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SKELETAL REARRANGEMENT OF A 2,6-DITHIAADAMANTANE-2,2,6,6-TETRAOXIDE DERIVATIVE DURING THERMAL AND PHOTOCHEMICAL SULFUR DIOXIDE EXTRUSION[1].

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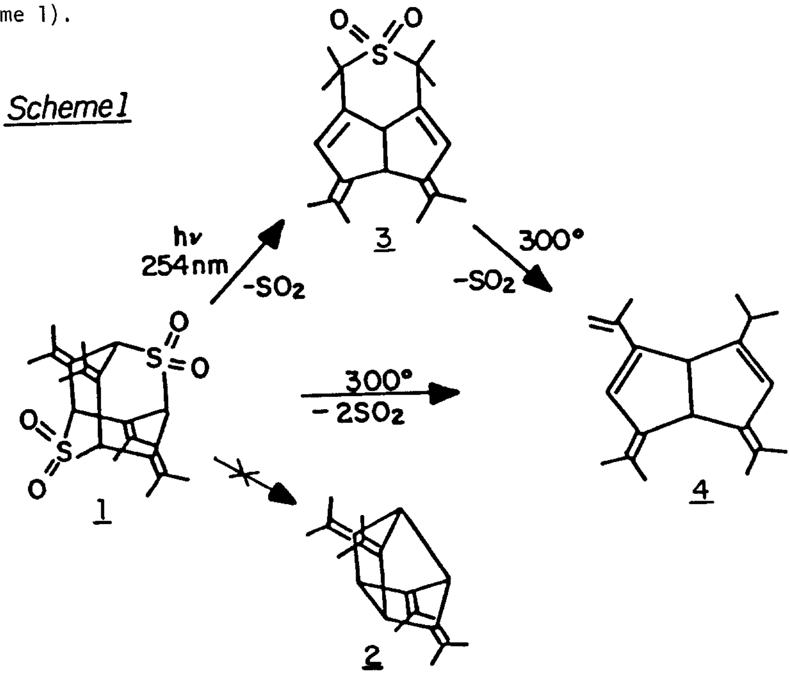
Summary: In contrast to the pyrolysis of 1 which results in loss of both SO_2 groups and formation of 4, the photolysis of 1 results in loss of only one SO_2 group, a double 1,3-shift of the second sulfonyl group and formation of 3. Pyrolysis of the latter also gives 4. The mechanistic significance and novelty of these results are discussed.

Previously, we have reported that bis-γ,γ-dimethylallenyl sulfone undergoes a novel and facile carbanionic cyclodimerization to the 2,6-dithiaadamantane bis-sulfone derivative 1[2]. Surprisingly, it was also found that compound 1 shows a strong ultraviolet absorption at λ_{max} = 236 nm with ε = 29,000 in acetonitrile, although none of its π systems are conjugated[3]. In view of this absorption as well as the considerable interest in the photolysis[4] and pyrolysis[5] of sulfones in the past, we have investigated the behaviour of compound 1 under photochemical and thermal conditions. Furthermore, in view of the application of the thermal and photochemical extrusion of sulfur dioxide as a synthetic method for the preparation of cyclic and polycyclic hydrocarbons in general and cyclophanes in particular[5-7], we were initially interested in exploiting this method in the conversion of adamantane bis-sulfone 1 to its five-membered homologue 2 (Scheme 1).

Scheme 1



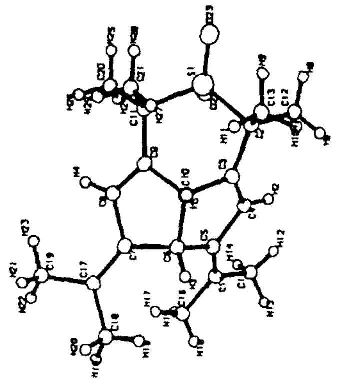


Figure 1. An ORTEP Drawing of the Molecular Structure of 3.

Contrary to our expectations, however, direct irradiation of 1 in acetonitrile at 254 nm for 6 hours results in the extrusion of only one molecule of sulfur dioxide together with a double allylic rearrangement of the second sulfonyl group and formation of the tricyclic sulfone 3 (Scheme 1), separated by column chromatography (silica, methylene chloride) and recrystallized from hexane: mp 170-171°; ^1H nmr ($CDCl_3$, 100 MHz): δ 1.60 (s, 6H), 1.80 (s, 12H) 4.03 (bs, 2H), 6.27 (s, 2H); ^{13}C nmr ($CDCl_3$, 20 MHz): 19.9, 22.4, 24.4 (Me), 47.4, 53.4 (=C-$\underline{C}$-H), 65.8 (C-SO_2), 128.4 (H-C=), 127.0, 139.3, 142.4 (C); ir ($CHCl_3$, cm^{-1}): 905(s), 1090(s), 1280(s); ms (m/e): 332 (M^+, 1%) 268 (M-SO_2, 100%), 253 (M-CH_3SO_2, 20%), 225 (M-$C_3H_7SO_2$, 33%), 183 (M-C_6H_{13}, 18%); uv (CH_3CN, λ_{max}, nm): 244 (ε_{max} = 21,200); Calcd. for $C_{20}H_{28}SO_2$: C, 72.79; H, 8.43; S, 9.64%. Found: C, 72.37; H, 8.42; S, 9.72% (yield 65%).

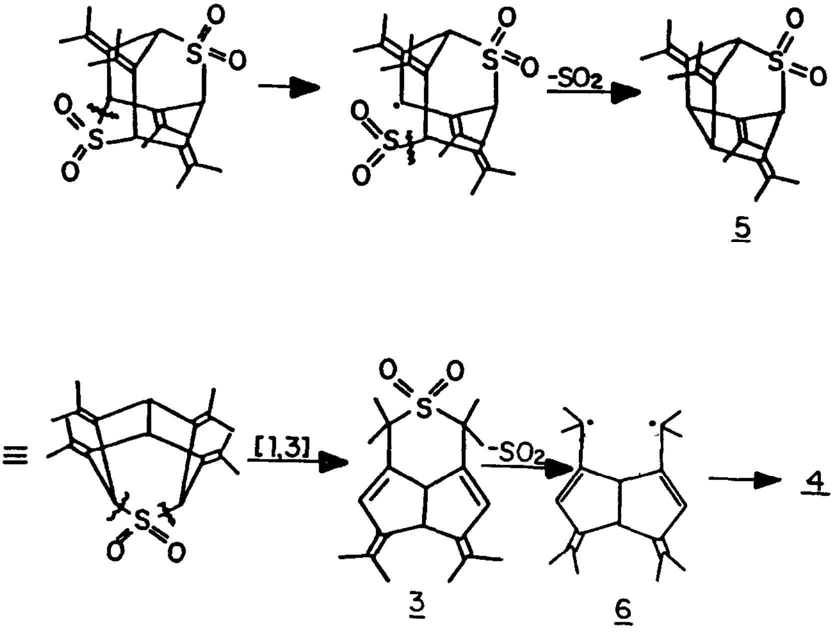
Although the spectral evidence was in accord with the assigned structure of 3, unequivocal structure proof was obtained by X-ray crystallographic analysis (Figure 1).

Irradiation of compound 1-d-1 [8] i.e., deuterated at only one of its four α-sulfonyl positions under identical conditions resulted in complete scrambling of the label among the two methine and two vinylic positions of the product (3). This result may be explained by the symmetry of 1 and the identity of the two sulfonyl groups with regard to both SO_2 extrusion and rearrangement. In principle, the extrusion of one SO_2 group may be preceded or followed by the skeletal rearrangement of the other sulfonyl group. The results so far obtained, including deuterium labeling, do not enable a distinction between these two possibilities. Nevertheless, a tentative mechanism based on the second possibility is presented in Scheme 2.

The photochemical behaviour of sulfones in general is dominated by the initial α-cleavage process[4]. Although the question of stepwise[9] or simultaneous[10] cleavage of the two carbon-sulfur bonds cannot be answered, there is ample precedence to suggest the involvement of a free radical mechanism for the photoextrusion of SO_2 from both cyclic[11] and acyclic[12] sulfones. This includes detection by uv spectroscopy[13], trapping of radicals[14] and isolation of radical coupling products[11,12]. The formation of relatively stable bis-allylic mono or diradicals, such as in the present case (Scheme 2) may provide further drive for a free radical mechanism.

The failure of the intermediate monosulfone 5 to undergo further loss of SO_2 to give the expected product (2) is not very surprising, in view of its excessive angular strain, also indicated by the difficulties involved in making a Dreiding model, of this molecule.

Scheme 2



Consequently, monosulfone 5 prefers to undergo a double 1,3-sulfonyl migration to release some of its strain, with formation of the observed photoproduct (3). This result is of considerable interest and novelty since thermal and ionic 1,3-sulfonyl migrations of allylic sulfones are well documented[15], while the photochemical version is practically unknown. Another significant aspect which deserves attention in the conversion of 1 to 3 is the exclusive photoextrusion of only one SO_2 molecule. This is in sharp contrast with the behaviour of other bis-sulfones which undergo photoextrusion of both SO_2 molecules, and only rarely are monosulfones detected[7] as reaction intermediates in the synthesis of cyclophanes. This behaviour has been the basis for the discussion of the sequential or simultaneous SO_2 loss, frequently encountered in the literature[7]. The exclusive conversion of 1 to 3, dictated by the structural constraints previously discussed, is thus a unique and novel evidence for the sequential loss of SO_2 interpretation.

Prompted by the photochemical results presented above, we decided to investigate the thermal extrusion of SO_2 from 1, as well. In contrast to the photochemical results, pyrolysis *of compound* 1 *at ca.* 300° *results in extrusion of both* SO_2 *groups and formation of the bicyclic* hydrocarbon 4 (mp, 99.5-101.5°) [8], with the same rearranged carbon skeleton as in product 3. Furthermore, since pyrolysis of the latter under the same conditions, also results in the formation of the same product (4, Scheme 1), one may conclude that direct pyrolysis of 1 involves the formation of monosulfone 3 as an intermediate.

In view of the free radical mechanism usually proposed for both the thermal sulfur dioxide extrusion[5] and 1,3 sulfonyl migrations[15,16] of allylic sulfones, the mechanism suggested above for the photochemical transformation of 1 to 3 (Scheme 2) may also apply for the thermal transformation of 1 to (undetected) 3. For the second extrusion of SO_2, observed only under pyrolysis, we suggest the involvement of a relatively stable and extended tetramethyleneethane (TME)-

diradical (6, Scheme 2) which may undergo disproportionation by internal hydrogen abstraction and formation of the observed product (4). TME or 2,2'-bisallyl diradicals are the generally accepted intermediates in the well known dimerization of allenes to 1,2-dimethylenecyclobutanes[17], the thermally induced rearrangements of the latter[18], and have been the subject of considerable theoretical discussion[19].

The occurrence of hydrogen transfer instead of ring closure of diradical 6 can be explained by steric effects, and is completely analogous to previous observations on such species[20]. Similar to their photochemical behaviour bis-sulfones also undergo thermal extrusion of both SO_2 groups and only rarely are monosulfones isolated as minor products in the synthesis of cyclophanes. This and other evidence has been the basis for the discussion of a one-step or two-step mechanism[5]. The thermal conversion of 1 to 4, involving the intermediacy of monosulfone 3, provides a unique example of a two-step elimination of SO_2 from a bis-sulfone.

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