The Pummerer Rearrangement of 1,5-Dithiacyclo-octane 1-Oxide with Acetic Anhydride: Evidence for Formation of the Disulphide Dication

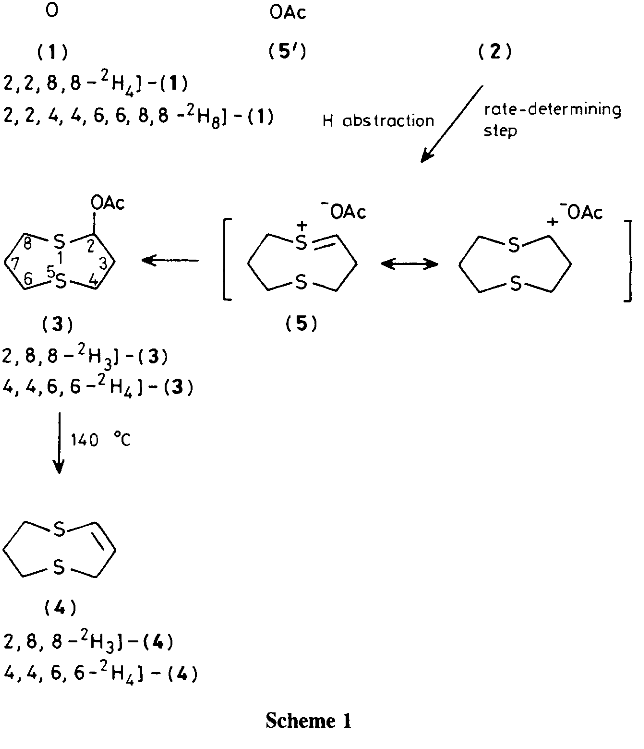
Naomichi Furukawa,* Akira Kawada, Tsutomu Kawai, and Hisashi Fujihara

Department of Chemistry, The University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

The Pummerer reaction of 1,5-dithiacyclo-octane 1-oxide with acetic anhydride afforded the α-acetylated cyclo-octane *via* the intermediate formation of the disulphide dication.

The Pummerer reaction of sulphoxides with acid anhydride has attracted attention for many years.[1] Recently, we found that 1,5-dithiacyclo-octane 1-oxide (**1**) reacts with conc. H_2SO_4 to give the disulphide dication (**2**).[2] Musker *et al.* also reported the formation of (**2**) when the sulphoxide (**1**) was reduced to the sulphide by treatment with aqueous HI.[3] These results indicate that both the sulphur atoms in the sulphoxide (**1**) interact transannularly. A similar $\geq\overset{+}{N}-\overset{+}{N}\leq$ dication has also been reported by Alder and his co-workers.[4] We have investigated the Pummerer reaction of (**1**) with acetic anhydride in order to elucidate whether the transannular S–S interaction participates in the Pummerer reaction of (**1**), and now report that this reaction proceeds *via* the disulphide dication (**2**).

Typically, the sulphoxide (**1**) was refluxed with acetic anhydride (5 mol. equiv.) in the presence of 5% sodium acetate in benzene for 24 h under an N_2 stream. After the usual work-up, the Pummerer product (**3**) was obtained in 75% isolated yield.† The product (**3**) decomposed on heating at 140 °C *in situ* resulting in 1,5-dithiacyclo-oct-2-ene (**4**) in 50% isolated yield, identified by its i.r. and ^1H n.m.r. spectra and elemental analysis.† Furthermore, a similar reaction of



Scheme 1

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† (**3**), m.p. 30.5—31.5 °C; i.r.(neat) 1740 and 1230 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 5.98 (1H, t, SC*H*OAc), 3.39—2.59 (6H, m, CH_2S), 2.53—1.78 (4H, m, CCH_2C), and 2.07 (3H, s, $MeCO_2$); (**4**), ^1H n.m.r. δ($CDCl_3$) 6.36 (1H, d, *J* 10 Hz, SC*H*=CH), 6.14—5.63 (1H, m, SCH=C*H*), 3.59 (2H, d, *J* 10 Hz, SCH_2CH=CH), 3.17—2.66 (4H, m, SCH_2CH$_2$CH_2S), and 2.50—2.11 (2H, m, CCH_2C); M^+ *m/z* 146. Satisfactory elemental analyses (C, H, S) were obtained for (**3**) and (**4**).

the 2,2,8,8-tetradeuteriated sulphoxide [$^2H_4$]-(**1**)[2] gave a *ca.* 1:1.7 mixture of the 2,8,8-trideuteriated and 4,4,6,6-tetradeuteriated products (**3**) obtained in 76% yield. Pyrolysis of the acetates [$^2H_3$]-(**3**) and [$^2H_4$]-(**3**) afforded a mixture of the alkenes [$^2H_3$]-(**4**) and [$^2H_4$]-(**4**), the ratio of which could be determined readily by ^{1}H n.m.r. spectroscopy, confirming the ratio of [$^2H_3$]-(**3**) and [$^2H_4$]-(**3**). This product ratio corresponds to the intramolecular isotope effect $k_H/k_D = 1.7$ and suggests that proton abstraction is associated with the rate-determining step. Furthermore, when the reaction using [$^2H_4$]-(**1**) was stopped at *ca.* 10 and *ca.* 50% conversion, the recovered sulphoxide was found to be a 1:1 mixture of 2,2,8,8- and 4,4,6,6-tetradeuteriated derivatives. During this reaction deuterium loss was not observed at all. These results demonstrate clearly that the Pummerer reaction proceeds *via* the initial formation of the acyloxy sulphonium salt which is converted into the disulphide dication (**2**) with rapid equilibration with (**1**) since complete deuterium scrambling was observed in the recovered sulphoxide. The dication (**2**) once formed should be converted into the intermediate (**5**) by α-proton removal at the rate-determining step which then subsequently reacts with acetate anion to give (**3**). In order to confirm the rate-determining step, we prepared 2,2,4,4,6,6,8,8-octadeuteriated sulphoxide (**1**)‡ and compared the rate of rearrangement with that of the protiated (**1**). The intermolecular kinetic isotope effect k_H/k_D thus obtained was found to be 1.74 which is consistent with the intramolecular value of 1.7 described above. These isotope effects indicate clearly that α-proton abstraction from the dication (**2**) is involved in the rate-determining step.

Further mechanistic information was gained from the reaction of the ^{18}O-labelled sulphoxide (**1**) (36.5% ^{18}O excess)§ with acetic anhydride in benzene for 2 h. After the reaction, the ^{18}O-contents of the rearranged product and the recovered sulphoxide were determined by mass spectroscopy. The rearranged product contained a 2.6% excess of ^{18}O (7.1% with respect to the original 36.5%) while in the recovered sulphoxide there remained a 12.5% excess of ^{18}O (34.2% with respect to the original). The ^{18}O experiment suggests that the dication (**2**) is probably a tight ion pair (sulphonium salt) which reverts readily to (**1**), while before reacting with the α-sulphenylated cation (**5**), the acetate anion scrambles completely with the anhydride. Thus, these ^{18}O experimental results also support the mechanism of the Pummerer reaction of (**1**) as illustrated in Scheme 1.

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‡ [$^2H_8$]-(**1**) was prepared by oxidation using *m*-chloroperbenzoic acid of the octadeuteriated sulphide which was obtained by reduction of octadeuteriated 1,5-dioxide.

§ The ^{18}O-labelled sulphoxide was prepared by oxidation of 1,5-dithiacyclo-octane with 1,5-diazabicyclo-octane–Br_2 and $H_2{}^{18}O$ (98.0% ^{18}O) in a 1:1 molar ratio.