

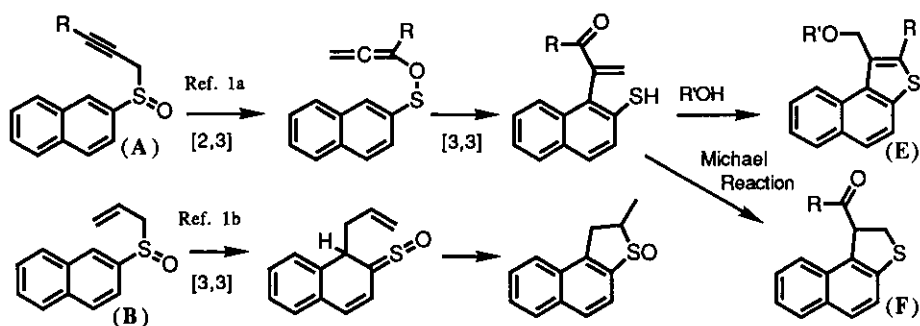
INTRAMOLECULAR REARRANGEMENT OF 2-(2-PROPYNYL-SULFINYL)TROPONE AND ITS HOMOLOGUES TO CYCLO-HEPTA[b]THIOPHEN-8-ONES

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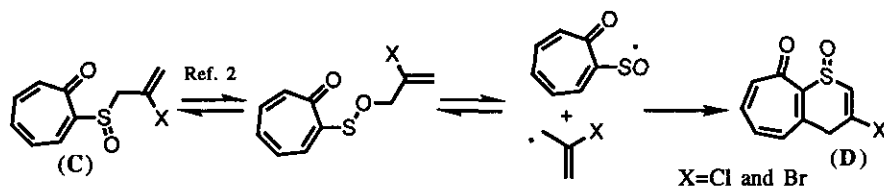
Abstract—Thermal reaction of 2-(2-alkynylsulfinyl)tropones afforded 3-acylcyclohepta[b]thiophen-8-ones, their dihydro derivatives as well as deacylated 2,3-dihydrocyclohepta[b]thiophen-8-ones. Deuterium labelling experiment confirmed the intramolecular reaction mode, which is different from the mechanism reported for the reaction of 2-(2-propenylsulfinyl)tropones.

Thermal rearrangements of allyl- and propargylsulfinylarenes are of considerable interest. In 1974, Makisumi *et al.*¹ reported sharply contrasting results between (2-alkynylsulfinyl)arenes (A) and (2-alkenylsulfinyl)arenes (B) to give products with or without [2,3] sigmatropic S-O fission.



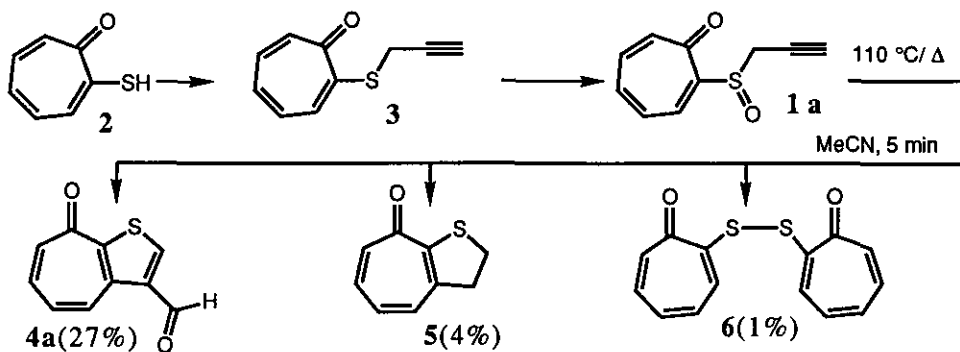
In 1984, we found that thermolysis of 2-(2-halo-2-propenylsulfinyl)tropones (C) to 3-

halo-1-oxo-4H-cyclohepta[b]thiopyran-9-ones (D) proceeded via radical chain process.² The cross-over labelling experiments indeed confirmed this intermolecular pathway.



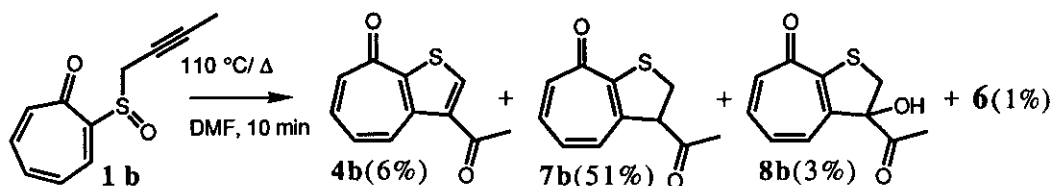
Very mild conditions of our rearrangement³ when compared with those employed by Makisumi and the different mode of product formation are worthy of further investigation of 2-(2-alkynylsulfinyl)tropones (1), of which the results are described herein. The substrates (1) were prepared by propargylation of 2-mercaptotroponone (2)⁴ and subsequent *m*-chloroperbenzoic acid oxidation of the resultant 2-(2-alkynylthio)tropones (3).⁵

An acetonitrile solution⁶ of 2-(2-propynylsulfinyl)troponone⁷ (1a, mp 135-136 °C) was heated in a sealed tube at 110 °C for 5 min. The products (4-6) thus formed were isolated via high pressure liquid chromatography; the major product was identified as 3-formylcyclohepta[b]thiophen-8-one (4a, mp 197-199 °C) on the basis of the ¹H nmr analysis. Also identified were 2,3-dihydrocyclohepta[b]thiophen-8-one (5, mp 104-105 °C) and the known bis(2-troponyl) disulfide [6, mp 224-226 °C (lit.,⁸ mp 206 °C)], a radical recombination product.

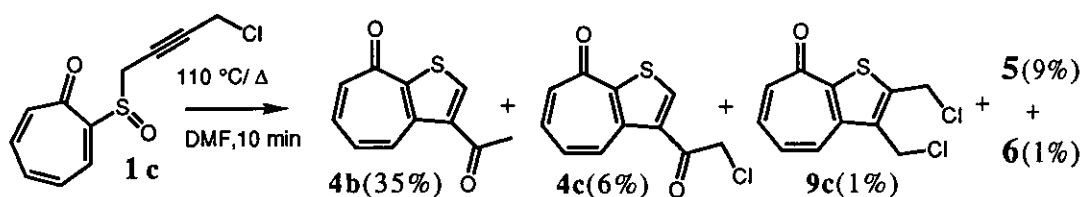


A similar treatment of 2-(2-butynylsulfinyl)troponone (1b, mp 124-126 °C) in *N,N*-dimethylformamide (DMF) afforded 3-acetylcyclohepta[b]thiophen-8-one (4b, mp 160-

161 °C) and **6**, along with new types of products, 3-acetyl-2,3-dihydrocyclohepta[b]-thiophen-8-one (**7b**, mp 96-97 °C) and 3-acetyl-3-hydroxy-2,3-dihydrocyclohepta[b]-thiophen-8-one (**8b**, a yellow oil). The DDQ dehydrogenation of the major product (**7b**) gave **4b** quantitatively.



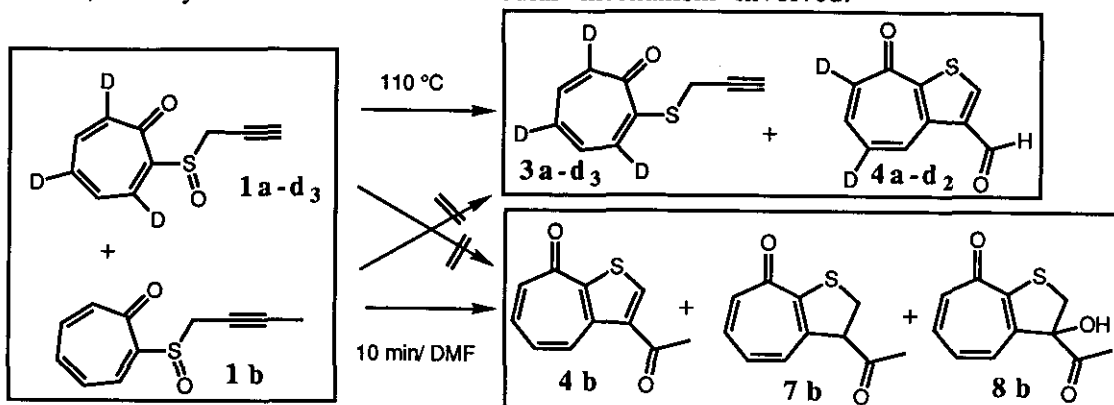
An extension of the reaction to 2-(4-chloro-2-butynylsulfinyl)troponone (**1c**, mp 97-99 °C) in DMF afforded similar thermolysates; 3-chloroacetylcyclohepta[b]thiophen-8-one (**4c**, mp 215-217 °C), **5**, and **6**. However, the presence of the allylic chlorine atom caused a complicated product distribution to give a chlorine-free **4b** and a dichloro compound, 2,3-bis(chloromethyl)cyclohepta[b]thiophen-8-one (**9c**, mp 164-166 °C), with an inferior material balance.



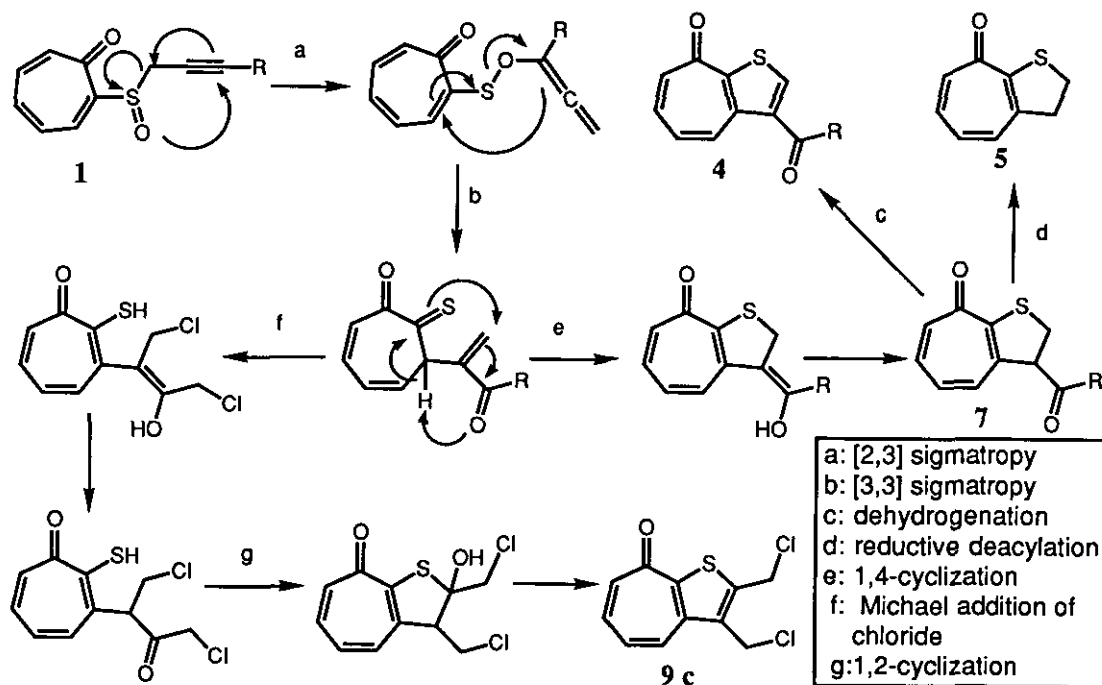
A marked contrast in the product distributions of the present results to those of **C**, previously investigated, suggests different mechanisms involved. Although the formation of the same compounds (**5** and **6**) from **1a** and **1c**, and the concomitant formation of **4** and **7** having different oxidation states from **1b** seem to suggest a radical mechanism, the absence of the thiopyran derivatives might be difficult to explain in terms of the radical dissociation-recombination mechanism.

Thus, to differentiate the intra- and inter-molecular processes, a cross-over experiment by an aid of deuterio derivative was then carried out. An equimolar mixture of **1a**-3,5,7- d_3 and **1b** was heated in DMF for 10 min, the mixture was fractionated in a

similar manner, and the products were analyzed mass-spectrometrically. The deuterium distribution patterns of the products (4a, 4b, 7b and 8b) along with deoxygenated 3a, clearly showed the intramolecular mechanism involved.



The [2,3] sigmatropy and the subsequent oxa-thia-Cope rearrangement ([3,3] sigmatropy) of these reactants are quite rapid, and the formation of 3-acylcyclohepta[b]-thiophen-8-ones (**4**) can be depicted as follows:



At the same time, the difference of the type of products between A and 1 should be

mentioned here: after the [2,3] and [3,3] sigmatropies, A gave both the 1,2- and 1,4-cyclization products (E and F), but all the products are in the same oxidation state. On the other hand, from 1 only 1,4-cyclization products (4, 5 and 8) were identified, except for 9c from 1c, and their oxidation states are different. This may be due to the difference of the solvents used; Makisumi¹ used protic solvents, and their 1,4-cyclization products showed incorporations of the solvent residues. We used aprotic solvents to prevent an incorporation of the solvent. However, in the reaction with 1c, liberated chloride serves as a nucleophile to give 9c via a Michael addition. Therefore, in the absence of nucleophilic species in the medium, intramolecular cyclization to 3-acylcyclohepta[b]thiophen-8-ones occurred preferentially. It may also be suggested that the proto-cyclization products, 7 or their equivalents, undergo radical abstraction process to give various types of products. As the acyl groups of unidentified 3-formyl- and 3-chloroacetyl-2,3-dihydrocyclohepta[b]thiophen-8-ones (7a and 7c) are radical sensitive, this radical process may be attributable to poor material balance observed particularly in the reaction with 1a and 1c.

Finally, it is interesting that, unlike the cases of A and B, the thermolysis of 1 and C resulted in the formation of different heterocycles, cyclohepta[b]thiophen-8-ones (4, 5, 7, 8, and 9) and cyclohepta[b]thiopyran-9-ones (D).

REFERENCES AND NOTES

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2. H. Takeshita, H. Motomura, and H. Mametsuka, Heterocycles, 1984, 22, 467.
3. In ref. 1, Makisumi carried out the reaction in protic solvents, e.g., EtOH and AcOH, at 80 °C for 1 to 2 h. At least in cases of our C and 1, the longer reaction time caused the more decomposition.
4. H. Takeshita, H. Mametsuka, and K. Uchida, Heterocycles, 1983, 20, 1709.
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6. After a survey of the reaction solvents, MeCN gave the highest yields for this 1a. In DMF, the yields of 4a, 5, and 6 were 14, 4, and 1%, respectively. The reaction in

non-polar solvents, such as benzene, caused an extensive decomposition.

7. All new compounds were fully characterized. The representative ^1H nmr spectral data (CDCl_3) are collected as follows:

1a: $\delta=2.35(1\text{H}, \text{t}, J=2.6 \text{ Hz}), 4.00(1\text{H}, \text{dd}, J=16.5, 2.6 \text{ Hz}), 4.01(1\text{H}, \text{dd}, J=16.5, 2.6 \text{ Hz}), 7.11(1\text{H}, \text{dm}, J=11.6 \text{ Hz}), 7.25(1\text{H}, \text{ddm}, J=10.2, 8.4 \text{ Hz}), 7.34-7.44(2\text{H}, \text{m}),$ and $7.80(1\text{H}, \text{dd}, J=10.2, 1.1 \text{ Hz}).$

1b: $\delta=1.79(3\text{H}, \text{td}, J=2.6, 0.7 \text{ Hz}), 3.87(1\text{H}, \text{dq}, J=16.1, 2.6 \text{ Hz}), 3.98(1\text{H}, \text{dq}, J=16.1, 2.6 \text{ Hz}), 7.10(1\text{H}, \text{dd}, J=11.7, 0.7 \text{ Hz}), 7.23(1\text{H}, \text{ddm}, J=10.3, 8.4 \text{ Hz}), 7.23-7.43(2\text{H}, \text{m}),$ and $7.77(1\text{H}, \text{dm}, J=9.8 \text{ Hz}).$

1c: $\delta=4.04(2\text{H}, \text{m}), 4.08(2\text{H}, \text{m}), 7.11(1\text{H}, \text{dm}, J=11.4 \text{ Hz}), 7.26(1\text{H}, \text{ddm}, J=10.6, 8.4 \text{ Hz}), 7.41(2\text{H}, \text{ddm}, J=11.4, 8.4 \text{ Hz}),$ and $7.81(1\text{H}, \text{d}, J=10.6 \text{ Hz}).$

4a: $\delta=7.10(1\text{H}, \text{ddd}, J=11.4, 8.1, 1.1 \text{ Hz}), 7.13(1\text{H}, \text{dd}, J=12.1, 1.1 \text{ Hz}), 7.38(1\text{H}, \text{ddd}, J=12.1, 8.1, 1.1 \text{ Hz}), 8.57(1\text{H}, \text{s}), 8.75(1\text{H}, \text{dd}, J=11.4, 1.1 \text{ Hz}),$ and $10.15(1\text{H}, \text{s}).$

4b: $\delta=2.68(3\text{H}, \text{s}), 7.06(1\text{H}, \text{ddd}, J=11.4, 8.4, 1.1 \text{ Hz}), 7.10(1\text{H}, \text{dd}, J=12.1, 1.1 \text{ Hz}), 7.36(1\text{H}, \text{ddd}, J=12.1, 8.4, 1.1 \text{ Hz}), 8.53(1\text{H}, \text{s}),$ and $8.78(1\text{H}, \text{dd}, J=11.4, 1.1 \text{ Hz}).$

4c: $\delta=4.70(2\text{H}, \text{s}), 7.08(1\text{H}, \text{ddd}, J=11.4, 8.5, 1.1 \text{ Hz}), 7.11(1\text{H}, \text{dd}, J=12.4, 1.1 \text{ Hz}), 7.38(1\text{H}, \text{ddd}, J=12.4, 8.5, 1.1 \text{ Hz}), 8.57(1\text{H}, \text{s}),$ and $8.67(1\text{H}, \text{dd}, J=11.4, 1.1 \text{ Hz}).$

7b: $\delta=2.31(3\text{H}, \text{s}), 3.48(1\text{H}, \text{dd}, J=12.1, 4.4 \text{ Hz}), 3.58(1\text{H}, \text{dd}, J=12.1, 9.5 \text{ Hz}), 4.48(1\text{H}, \text{dd}, J=9.5, 4.4 \text{ Hz}), 6.90(1\text{H}, \text{ddd}, J=11.0, 8.4, 1.1 \text{ Hz}), 7.01(1\text{H}, \text{dd}, J=11.0, 1.1 \text{ Hz}), 7.02(1\text{H}, \text{dd}, J=12.4, 1.5 \text{ Hz}),$ and $7.23(1\text{H}, \text{ddd}, J=12.4, 8.4, 1.5 \text{ Hz}).$

5: $\delta=3.24(2\text{H}, \text{t}, J=8.5 \text{ Hz}), 3.63(2\text{H}, \text{t}, J=8.5 \text{ Hz}), 6.83(1\text{H}, \text{ddd}, J=11.0, 8.4, 1.1 \text{ Hz}), 7.01(1\text{H}, \text{dd}, J=12.1, 1.1 \text{ Hz}), 7.03(1\text{H}, \text{dd}, J=11.0, 1.1 \text{ Hz}),$ and $7.17(1\text{H}, \text{ddd}, J=12.1, 8.4, 1.1 \text{ Hz}).$

8b: $\delta=2.36(3\text{H}, \text{s}), 3.41(1\text{H}, \text{d}, J=13.2 \text{ Hz}), 3.49(1\text{H}, \text{d}, J=13.2 \text{ Hz}), 5.17(1\text{H}, \text{s}), 6.67(1\text{H}, \text{dd}, J=10.6, 1.1 \text{ Hz}), 6.94(1\text{H}, \text{dd}, J=10.6, 8.4, 0.7 \text{ Hz}), 7.06(1\text{H}, \text{dd}, J=12.1, 0.7 \text{ Hz}),$ and $7.26(1\text{H}, \text{ddd}, J=12.1, 8.4, 1.1 \text{ Hz}).$

9c: $\delta=4.81(2\text{H}, \text{s}), 4.86(2\text{H}, \text{s}), 7.06(1\text{H}, \text{ddd}, J=11.0, 8.4, 1.1 \text{ Hz}), 7.09(1\text{H}, \text{dd}, J=12.1, 1.1 \text{ Hz}), 7.34(1\text{H}, \text{ddd}, J=12.1, 8.4, 1.1 \text{ Hz}),$ and $7.61(1\text{H}, \text{dd}, J=11.0, 1.1 \text{ Hz}).$

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