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SULFUR HETEROCYCLES. II.
THE HYDROXYOXATHIOLANE TO ACYLOIN REARRANGEMENT

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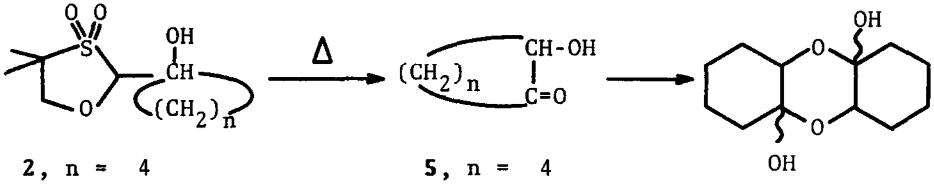
Summary: Thermal control of demasking conditions may be used to convert hydroxyoxathiolanes into either α-hydroxyaldehydes or the corresponding ring-expanded acyloins.

The pyrolysis of 2-substituted-4,4-dimethyl-1,3-oxathiolane-3,3-dioxides generally yields aldehydes in which the 2-substituent in the oxathiolane is identical to the organic residue in the aldehyde.[1] When the 2-substituent is a tertiary carbinol (arising from a ketone) either an aldehyde or an acyloin may be isolated depending on the substrate and conditions. We have obtained some preliminary information concerning the requirements of this reaction and report them herein.

When the anion of 4,4-dimethyl-1,3-oxathiolane-3,3-dioxide (**1**) is allowed to react with cyclopentanone, cyclohexanone or cyclododecanone, the adducts **2**, **3**, and **4**, respectively, are all obtained in greater than 90% yield in purity sufficient for direct pyrolysis. When these adducts are sublimed (internal pressure ca. 0.1-0.2 torr) through a 20-cm Vigreux column loosely packed with 4 x 15 mm Pyrex tubes and maintained at a temperature of ca. 400°C, adipoin (**5**),[2] 2-hydroxycycloheptanone (**6**),[3] and 2-hydroxycyclotridecanone (**7**, brassyloin)[4] were isolated. In the case of adipoin, the dimer **8**[5] rather than the monomeric compound was isolated. In the adipoin case, it was difficult to exactly reproduce the published infrared spectrum but that of adipoin produced by our method was indistinguishable from that of commercially available[6] material. The seven- and thirteen-membered rings tended to remain monomeric.



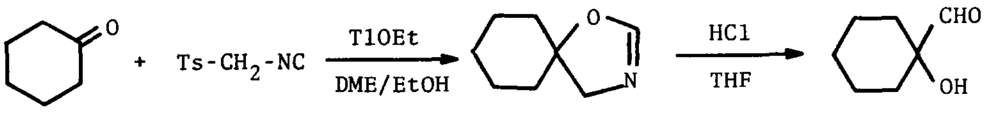
2, n = 4
3, n = 5
4, n = 12

5, n = 4
6, n = 5
7, n = 12

8 = dimer of **5**

2-Hydroxycyclotridecanone is a known monomeric acyloin[4] and could be characterized readily. 2-Hydroxycycloheptanone (**6**, pimeloin) is also known, but additional characterization was desired since its spectral properties are so similar to those of **5**. When the pyrolysis product (**6**) was reduced ($NaBH_4$) immediately, 1,2-dihydroxycycloheptane (pure by ^{1}H-nmr; bis-nitrobenzoate, mp 188-189°) was obtained in 92% overall yield.

It is possible that compounds **2**, **3**, and **4** undergo direct, concerted rearrangement and ring expansion as sulfur dioxide and isobutylene are extruded. It seemed somewhat more likely, however, that the thermal demasking occurred first, and the α-hydroxyketone undergoes an acid catalyzed ring expansion. The source of the acid catalyst might be either sulfur dioxide or the hot glass surface. In order to obtain somewhat more information on the latter possibilities, we prepared 1-formylcyclohexanol[7] by the method of Oldenziel and van Leusen[8] as shown in the equation below. Hydroxyaldehyde **9** was then subjected to pyrolysis under a variety of conditions.



9

When an authentic sample of **9** was sublimed through the pyrolysis column (maintained at 400°C), only the starting material was isolated. This seemed to imply that SO_2 produced during the pyrolysis catalyzes the ring expansion of the intermediate hydroxyaldehyde. In order to test this hypothesis, SO_2 was passed through the pyrolysis column for several minutes prior to conducting the pyrolysis. Compound **9** was sublimed into the conditioned column and product was collected on a liquid nitrogen-cooled coldfinger condenser. No acyloin could be detected; the aldehyde appeared to survive. In a slight variation of this approach, the column was again pretreated with SO_2 which was then allowed to condense on the coldfinger. It was thought that the aldehyde might survive the actual pyrolysis, but that contact with sulfur dioxide could effect the rearrangement on the coldfinger itself. Under the conditions described above, a mixture of compound **9** and its dimer were isolated from the coldfinger. Further dimerization of **9** could be monitored by disappearence of carbonyl absorption in the infrared spectrum. Assuming that proximity of SO_2 and the hydroxyaldehyde in the gas phase is required for the rearrangement to occur, a copyrolysis of **3** and **9** was attempted. Unfortunately, this experiment proved inconclusive and definitive discussion of this question must await the full report of this work.

Certain empirical observations are relevant and lead to a useful method for controlling this pyrolysis reaction. It was found that reactive compound **2** generally underwent ring expansion even at 400°C and even when a short pyrolysis column (10 cm) was used. Compound 3, which is somewhat less reactive, yields 2-formylcycloheptanone (**9**) in almost quantitative yield (crude) when pyrolyzed at 400°C in a short column (10 cm). When pyrolysis was conducted at the same temperature but using a longer column (30 cm), **9** was obtained in 96% crude yield. The observations indicate that although additional work is required before a detailed understanding of this reaction is in hand, it may be controlled effectively by minor variations in reaction conditions.

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NOTES AND REFERENCES

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5. The structure of dimer **8** was suggested by Sheehan and coworkers in reference 2.

6. The commercial material was obtained from the Aldrich Chemical Company.

7. Compound **9** could be obtained in 67% yield by the published (ref. 8) method if a somewhat more vigorous distillation than that described in the original work was conducted.

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