Notes

Formation of Cyclic Disulfide Cation Radicals in the Electron Impact Induced Fragmentation of Mesocyclic Dithioethers

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Recently, we reported[1] that long-lived cation radicals are formed at room temperature in acetonitrile when certain mesocyclic dithioethers are treated with one-electron oxidizing agents such as NO^+ or Cu^{2+}. The enhanced stability of these cation radicals derived from mesocyclic dithioethers is attributed to an interaction between the transannular thioether group and the oxidized thioether to give a ring-fused system with an S–S bond. Because of this unusual behavior, we decided to investigate the mass spectra of mesocyclic dithioethers to determine if a similar transannular interaction gives fragmentation products containing S–S bonds.

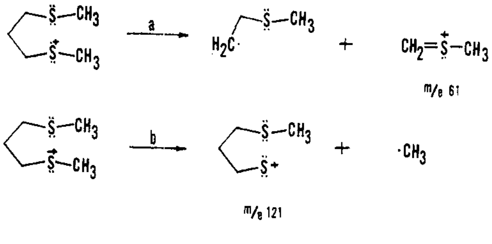
The compounds examined are 1,4-dithiane (1,4-DT), 1,4-dithiacycloheptane (1,4-DTCH), 1,5-dithiacyclooctane (1,5-DTCO), 1,4-dithiacyclooctane (1,4-DTCO), 1,5-dithiacyclononane (1,5-DTCN), 1,4-dithiacyclononane (1,4-DTCN), 1,6-dithiacyclodecane (1,6-DTCD), 2,5-dithiahexane (2,5-DTH), 2,6-dithiaheptane (2,6-DTHP), 2,7-dithiaoctane (2,7-DTO), and 2,8-dithianonane (2,8-DTN).

Results and Discussion

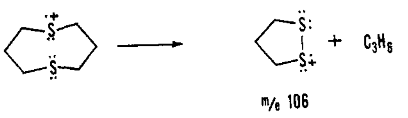
The mass spectra of most thioethers are similar to those of ethers. Normally, cleavage occurs either between the sulfur–carbon bond or the α,β carbon–carbon bond.[2] For example, the mass spectrum of 2,6-dithiaheptane (Scheme I) exhibits strong peaks at *m/e* 121 and 61. However, mesocyclic dithioethers exhibit intense peaks at *m/e* 106 when five-membered ring (1,2-dithiolane) and at *m/e* 120 when six-membered ring (1,2-dithiane) cation radicals can be formed by a transannular interaction. In Scheme II, the formation of the 1,2-dithiolane cation radical from 1,5-dithiacyclooctane is illustrated. This cation radical dominates the spectrum and is more than twice as intense as the parent. A similar decomposition to give the *m/e* 106 peak can be seen in both 1,5-dithiacyclononane and 1,4-dithiacycloheptane where a trimethylene chain also spans the two thioether groups.

The 1,2-dithiane cation radical forms when a tetramethylene chain spans the two thioether groups. In 1,5-dithiacyclononane, both 1,2-dithiolane and 1,2-dithiane cation radicals are observed (Scheme III), whereas 1,6-dithiacyclodecane and 1,4-dithiacyclooctane give only the 1,2-dithiane cation radical. Subsequent cleavage of the 1,2-dithiane cation radical gives an intense peak at *m/e* 55 which is identical with that reported in the fragmentation of 1,2-dithiane itself.[3]

Scheme I. Cleavage of 2,6-Dithiaheptane: (a) α,β C–C Cleavage; (b) S–C Cleavage



Scheme II. Cleavage of 1,5-Dithiacyclooctane



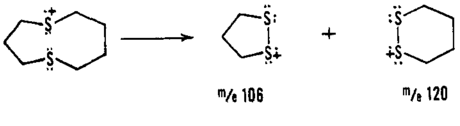
1,2-Dithiolane and 1,2-dithiane radical cations are also observed in the mass spectra of macrocyclic tetrathioethers, where a trimethylene chain (1,5,9,13-tetrathiacyclohexadecane) or a tetramethylene chain (1,6,11,16-tetrathiacycloeicosane), respectively, spans two sulfur atoms.

Only a weak peak due to a four-membered ring cyclic disulfide cation radical (*m/e* 92) is observed when a dimethylene bridge spans the two thioether groups (i.e., in 1,4-dithiacyclooctane, 1,4-dithiacycloheptane, and 1,4-dithiane). Apparently, the strain involved in forming a four-membered ring is so large that alternative cleavage modes predominate. To determine whether cation radicals with ring size greater than six form when the two thioether groups are separated by five methylene groups, 1,4-dithiacyclononane was examined. No seven-membered ring formation was observed as evidenced by the lack of a peak at *m/e* 134.

As part of a study of the photochemistry of dithioketals, Willett[4] also examined the mass spectra of a series of bicyclic dithioethers in which the two sulfur atoms are separated by two and three methylene groups. He reported that the 1,2-dithiolane cation radical and the 1,2-dithiacyclobutane cation radical are formed when the distance between the two sulfur atoms is relatively short. For example, he showed that in the two isomeric 2,6-dithiabicyclo[5.3.0]decanes, the cis isomer exhibits a more intense peak at *m/e* 106 than the trans isomer. However, when he examined the spectrum of 2,6-dithiabicyclo[5.3.1]undecane, a molecule in which the distance between the two sulfur atoms is longer, no peak appeared at *m/e* 106.[4]

These results suggest that an interaction between the two sulfur atoms must occur prior to any bond breaking process in order to produce cyclic disulfide cation radicals.

Scheme III. Cleavage of 1,5-Dithiacyclononane



In 1,5-dithiacyclooctane a small peak is observed at *m/e* 74. Since this peak is at one-half the molecular weight of 1,5-dithiacyclooctane, the possibility that this peak is due to the dication of 1,5-dithiacyclooctane was considered.[5] However, since the relative intensity of the peak at *m/e* 74 did not change at different ionizing voltages, this peak is probably due to a normal fragmentation path of simple thioethers. A series of peaks at 45–47, 59–61, 73–75, and 87–89 are observed in the decomposition of thioethers when one, two, three, and four methylene groups are originally present on the sulfur atom. Thus the strong peak at *m/e* 88 in 1,6-dithiacyclodecane, one-half its molecular weight, and the small peaks at *m/e* 74

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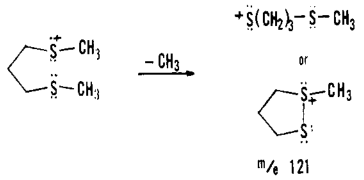
Scheme IV. Cleavage of 2,6-Dithiaheptane



in 1,4-dithiacyclooctane and at m/e 60 in 1,4-dithiane are most likely due to fragments in this series rather than to the dications. To further support the belief that no dicationic species are formed in any of these dithioethers, it is noted that there is *no peak* at m/e 81 in the spectrum of 1,5-dithiacyclononane or 1,4-dithiacyclononane or at m/e 67 in 1,4-dithiacycloheptane.

The mass spectra of some acyclic dithioethers were obtained by Shuttleworth,[6] who reported relatively intense peaks at m/e 121 in 2,6-dithiaheptane (Scheme IV) and m/e 135 in 2,7-dithiaoctane corresponding to loss of a CH_3 group from the cation radical. However, the intensity of the peaks at m/e 107 in 2,5-dithiahexane and at m/e 149 in 2,8-dithianonane, which are attributed to the loss of one CH_3 group from the parent, were lower. Budzikewicz, Djerassi, and Williams[2] suggested that the m/e 121 peak in 2,6-dithiaheptane might be due to a cyclic ion rather than to a linear ion. In view of our results on mesocyclic dithioethers, the formation of cyclic ions in 2,6-dithiaheptane and 2,7-dithiaoctane appears more plausible. Since we did not observe either four-membered or seven-membered ring formation in mesocyclic systems in which two thioether sulfurs were bridged by two and five methylene groups, the rather low intensity of the peaks at m/e 107 and 149 in the mass spectrum of 2,5-dithiahexane and 2,8-dithianonane, respectively, are expected.

Experimental Section

The mass spectra were run on a CE 21-104. The 1,4-dithiane was purchased from the Aldrich Chemical Co., Inc., and was sublimed before use. 1,4-Dithiacycloheptane,[7] 1,5-dithiacyclooctane,[8] 1,4-dithiacyclooctane,[9] 1,5-dithiacyclononane,[9] 1,6-dithiacyclodecane,[10] 2,5-dithiahexane,[11] 2,6-dithiaheptane,[12] and 2,7-dithiaoctane[12] were synthesized following reported procedures.

1,4-Dithiacyclononane. Into a 3-neck 2-L Morton flask fitted with overhead stirrer, condenser, and adaptor for syringe pump was added 1 L of absolute ethanol. With stirring, 12 g (0.52 g-atom) of freshly cut sodium was added under nitrogen. The solution was heated to 50 °C and 21 mL (0.25 mol) of 1,2-ethanedithiol diluted to 100 mL with absolute ethanol and 57.5 g (0.25 mol) of 1,5-dibromopentane diluted to 100 mL with absolute ethanol were added simultaneously by a syringe pump at a rate of 0.30 mL/min. The mixture was refluxed for 0.5 h and then concentrated under vacuum. Water was added to the remaining thick oil, and the mixture was extracted three times with dichloromethane. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was distilled under vacuum to give 0.24 g (0.6%) of 1,4-dithiacyclononane: bp 65–67 °C (0.3 mm); mp 59–60 °C; ^{1}H NMR (CCl_4) δ 2.8 (m, 8, CH_2-S), 1.9 (m, 6, —CH_2—); ^{13}C NMR ($CDCl_3$) δ 34.8, 33.5, 27.9, 24.5.

Registry No.—1,4-DT, 505-29-3; 1,4-DTCH, 6008-55-5; 1,5-DTCO, 6572-95-8; 1,4-DTCO, 6572-94-7; 1,5-DTCN, 6573-47-3; 1,6-DTCD, 51472-64-1; 2,5-DTH, 6628-18-8; 2,6-DTHP, 24949-35-7; 2,7-DTO, 15394-33-9; 2,8-DTN, 54410-63-8; 1,2-dithiolane cation radical, 66609-63-0; 1,2-dithiane cation radical, 56587-33-8.

Supplementary Material Available: Bar graphs showing the mass spectra of all the dithioethers are presented (5 pages). Ordering information is given on any current masthead page.

References and Notes

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Mechanism of Oxidation of Alkylaromatic Compounds by Metal Ions. 4. Cerium(IV) Pyridinium Chloride. A Novel Reagent for Side-Chain Oxidation of Highly Substituted Methylbenzenes[1]

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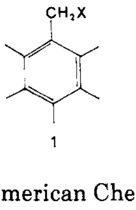
Several reports on oxidation reactions of methylbenzenes by Ce(IV) compounds are available in the recent literature.[2] We have shown that ceric ammonium nitrate (CAN) in oxygen-free AcOH leads to a mixture of side-chain acetoxylated and nitrooxylated products.[2] In view of the general interest of reactions leading to side-chain functionalization of alkyl aromatic compounds, we have investigated the behavior of a different oxidizing system, namely ceric pyridinium chloride $(C_5H_6N)_2CeCl_6$ (referred to as CPC), in either MeOH or EtOH solution. We now wish to report on a product study of the oxidation by this reagent of some highly substituted methylbenzenes, namely, hexamethylbenzene (HMB), durene (DUR), and mesitylene (MES).

The oxidation reactions were carried out under reflux in a nitrogen atmosphere with 2 mol of oxidant per mol of hydrocarbon. The results (Table I) show that with either HMB or DUR fair to good yields of side-chain chlorinated and/or alkoxylated products are formed. In contrast, MES does not seem to be reactive enough as to compete with the "spontaneous" reduction of CPC in boiling MeOH.[3] Because of its low reactivity, the oxidation of MES in EtOH solution was not attempted. Interestingly, both the oxidation reaction and the "spontaneous" reduction of CPC are at least two orders of magnitude faster in MeOH than in EtOH. This phenomenon might be related to different structures of the dissolved Ce(IV) species in the two solvents, possibly due to varying extents of displacement of loosely bound chloro ligands by solvent molecules (vide infra).

A dramatic change in the reaction mixture composition was observed when oxygen was bubbled through the solution during the oxidation of DUR in MeOH. 2,4,5-Trimethylbenzaldehyde, mp 38.5–40 °C,[4] was isolated in 65% yield. It was in fact detected in the ^{1}H-NMR spectrum of the crude reaction product mostly as its dimethyl acetal **3**.[5] The latter was also



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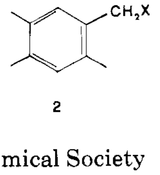

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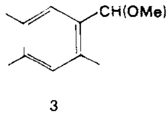

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