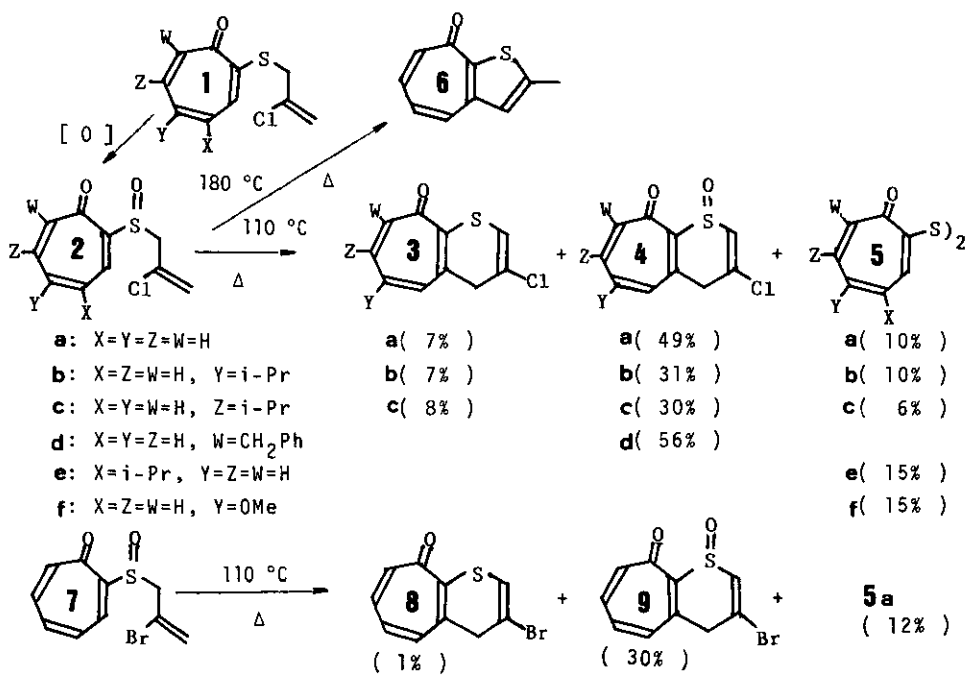
AN EXTREMELY MILD THERMOLYSIS OF SEVERAL 2-(2-HALOGENO-2-PROPENYL-SULFINYL)TROPONES

Hitoshi TAKESHITA,* Hideshi MOTOMURA,† Kingo UCHIDA,† and Hiroaki MAMETSUKA

Research Institute of Industrial Science, 86, and †Graduate School of Engineering Sciences, 39, Kyushu University, Sakamoto, Kasuga City, Fukuoka, 816, Japan

Abstract —— By heating 2-(2-chloro-2-propenylsulfinyl)tropones at above 110 °C afforded 3-chloro-4H,9H-cyclohepta[b]thiopyran-9-ones and their S-oxides. Accompanied formation of di(2-troponyl) disulfides indicated the thermolysis to be a radical, non-concerted intermolecular reaction.

Previously, we have reported the reinvestigations on some Claisen-type sigmatropic reactions of troponoids.[1,2] Contrary to the Matsui's early attempt on the *thio*-Claisen rearrangement,[3] 2-(allylthio)tropones (1) have caused a smooth reaction when heated in DMF.[4] In connection to this, we have extended the study to the reaction with 2-(allylsulfinyl)tropones (2),[5] of which the intermediate should be an α-keto sulfine if it occurred. However, the results have shown not to be the



case; all the products were formed *via* a non-concerted process as presented herein. When 2-(2-chloro-2-propenylsulfinyl)tropone (2a, yellow needles, mp 86-88 °C), prepared by *m*-chloroperbenzoic-acid-oxidation of 2-(2-chloro-2-propenylthio)tropone (1a), was heated in DMF at 110 °C for 10 min, a facile reaction occurred to give three products, 3a, 4a, and 5a. Under more drastic conditions (180 °C in a sealed tube), 2a merely gave a small amount of 2-methyl-8*H*-cyclohepta[*b*]thiophen-8-one (6a) which was identical in every respect with the authentic sample prepared from 1a.[4] The major product, 4a, yellow needles, still contained the chlorine atom, and according to mass-spectral determination of the molecular weight showed to be a dehydro derivative of 2a. Its ^{1}H-NMR spectrum[6] suggested the tropone ring remained, and its IR [ν: 1620, 1590, 1030 cm^{-1}] assured a presence of the sulfinyl group.

TABLE 1. THE PHYSICAL PROPERTIES OF THE THERMAL REACTION PRODUCTS OF 2-(2-HALOGENO-2-PROPENYLSULFINYL)TROPONES.

	Physical Properties
⟹ 3a	mp 164-165 °C. δ: 3.61(2H, d, J=1 Hz), 6.58(1H, t, J=1 Hz), 6.7-7.2(4H, m). δ(C): 31.2, 129.6, 129.7, 131.2, 132.5, 135.2, 135.4, 135.6, 150.1, 183.1.
2a ⟹ 4a	mp 151-152 °C. δ: 4.79(2H, d, J=1 Hz), 6.90(1H, ddd, J=11, 8, 1 Hz), 7.02(1H, dt, 12, 1 Hz), 7.28(1H, ddd, J=12, 8, 1 Hz), 7.35(1H, t, J=1 Hz), 7.45(1H, dt, J=11, 1 Hz). δ(C): 39.7, 128.0, 130.8, 132.7, 134.6, 136.4, 140.4, 147.8, 151.8, 180.6.
⟹ 5a	mp 227-229 °C.[6] δ: 6.9-7.5(10H, m).
⟹ 3b	mp 90-91 °C. δ: 1.22(6H, d), 2.74(1H, sept), 3.57(2H, d, J=1 Hz), 6.5-7.2(4H, m).
⟹ 4b	mp 95-96 °C. δ: 1.28(6H, d), 2.82(1H, sept), 4.78(2H, d, J=1 Hz), 7.01(1H, d, J=12 Hz), 7.24(1H, dd, J=12, 1 Hz), 7.32(1H, d, J=1 Hz), 7.32(1H, t, J=1 Hz). δ(C): 23.1(2C), 38.0, 39.8, 128.5, 131.3, 134.3, 138.1, 141.2, 147.5, 148.4, 149.6, 180.2.
2b ⟹ 5b	mp 145-146 °C. δ: 1.22(12H, d), 2.77(2H, sept), 6.90(2H, dd, J=10, 1 Hz), 7.04(2H, dd, J=12, 1 Hz), 7.07(2H, d, J=12 Hz), 7.36(2H, d, J=10 Hz).
⟹ 3c	mp 95-96 °C. δ: 1.23(6H, d), 2.75(1H, sept), 3.58(2H, d, J=1 Hz), 6.5-7.0(4H, m).
⟹ 4c	mp 92-93 °C. δ: 1.25(6H, d), 2.79(1H, sept), 4.77(2H, d, J=1 Hz), 6.82(1H, dd, J=11, 2 Hz), 6.96(1H, d, J=2 Hz), 7.29(1H, t, J=1 Hz), 7.37(1H, d, J=11 Hz). δ(C): 23.0(2C), 39.1, 39.7, 130.6, 130.9, 131.4(2C), 140.0, 147.4, 151.2, 157.4, 180.4.
2c ⟹ 5c	mp 208-209 °C.[7] δ: 1.24(12H, d), 2.77(2H, sept), 6.9-7.5(8H, m).
2d ⟹ 4d	mp 134-135 °C. δ: 4.04(2H, s), 4.71(2H, s), 6.79(1H, dd, J=11, 9 Hz), 7.1-7.5(8H, m). δ(C): 39.8, 40.7, 126.4(2C), 127.7, 128.5(2C), 129.4, 130.4, 130.9, 136.0, 139.4, 140.3, 146.1, 147.7, 151.5, 179.4.
2e ⟹ 5e	mp 154-155 °C.[7] δ: 1.00(12H, d), 2.68(2H, sept), 6.86(2H, dt, J=9, 2 Hz), 6.98 (2H, dd, J=12, 2 Hz), 7.22(2H, dd, J=12, 9 Hz), 7.28(2H, d, J=12 Hz).
2f ⟹ 5f	mp 184-185 °C. δ: 3.75(6H, s), 6.36(2H, ddd, J=10, 3, 1 Hz), 7.0-7.1(4H, m), 7.34 (2H, d, J=10 Hz).
7 ⟹ 9	mp 123-124 °C. δ: 4.68(2H, d, J=1 Hz), 6.90(1H, ddd, J=11, 8, 1 Hz), 7.02(1H, dt, J=12, 1 Hz), 7.28(1H, ddd, J=12, 8, 1 Hz), 7.35(1H, t, J=1 Hz), 7.45(1H, dt, J=11, 1 Hz). δ(C): 25.0, 128.0, 131.5, 132.7, 134.7, 136.3, 140.5, 148.1, 152.0, 180.7.

Therefore, the structure can be assigned as depicted, the S-oxide of 3-chloro-4*H*,9*H*-cyclohepta[*b*]thiopyran-9-one. The minor product, **3a**, yellow needles, was also retained the tropone ring and chlorine atom; the ^{1}H-NMR spectrum showed a presence of a methylene group, which is spin-coupled to the vinylic protons, and its IR spectrum [ν^{KBr}: 1620, 1540, 1460, 1230, 925, 860, 795 cm^{-1}] did not exhibit any absorption due to the sulfinyl, hydroxy, or thiol group, and the mass spectrum indicated it to be the deoxo derivative of **4a**.

Beside these, di(2-troponyl) disulfide (**5a**), yellow needles (lit.[7] brown crystals, mp 206 °C), in 10% yield, was an accompanied product.

The thermal reaction of 2-(2-bromo-2-propenylsulfinyl)tropone (**7**), although less stable than **2** toward air, revealed a similar product distributions; very low yield of 3-bromo-4*H*,9*H*-cyclohepta[*b*]thiopyran-9-one (**8**) and a considerable yield of its S-oxide (**9**) [δ: 4.68(2H, d, J=1 Hz), 6.90(1H, ddd, J=11, 8, 1 Hz), 7.02(1H, dt, J=12, 1 Hz), 7.28(1H, ddd, J=12, 8, 1 Hz), 7.35(1H, t, J=1 Hz), and 7.45(1H, dt, J=11, 1 Hz)], pale yellow needles, along with **5a**.

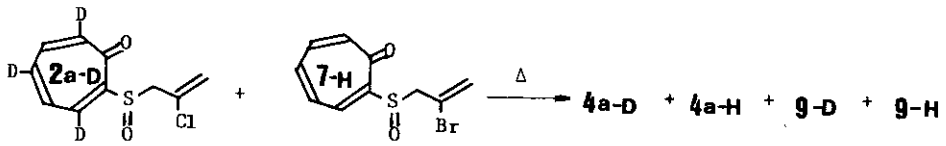
To know the scope and limitation, we have checked the reaction with several 2-(2-chloro-2-propenylsulfinyl)tropones: 5-isopropyl (**2b**), 6-isopropyl (**2c**), and 7-benzyl (**2d**) derivatives. The results obtained were displayed in Scheme 1.

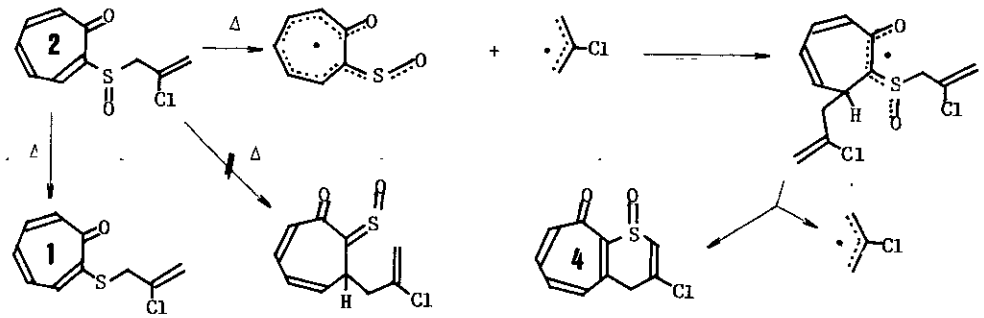
In cases of the 4-isopropyl (**2e**) and 5-methoxyl (**2f**) derivatives, none of thiopyran could be detected; the major product isolated from **2e** was di(4-isopropyl-2-troponyl) disulfide (**5e**),[8] yellow needles, which accompanied deoxygenated 2-(2-chloro-2-propenylthio)-4-isopropyltropone (**1e**), while from **2f** only di(5-methoxy-2-troponyl) disulfide (**5f**), yellow needles, was identified.[9]

For the formation of thermolysates, two major different mechanisms, concerted and non-concerted, should be differentiated. The formation of substantial amounts of **5**,[10] and different structural features between the thermolysates from **1** and **2** are strongly in favor of the non-concerted mechanism, but rigorous elimination of the concerted mechanism should be desirable. Thus, a cross-over experiment with the 1:1-mixture of 3,5,7-trideuterio derivative of **2a** (**2a**-d_3) and **7** under the same conditions was carried out. After fractionations by the high-pressure liquid chromatography (μ-Polasil/ ethyl acetate), an inseparable mixture of **4a** and **9** was obtained. The mass spectrum[11] of this sample has not shown the molecular peaks, but the deoxygenation fragments, M^+-16, were the base peaks. Nevertheless, after the correction for isotope abundance of halogens, they have clearly indicated its intermolecular nature of the reaction; *i.e.*, the ratio of d_0:d_1:d_2 for **4a** was 51:11:38. Similarly, that of d_0:d_1:d_2 for **9** was 58:10:32.

In view of this facile deoxygenation from **2** upon electron impact, the formation of **6a** on the thermolysis at 180 °C might be an outcome of such deoxygenation from **2a**. This might be even the case of the thermolysis of **2e** at 110 °C, where, under the insufficient temperature for the cycloheptathiophenone formation, the resultant propenylthiotropone, **1e**, could be isolated after the reaction in 20% yield.

As shown above, the creavage of S-C bond of **2** and **7** under unusually mild conditions led a new radical rearrangement to give cycloheptathiopyran oxide derivatives. The occurrence of this non-concerted radical substitution reaction under such mild conditions is indeed a surprise as the structural features of troponoids permit the concerted electrocyclic process according to the Woodward-Hoffmann rule.





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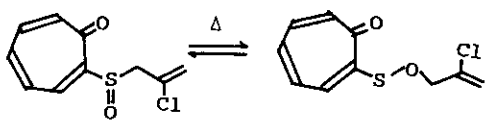
4. H. Takeshita, H. Mametsuka, and K. Uchida, *Heterocycles*, 20, 1709 (1983).
5. The substrates, 2 and 7, were prepared by m-chloroperbenzoic acid oxidation of 1.[1,3]
6. The NMR spectra were measured by a Nippon Denshi Co. (JEOL) FX 100 Model spectrometer in $CDCl_3$ solutions unless otherwise stated, and the chemical shifts were expressed in the δ units from the internal Me_4Si.
7. T. Muroi, *Nippon Kagaku Zasshi*, 80, 185 (1959).
8. K. Matsui (*Bull. Chem. Soc. Jpn.*, 33, 1448 (1960)) has given the mp of 5e and 5c as 155-156 °C and 210-211 °C, respectively.
9. Other than these 2-chloro-2-propenyl derivatives, the reaction was investigated with several allyl derivatives; *i.e.*, 2-(3-chloro-2-propenylsulfinyl)tropone, 2-(allylsulfinyl)tropone, and 2-(methallylsulfinyl)tropone were subjected for the reaction, but they have resulted in an extensive decomposition of the materials.
10. Formation of 5 requires S-O fission and C-S fission, therefore, a well known concerted process, a 2,3-sigmatropy,[12] might be taken place prior to S-O homolysis. However, it is not certain that all the pyrolysates are products of this type of intermediates.



11. The mass spectra were measured by a JEOL OS1G Model spectrometer.
12. D. A. Evans and G. C. Andrews, *Accounts Chem. Research*, 7, 147 (1974).

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