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The dimerization and photochemical rearrangement of pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8-thione

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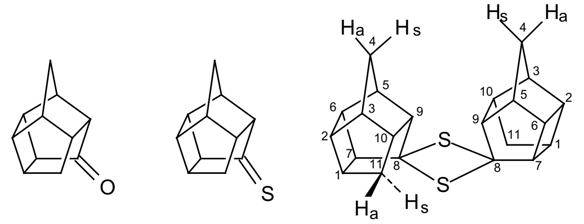
Abstract—Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one **1** is readily sulfurated into pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8-thione **2** with Lawesson's reagent in dry THF. Upon standing at ambient temperature the thione **2** formed the corresponding thio-dimer **3** within 10 days. When the thio-dimer **3** was exposed to oxygen and ultraviolet light an unexpected photochemical oxidation and rearrangement took place to form the stable disulfenate **5**.

It was previously reported that the thione **2** can be obtained in good yield (70%) from treatment of the ketone **1** with P_2S_5 in pyridine, but it was claimed that Lawesson's reagent does not react productively with **1**.[1] However, in our hands Lawesson's reagent appears to be a far superior reagent for this conversion and produced the thione **2** in 85% yield.

The thione **2** is stable if stored under nitrogen at low temperatures (0 °C). At room temperature the orange coloured crystals of the thione **2** gradually decolourise as a result of dimerization to form the dimer **3** (yield: 95%; melting point: 160–163 °C). Complete transformation of **2** to **3** at room temperature can be observed after 10 days. The mass spectrum (EI) of **3** exhibits a molecular ion at *m*/*z* 352, which corresponds to a molecular composition of $C_{22}H_{24}S_2$ (calculated mass for $C_{22}H_{24}S_2$: C, 74.95; H, 6.86; S, 18.19. Found: C, 74.91; H, 6.89; S, 18.17). The dimeric character of **3** was clearly demonstrated by fragmentation in the mass spectrometer to a fragment ion at *m*/*z* 176 (monomer).

The ^{13}C NMR spectrum ($CDCl_3$) of **3** shows 11 carbon signals consisting of two methylene carbon signals at δ_C 29.4 and δ_C 33.2 and a quaternary carbon signal at δ_C 64.4 as well as eight methine carbon signals.



1 **2** **3**

Figure 1.

The ^1H NMR spectrum of **3** exhibits two AX-spin systems at high field, which can be associated with two different methylene groups. The doublets at δ_H 1.20 and δ_H 1.62 (J = 10.5 Hz) are associated with the methylene protons of C-4 (Fig. 1). The doublet at δ_H 1.20 is associated with H-4a (Fig. 1) and the doublet at δ_H 1.62 with H-4s (Fig. 1). The high field chemical shifts at δ_H 0.97 (doublet of triplets; J = 13.0 and 3.1 Hz) and δ_H 2.54 (doublet; $J_{a.s}$ = 13.0 Hz) can, respectively, be assigned to the protons H-11a and H-11s (Fig. 1) of the methylene carbon atom C-11.

The assignments of the remainder of the signals in the ^1H and ^{13}C NMR spectra of **3** to specific nuclei were derived from COSY and HETCOR 2D experiments and are given in Table 1.

It is known that aliphatic sulfides can suffer photo-oxidation in solution or in the solid phase by which sulfoxides are formed in quantitative yield.[2,3] It is expected

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Keywords: Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8-thione; Disulfenate; Disulfoxide; Lawesson's reagent; Photochemical rearrangement.

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Table 1. ^{1}H and ^{13}C NMR spectroscopic data[a] of **3**

Carbon, hydrogen	δ_H[b] (ppm)	J (Hz)	δ_C[b] (ppm)	^1J (Hz)
1	2.62 m		37.1 D	139.2
2	2.49 m		40.7 D	143.8
3	2.22 m		47.5 D	140.3
4 a	1.20 d	10.5	33.2 T	129.6
4 s	1.62 d	10.5		
5	2.71 m		45.3 D	140.5
6	2.38 m		43.8 D	142.7
7	2.60		41.7 D	146.5
8			64.4 S	
9	3.00 m		48.1 D	144.9
10	2.67 m		52.6 D	137.4
11 a	0.97 dt	13.0; 3.1	29.4 T	126.8
11 s	2.54 d	13.0		

[a] ^{1}H spectrum: 300 MHz; ^{13}C spectrum: 75 MHz.

[b] Solvent $CDCl_3$. Capital letters refer to splitting patterns, which are attributed to direct coupled protons and small letters refer to couplings over more than one bond. S = singlet, D/d = doublet, T/t = triplet and m = multiplet.

that the product of the photochemical oxidation of **3** should have structure **4** (Scheme 1). However, attempted photochemical oxidation of the dimer **3** led to an unexpected photochemical rearrangement. A solution of **3** (1 g; 2.84 mmol) in benzene (100 cm^3) was irradiated with a medium pressure UV lamp for 3 h while air was bubbled through the reaction mixture. The mass spectrum (EI) of the photo-product exhibits a molecular ion at *m*/*z* 384, which corresponds to the structure of **4**. However, the IR spectrum of the product showed no characteristic absorptions of a sulfoxide group in the 1070–1030 cm^{-1} region. This suggested that the disulfoxide **4** is unstable and probably undergoes photochemical rearrangement to form the disulfenate **5** (Scheme 1; yield: 97%; melting point: 237–240 °C; calculated mass for $C_{22}H_{24}O_2S_2$: C, 68.71; H, 6.29; O, 8.32; S, 16.68. Found: C, 68.67; H, 6.23; O, 8.31; S, 16.73).

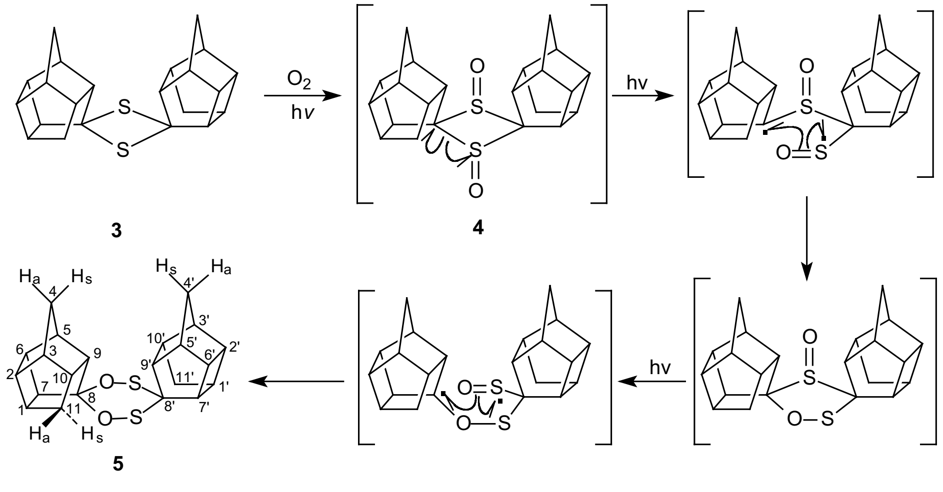
Support for the structure of **5** was found from ^{13}C and ^{1}H NMR studies. The ^{13}C NMR spectrum ($CDCl_3$) of **5** exhibits 22 signals, which are supportive of the asymmetrical character of the compound. The ^{13}C NMR spectrum ($CDCl_3$) of **5** also exhibits two quaternary carbon signals at δ_C 80.2 and δ_C 89.4. The signal at δ_C 89.4 can be associated with the carbon atom coupled with the two oxygen atoms while the signal at δ_C 80.2 is associated with the carbon atom coupled to the two less electronegative sulfur atoms.

The ^{1}H NMR spectrum ($CDCl_3$) of **5** showed characteristic signals for four methylene groups. The signals of the methylene groups of C-4 overlap and are registered as two doublets at δ_H 1.25 (H-4a, J = 10.6 Hz) and δ_H 1.69 (H-4s, J = 10.6 Hz). The coupling constants of 10.6 Hz are typical of the bridgehead methylene protons of pentacyclo-undecane derivatives.[8–11]

Two lower field doublets, which are associated with two sets of doublets of triplets are seen on the ^{1}H NMR spectrum of **5**. The doublet at δ_H 2.55 (J = 12.9 Hz) is at a lower field than the doublet at δ_H 1.85 (J = 13.1 Hz). In the case of the dimer **3** the resonance of H-11s was registered at δ_H 2.54 (J = 13.0 Hz). The doublet at δ_H 2.55 (J = 12.9 Hz) can thus be assigned to H-11's while the doublet at δ_H 1.85 (J = 13.1 Hz) to H-11s.

As a result of overlapping of methine proton signals of the two polycyclic units no assignment of resonance signals to specific nuclei could be made. Resonance signals in the ^{1}H NMR spectrum ($CDCl_3$) of **5** were observed at δ = 1.14 (dt; J = 13.0 Hz), 1.05 (dt; J = 12.0 Hz), 2.16–2.30 (m, 2H), 2.31–2.45 (m, 3H), 2.45–2.62 (m, 5H), 2.62–2.76 (m, 4H), 2.83–2.99 (m, 1H) and 3.01–3.15 (m, 1H). The ^{13}C NMR ($CDCl_3$) signals are registered at δ = 34.6 (T, J = 129.5/129.0 Hz), 34.5 (T), 30.3 (T, J = 128.4 Hz), 27.6 (T, J = 130.2 Hz), 36.8 (D), 37.4 (D), 40.6 (D), 40.6 (D), 42.7 (D), 42.8 (D), 43.8 (D), 44.0 (D), 44.9 (D), 46.9 (D), 47.0 (D), 47.3 (D), 47.3 (D), 50.2 (D), 52.3 (D) and 53.4 (D).

It was shown previously that sulfenate intermediates play a vital role in rearrangement reactions of sulfoxide derivatives.[4–7] It is not sure whether the rearrangement of the disulfoxide to the disulfenate takes place via an



Scheme 1.

α-splitting of the disulfoxide (Scheme 1) or via a one step[2,3]-sigmatropic process. α-Splitting is probably favoured under photochemical conditions. The transformation of the dimer **3** to the stable disulfenate **5** is remarkable in the sense that disulfenate derivatives are uncommon in the literature and that **5** shows an unexpected high stability.

The proposed mechanism for the formation of the disulfenate **5** from the dimer **3** can be explained schematically as shown in Scheme 1. The possibility of a sulfoxidation-rearrangement–sulfoxidation-rearrangement mechanistic pathway can, however, not be excluded.

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