INTRAMOLECULAR REARRANGEMENT OF 2-(2-PROPYNYLSULFINYL)TROPONE AND ITS HOMOLOGUES TO CYCLOHEPTA[b]THIOPHEN-8-ONES

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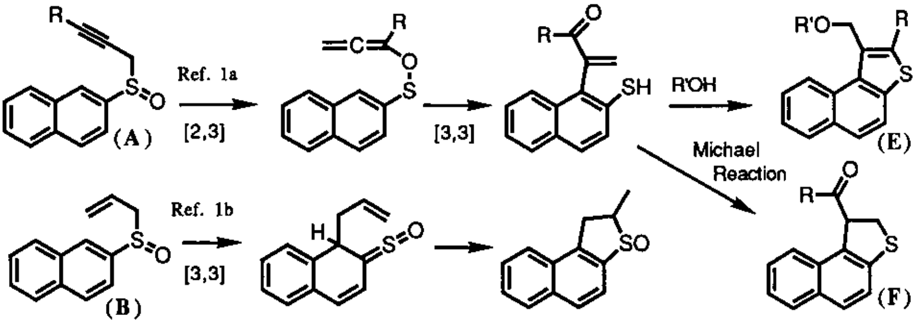
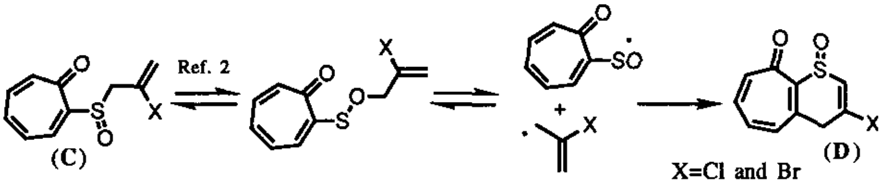
Abstract—Thermal reaction of 2-(2-alkynylsulfinyl)tropones afforded 3-acylcyclohepta[b]thiophen-8-ones, their dihydro derivatives as well as deacylated 2,3-dihydrocyclohepta[b]thiophen-8-ones. Deuterium labelling experiment confirmed the intramolecular reaction mode, which is different from the mechanism 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-alkynysulfinyl)arenes (**A**) and (2-alkenylsulfinyl)arenes (**B**) to give products with or without [2,3] sigmatropic S-O fission.



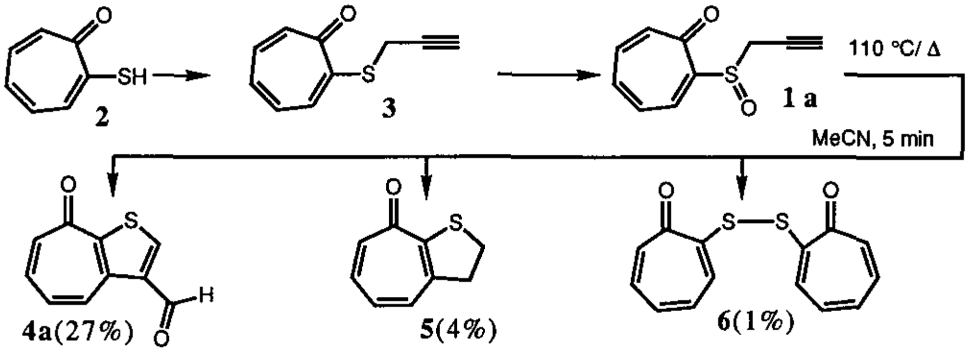
In 1984, we found that thermolysis of 2-(2-halo-2-propenylsulfinyl)tropones (**C**) to 3-

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.



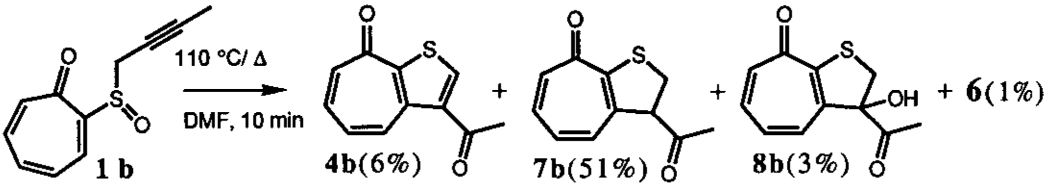
Very mild conditions of our rearrangement[3] when compared with those employed by Makisumi and the different mode of product formation are worthy of further investigation of 2-(2-alkynylsulfinyl)tropones (1), of which the results are described herein. The substrates (1) were prepared by propargylation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

An acetonitrile solution[6] of 2-(2-propynylsulfinyl)tropone[7] (**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.

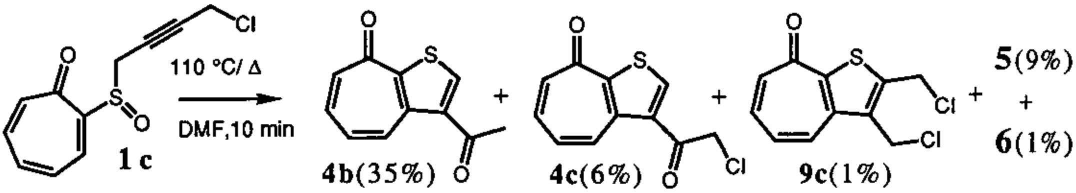


A similar treatment of 2-(2-butynylsulfinyl)tropone (**1b**, mp 124-126 °C) in N,N-dimethylformamide (DMF) afforded 3-acetylcyclohepta[b]thiophen-8-one (**4b**, mp 160-

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.

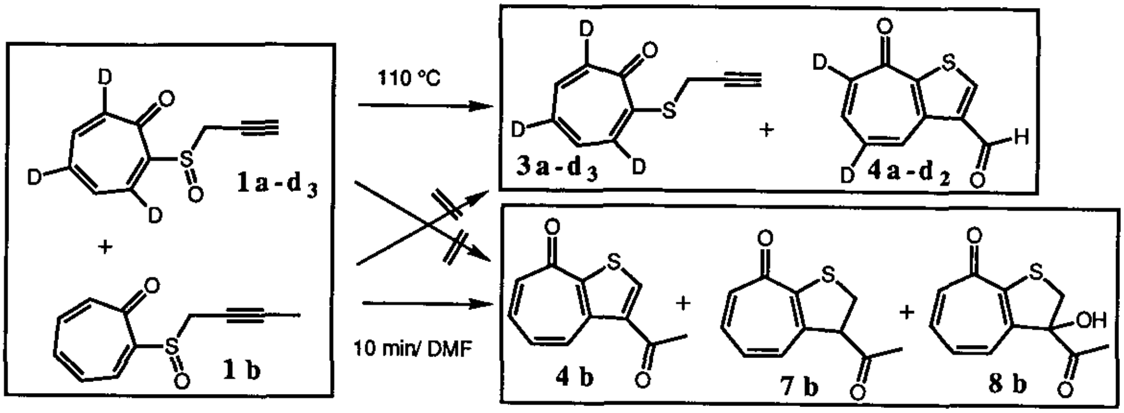


An extension of the reaction to 2-(4-chloro-2-butynylsulfinyl)tropone (**1c**, mp 97-99 °C) in DMF afforded similar thermolysates; 3-chloroacetylcyclohepta[b]thiophen-8-one (**4c**, mp 215-217 °C), **5**, and **6**. However, the presence of the allylic chlorine atom caused a complicated product distribution 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.

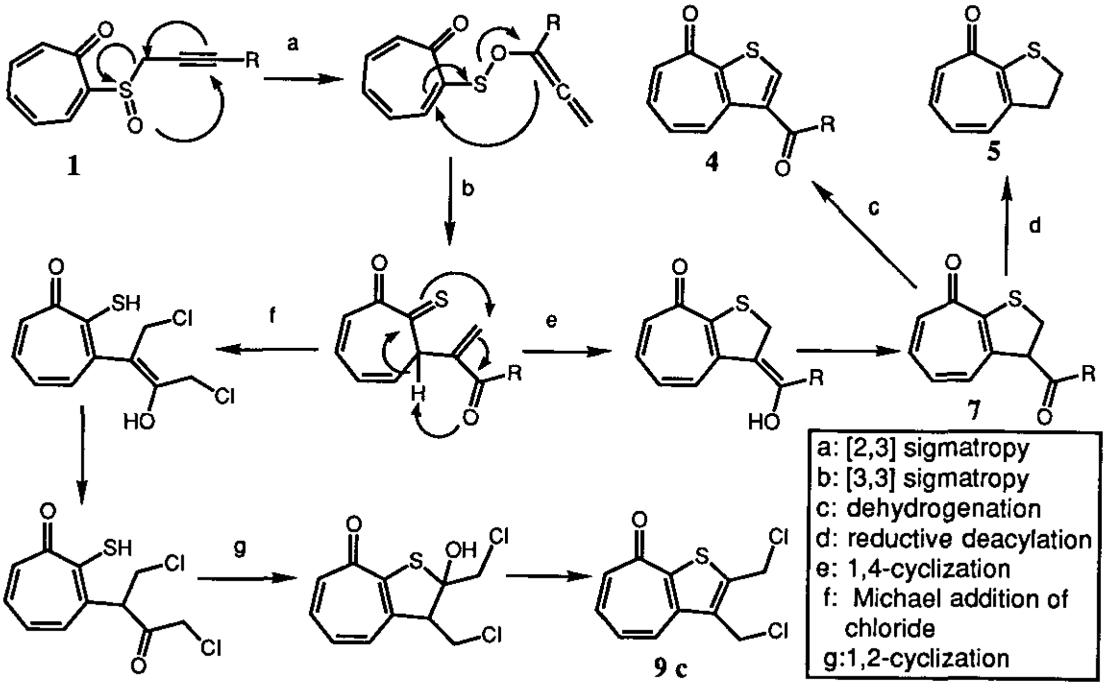


A marked contrast in the product distributions of the present results to those of **C**, previously investigated, suggests different mechanisms involved. Although the formation of the same compounds (**5** and **6**) from **1a** and **1c**, and the concomitant formation of **4** and **7** having different 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; Makisumi[1] 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

1. a) Y. Makisumi and S. Takada, J. Chem. Soc., Chem. Commun., **1974**, 848; 1b) Y. Makisumi, S. Takada, and Y. Matsukura, J. Chem. Soc., Chem. Commun., **1974**, 850.

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.

5. H. Takeshita, H. Motomura, and H. Mametsuka, Bull. Chem. Soc. Jpn., 1984, **57**, 3157.

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 ^{1}H nmr spectral data ($CDCl_3$) are collected as follows:

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

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

1c: δ=4.04(2H, m), 4.08(2H, m), 7.11(1H, dm, J=11.4 Hz), 7.26(1H, ddm, J=10.6, 8.4 Hz), 7.41(2H, ddm, J=11.4, 8.4 Hz), and 7.81(1H, d, J=10.6 Hz).

4a: δ=7.10(1H, ddd, J=11.4, 8.1, 1.1 Hz), 7.13(1H, dd, J=12.1, 1.1 Hz), 7.38(1H, ddd, J=12.1, 8.1, 1.1 Hz), 8.57(1H, s), 8.75(1H, dd, J=11.4, 1.1 Hz), and 10.15(1H, s).

4b: δ=2.68(3H, s), 7.06(1H, ddd, J=11.4, 8.4, 1.1 Hz), 7.10(1H, dd, J=12.1,1.1 Hz), 7.36(1H, ddd, J= 12.1, 8.4, 1.1 Hz), 8.53(1H, s), and 8.78(1H, dd, J=11.4, 1.1 Hz).

4c: δ=4.70(2H, s), 7.08(1H, ddd, J=11.4, 8.5, 1.1 Hz), 7.11(1H, dd, J=12.4, 1.1 Hz), 7.38(1H, ddd, J=12.4, 8.5, 1.1 Hz), 8.57(1H, s), and 8.67(1H, dd, J=11.4, 1.1 Hz).

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

5: δ=3.24(2H, t, J=8.5 Hz), 3.63(2H, t, J=8.5 Hz), 6.83(1H, ddd, J=11.0, 8.4, 1.1 Hz), 7.01(1H, dd, J=12.1, 1.1 Hz), 7.03(1H, dd, J=11.0, 1.1 Hz), and 7.17(1H, ddd, J=12.1, 8.4, 1.1 Hz).

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

9c: δ=4.81(2H, s), 4.86(2H, s), 7.06(1H, ddd, J=11.0, 8.4, 1.1 Hz), 7.09(1H, dd, J=12.1, 1.1 Hz), 7.34(1H, ddd, J=12.1, 8.4, 1.1 Hz), and 7.61(1H, dd, J=11.0, 1.1 Hz).

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