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

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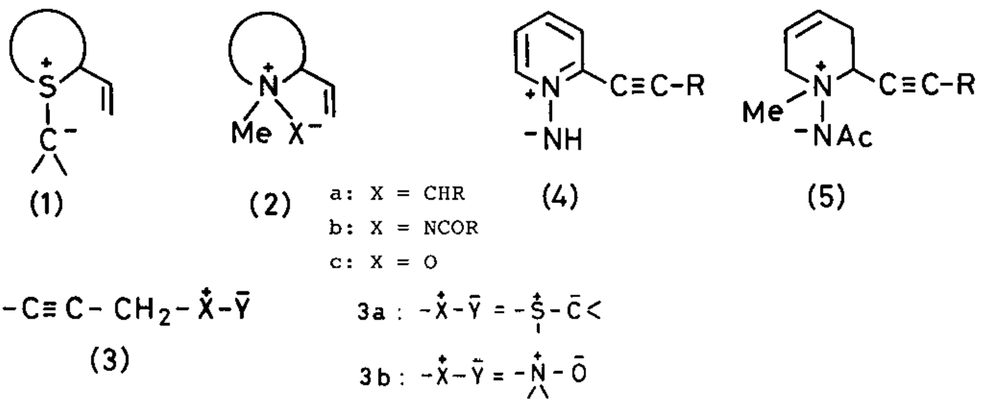
Abstract ——— Treatment of the α-ethynyl cyclic sulfonium salts (8) with DBU gave the corresponding ring-expansion products (11), presumably via the allenic intermediates (10) derived from the initially formed S-ylides (9) by [2,3]-sigmatropic rearrangement.

Ylides have been used as reactive intermediates in organic syntheses, particularly in reactions involving either thermal[1] or photochemical[2] 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.



$-C\equiv C-CH_2-\overset{+}{X}-\overset{-}{Y}$

3a : $-\overset{+}{X}-\overset{-}{Y} = -\overset{+}{S}-\overset{-}{C}<$

3b : $-\overset{+}{X}-\overset{-}{Y} = -\overset{+}{N}-\overset{-}{O}$

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[10] and that of 6-ethynyl-1,2,5,6-tetrahydropyridine N-imides (5) into dihydrodiazonines.[11] In connection with these results, we studied the thermolysis of cyclic sulfonium ylides having an ethynyl group in the α-position in the ring and now report our new results.

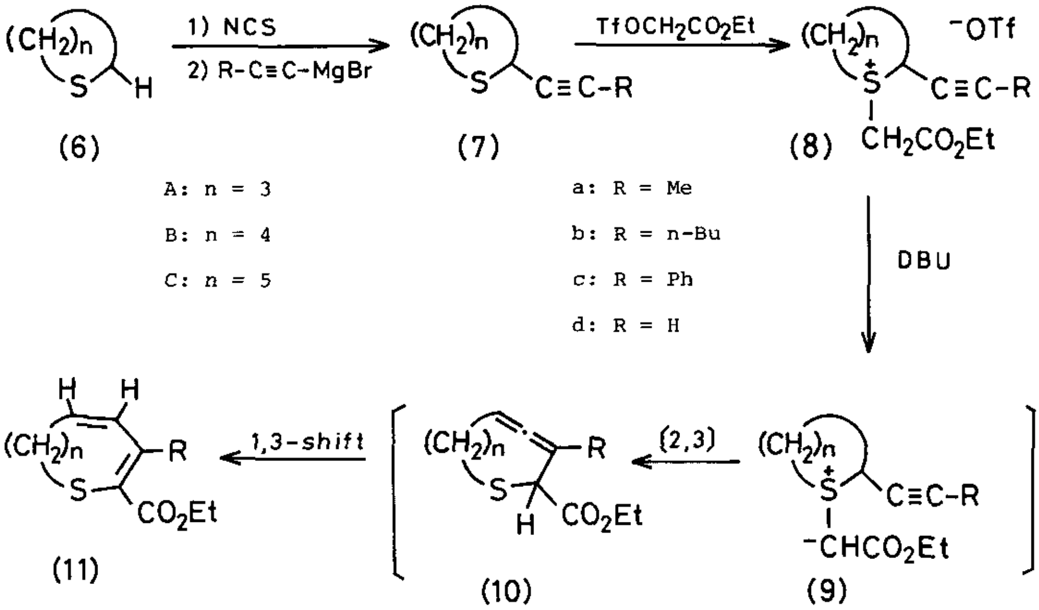
The ethynyl thiacycloalkanes (7Aa-d, 7Ba-c, and 7Ca-c) were prepared from the corresponding five- (6A), six- (6B), and seven-membered (6C) thiacycloalkanes by successive treatment with N-chlorosuccinimide (NCS) and the ethynyl Grignard reagents in 50-80% yields, respectively, according to the reported method.[12] Treatment of 7 with ethoxycarbonylmethyl trifluoromethanesulfonate ($TfOCH_2CO_2Et$)[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.[13]

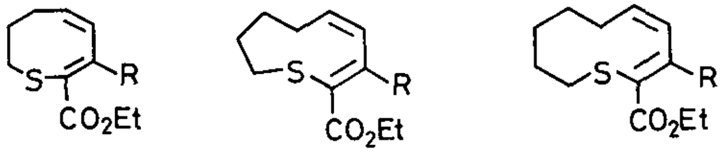
This three-carbon ring enlargement reaction of 8 into 11 may involve the allenic intermediates (10) which might be derived from the initially formed S-ylides (9) by the [2,3]-sigmatropic rearrangement with the ethynyl groups by analogy with the cases of the open-chain propargylic ylides (3)[8,9] and the tetrahydropyridine N-imides (5).[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 ($C_4 = C_5$) in all products (11) was proved to be cis by the vicinal coupling constant ($J_{4,5}$= 11 Hz) in the ^1H-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



		(11A)	(11B)	(11C)
a:	R = Me	38%	73%	62%
b:	R = n-Bu	40%	75%	63%
c:	R = Ph	68%	61%	75% i)
d:	R = H	33%	— ii)	—

i) mp 94-95 °C. All other compounds (11) are yellow oil.

ii) The salts (8B-d) and (8C-d) were not prepared.

Scheme 2

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