ca-c) were prepared from the corresponding five- (6A), six- (6B), and seven-membered (6C) thiacycloalkanes by successive treatment with N-chlorosuccinimide (NCS) and the ethynyl Grignard reagents in 50-80\% yields, respectively, according to the reported method.\textsuperscript{12} Treatment of 7 with ethoxycarbonylmethyl trifluoromethanesulfonate (TfOCH\textsubscript{2}C0\textsubscript{2}Et)\textsuperscript{5} in acetonitrile gave the corresponding sulfonium salts (8) quantitatively. The salts (8) thus obtained were treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) as the base in acetonitrile with stirring for 10-15 min at room temperature to give the corresponding ring-expansion products (11) in the yields shown in Scheme 2, respectively.\textsuperscript{13} This three-carbon ring enlargement reaction of 8 into 11 may involve the allenic intermediates (10) which might be derived from the initially formed S-ylides (9) by the [2,3]-sigmatropic rearrangement with the ethynyl groups by analogy with the cases of the open-chain propargylic ylides (3)\textsuperscript{8,9} and the tetrahydropyridine N-imides (5).\textsuperscript{11} The allenic intermediates (10) may then undergo 1,3-hydrogen shift to give the products (11) with a conjugated diene system.

In the present case, both key intermediates (9) and (10) could not be isolated in contrast to the cases of 3 and 5, in which either ylides or allenic compounds were isolated. This result shows that the S-ylides (9) are very reactive toward the rearrangement analogous to those observed for the cyclic allyl S-ylides (1) and the cyclic allenic compounds readily undergo 1,3-hydrogen shift to more stable dienes. The geometry of the double bonds (C\textsubscript{4} = C\textsubscript{5}) in all products (11) was proved to be cis by the vicinal coupling constant (J\textsubscript{4,5} = 11 Hz) in the \textsuperscript{1}H-NMR spectra. In addition, the same products (11) were obtained when potassium ethoxide or t-butoxide was used as a base, but the yields of 11 were lower than those for the present DBU-induced reactions.

Attempts to prepare fully unsaturated nine-membered cyclic sulfides, thionines, from 11B and further synthetic applications of this ring-expansion reaction to other systems are under investigation.
Yields of the Ring-expansion Products (11) from 8

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\begin{align*}
(11A) & \quad (11B) & \quad (11C) \\
a: R = Me & \quad 38\% & \quad 73\% & \quad 62\% \\
b: R = n-Bu & \quad 40\% & \quad 75\% & \quad 63\% \\
c: R = Ph & \quad 68\% & \quad 61\% & \quad 75^i) \\
d: R = H & \quad 33\% & \quad - & \quad - \\
i) mp 94-95 \degree C. All other compounds (11) are yellow oil. \\
ii) The salts (8B-d) and (8C-d) were not prepared.
\end{align*}
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Scheme 2
REFERENCES AND NOTES


13. Satisfactory elemental analyses and spectral data were obtained for all new compounds reported.

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