

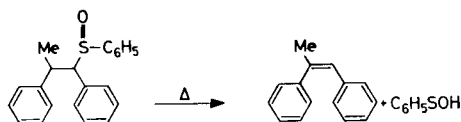
CYCLOPHANE BIS(SULFOXIDES) A THERMAL ANALYSIS STUDY

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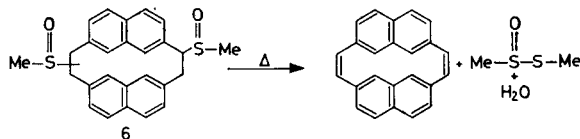
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A thermogravimetry study of a series of cyclophane bis(sulfoxides) (1–6) has shown that thermal decomposition of these compounds occurs in two stages with a stepwise loss of the sulfoxide groups at well defined decomposition temperatures. The stepwise thermal cleavage has been rationalized in terms of the stereochemistry of the sulfoxide groups and the strain associated with the resultant elimination products.

Thermal analysis of sulfoxide compounds has been used as a direct route for the introduction of olefinic bonds into organic substrates [1, 2]. The thermal decomposition has generally been effected in solvents (toluene, xylene) at temperatures between 100 and 150°, and the method has been used to prepare alkenes [3], α,β -unsaturated carbonyl compounds [2], stilbenes [4] (Scheme 1) and unsaturated



cyclophanes [5, 6]. Considerable investigations into the mechanism of the thermally induced elimination reaction have been made [7], and suggestions as to the nature of the transition state have been proposed [8]. The primary byproduct of the elimination of methyl sulfoxide compounds is considered to be methane sulfenic acid (CH_3SOH) which rapidly disproportionates to methyl methanethiol-sulfinate ($\text{CH}_3(\text{SO})\text{SCH}_3$) and water (e.g., Scheme 2).



We have used the thermal decomposition of cyclophane bis(sulfoxides) at temperatures up to 350° (5×10^{-4} mm) to prepare an extensive range of cyclophane dienes [9] (for example, Scheme 2). We report here a thermogravimetry study of the cyclophane bis(sulfoxides) 1–6 and suggest that a stepwise loss of the two

a high heating rate ($20^{\circ} \text{ min}^{-1}$) under nitrogen or a low heating rate ($4^{\circ} \text{ min}^{-1}$) under vacuum. The TG profiles for each compound are equivalent with these two sets of conditions.

Results and discussion

Thermal curves for the six cyclophane bis(sulfoxides) 1–6 were determined and a representative curve for one of these (compound 1) is shown in Fig. 1. Total mass loss data and theoretical mass loss data based on complete decomposition to the corresponding cyclophane-diene product together with the relevant decomposition temperatures T_1 and T_2 (Scheme 3) are given in the Table. T_1 and T_2 were determined from the relevant peak maxima in the DTG profile for these compounds.

The TG profiles for all six compounds are similar and two mass losses occur for each compound at characteristic decomposition temperatures T_1 and T_2 . Total

Table
TC data and decomposition temperatures for cyclophane bis(sulfoxides)

Compound	Total mass loss, %	Theoretical total mass loss, %	T_1 , °C	T_2 , °C
1	24	26.6	206	326
2	26	28.0	200	330
3	32	31.4	224	300
4	39	29.4	132	138
5	30	29.6	204	335
6	26	29.6	270	278

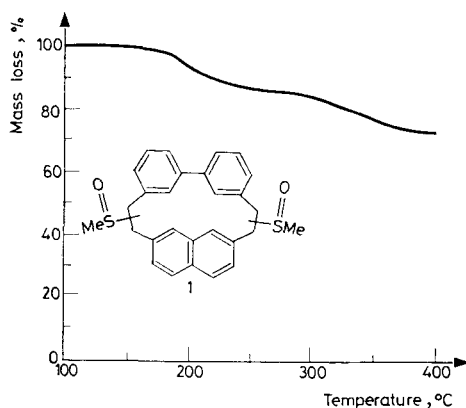
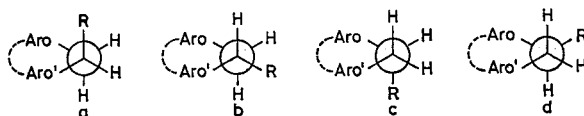


Fig. 1. Cyclophane bis(sulfoxides): A typical TG profile

mass losses are within 10% of the calculated values and discrepancies are due primarily to partial vapourization of the intermediate **8** and of the cyclophane diene **9** (Scheme 3).

It is important and relevant to provide some independent evidence for the existence of the cyclophane sulfoxide intermediate **8**, Scheme 3. The mass spectra (at 200°) of all six cyclophane bis(sulfoxides) studied show no parent molecular ion but a base peak is observed in each case located at 128 mass units lower than the molar mass of the cyclophane bis(sulfoxide) and thus represents the parent ion of the corresponding cyclophane diene **9** (Scheme 3). Also in each case, a low intensity peak is indicated at 64 mass units lower than the molar mass of the parent cyclophane bis(sulfoxide) and represents the parent ion of the corresponding cyclophane sulfoxide **8** (Scheme 3). Thus at 200°, 10⁻⁷ Torr, thermal cleavage of one and both sulfoxide functional groups occurs.

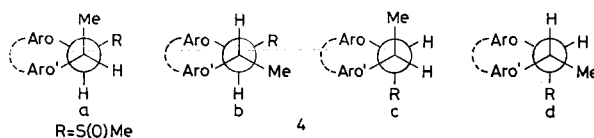
The method of preparation of each of the cyclophane bis(sulfoxides) yields a statistical distribution of isomers whose structures may be represented as **10a-d** in which only one bridge of the cyclophane is shown. Structures **10a** and **c** are pseudo-axial and **10b** and **d** are pseudo-equatorial. Consideration of the possible geometries for structures **10a-d** offers several possible explanations for stepwise



10

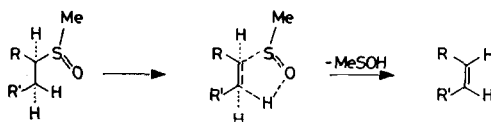
thermal cleavage of the sulfoxide functional groups. An important factor influencing the decomposition temperatures T_1 and T_2 is the resultant strain (due to intramolecular non-bonded interactions) in the products of each successive elimination. In most of the compounds studied, molecular models suggest that the strain in the intermediate products **8** is much less than that associated with the final cyclophane diene **9**. This accounts for the divergent values of T_1 and T_2 . However, in the case of compound **6**, molecular models indicate that the strain associated with the intermediate is approximately the same as that associated with the final cyclophane diene **9**, and the similarity of T_1 and T_2 (270 and 278°) reflect this prediction.

A second factor is the stereochemistry of the sulfoxide groups in the bridges of the cyclophanes. Compounds **4** is restricted to four configurations about each bridge, **4a-d**. Two of these structures have equatorial sulfoxide groups and the other two structures have axial sulfoxide groups. The temperatures of decomposi-



4

tion for compound 4 are 132 and 138° and the mass losses are in the ratio 3 : 1. This ratio suggests the decomposition of isomers 4a–c at the lower temperature T_1 and of 4d at T_2 . Thus the accessibility of a proton on the β -carbon to the sulfoxide group is the limiting factor rather than the stereochemistry of the sulfoxide group, i.e., whether it is axial or equatorial. This is in accord with a concerted process for the *syn* β -elimination of the type shown in Scheme 4 which has been proposed [13].



The presence of the methyl group on the β -carbon to the sulfoxide group in compound 4 also facilitates the decomposition. The temperatures of decomposition of 4 are significantly lower than those of 3. This may well reflect the increase in strain energy about the sp^3 carbon bridges in 4 relative to 3 due to non-bonded intramolecular interactions in the more highly substituted cyclophane 4.

Thus, in summary, TG data for six cyclophane bis(sulfoxides) confirm a two-step decomposition mechanism. The relevant mass losses and corresponding decomposition temperatures are rationalised in terms of the structure of the parent cyclophane bis(sulfoxide), the stereochemistry of the sulfoxide functional groups, and the relative strain associated with the elimination products.

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RÉSUMÉ — Une étude thermogravimétrique d'une série de bis (sulfoxydes) de cyclophane (1–6) a montré que la décomposition thermique de ces composés se déroule en deux étapes avec pertes graduelles des groupes sulfoxydes à des températures de décomposition bien définies. Le clivage thermique graduel est expliqué par la stéréochimie des groupes sulfoxydes et la contrainte associée aux produits éliminés.

ZUSAMMENFASSUNG — Eine thermogravimetrische Studie einer Reihe von Cyclophan-bis-(sulphoxiden) (1–6) zeigte, dass die thermische Zersetzung dieser Verbindungen in zwei Stufen unter stufenweisem Verlust der Sulphoxidgruppen bei gut definierten Zersetzungstemperaturen vor sich geht. Die stufenweise thermische Spaltung wurde aufgrund der Stereochemie der Sulphoxidgruppen und der mit den resultierenden Eliminationsprodukten verbundenen Belastung erörtert.

Резюме — Термогравиметрическое изучение ряда бис-сульфоксидов циклофана показало, что термическое разложение этих соединений происходит в две стадии, сопровождаемая ступенчатой потерей сульфоксидных групп, с хорошо выраженными температурами разложения. Ступенчатое термическое расщепление объяснено на основе стереохимии сульфоксидных групп и деформаций, обусловленных продуктами реакций расщепления.