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

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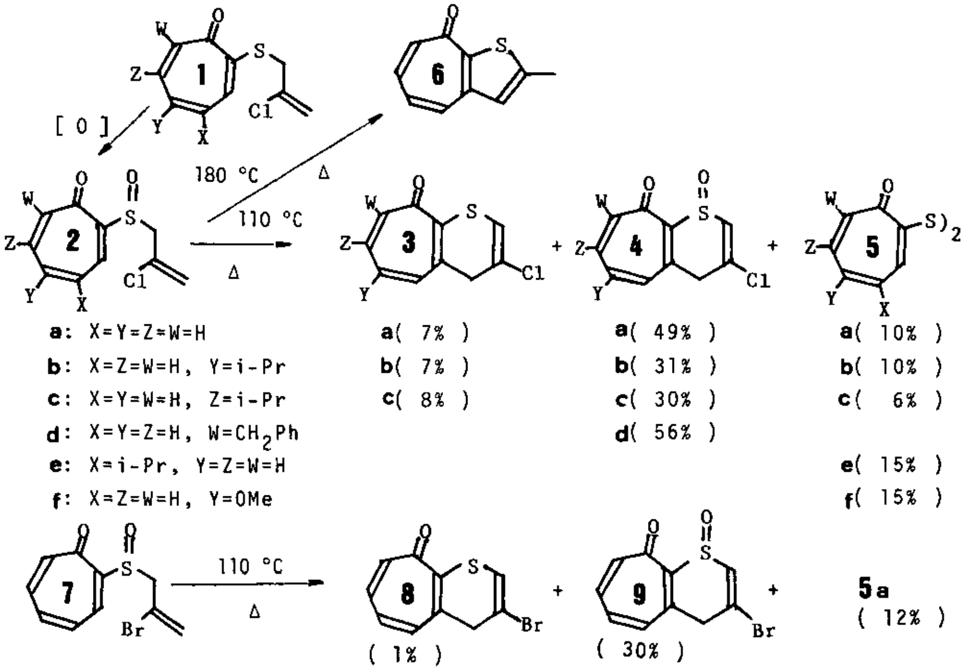
Abstract —— By heating 2-(2-chloro-2-propenylsulfinyl)tropones at above 110 °C afforded 3-chloro-4H,9H-cyclohepta[b]thiopyran-9-ones and their S-oxides. Accompanied formation of di(2-troponyl) disulfides indicated the thermolysis to be a radical, non-concerted intermolecular reaction.

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
2a ⟹ 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.
2a ⟹ 5a	mp 227-229 °C.6) δ: 6.9-7.5(10H, m).
2b ⟹ 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).
2b ⟹ 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).
2c ⟹ 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).
2c ⟹ 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**.

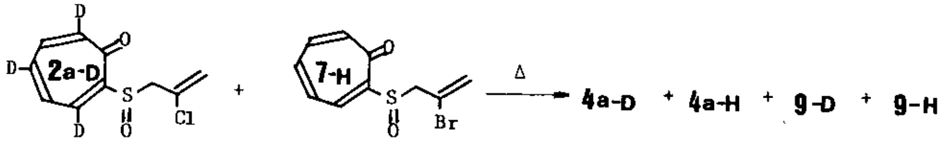
To know the scope and limitation, we have checked the reaction with several 2-(2-chloro-2-propenylsulfinyl)tropones: 5-isopropyl (**2b**), 6-isopropyl (**2c**), and 7-benzyl (**2d**) derivatives. The results obtained were displayed in Scheme 1.

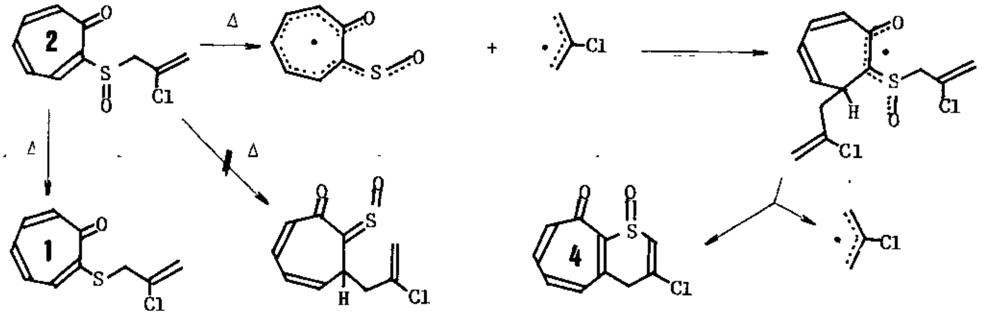
In cases of the 4-isopropyl (**2e**) and 5-methoxyl (**2f**) derivatives, none of thiopyran could be detected; the major product isolated from **2e** was di(4-isopropyl-2-troponyl) disulfide (**5e**),[8] yellow needles, which accompanied deoxygenated 2-(2-chloro-2-propenylthio)-4-isopropyltropone (**1e**), 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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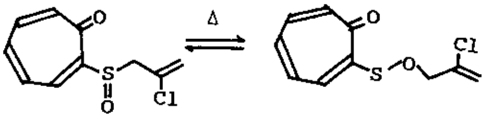
3. K. Matsui, *Sci. Repts. Tohoku Univ., Ser. I*, 43, 223 (1959).
4. H. Takeshita, H. Mametsuka, and K. Uchida, *Heterocycles*, 20, 1709 (1983).
5. The substrates, **2** and **7**, were prepared by m-chloroperbenzoic acid oxidation of **1**.[1,3]
6. The NMR spectra were measured by a Nippon Denshi Co. (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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