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Oxidative Cleavage of *cis*-1,2-Diamino-1,2-Dimethylcyclobutane to 2,5-Hexanedione

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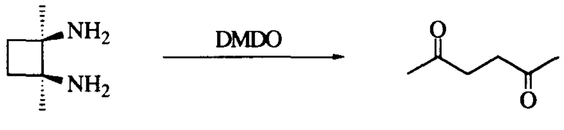
Abstract: *cis*-1,2-Diamino-1,2-dimethylcyclobutane is oxidatively cleaved by dimethyldioxirane to 2,5-hexanedione.

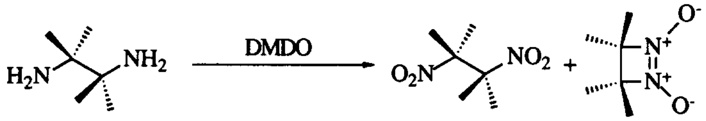
There has been considerable interest in the synthesis of highly strained polynitropolycyclic cage compounds because of their potential as high energy density materials.[1] Amongst the most desirable of these compounds are the polynitrated cubanes.[2] The syntheses of 1,3-dinitro, 1,4-dinitro, 1,3,5-trinitro and 1,3,5,7-tetranitrocubanes have been accomplished by the oxidation of the corresponding amines.[3] Thus far all attempts to synthesize 1,2-dinitrocubanes by the oxidation of the corresponding 1,2-diaminocubanes have failed due to cage cleavage reactions. One possible way that ring cleavage might occur would involve oxidation of one of the amino groups to a hydroxylamino group followed by a Grob fragmentation.[4] To date, there is no experimental evidence to substantiate this hypothesis even though the destablizing effect of adjacent amino and nitro groups in cubane has been supported by *ab initio* calculations.[5] We now wish to report the first experimental evidence which supports the contention that ring cleavage does in fact occur during the oxidation of vicinal diamines. We have found that dimethyldioxirane (DMDO) oxidizes *cis*-1,2-diamino-1,2-dimethylcyclobutane (1)[6] to 2,5-hexanedione (2, 86%).[7] This result is significant since it is the first time in which the cleavage product resulting from the oxidation of a vicinal diamine has been isolated and identified. On the other hand, the open chain analogue, 2,3-diamino-2,3-dimethylbutane (3) yields a mixture of 2,3-dimethyl-2,3-dinitrobutane (4, 13%) and the cyclic nitroso dimer 3,3,4,4-tetramethyl-1,2-diazetine-1,2-dioxide (5, 49%). Unfortunately, the oxidative cleavage product in this case would be acetone which can not be detected since the oxidant is prepared as an acetone solution. It should also be

(1)



1 2

(2)



3 4 5

noted that the DMDO oxidation of *o*-phenylenediamine to *o*-dinitrobenzene occurs quantitatively.[8]

Two further questions still need to be addressed in order to fully understand the nature of this oxidative cleavage. (a) How much strain within a cyclic system can be tolerated before oxidative ring cleavage will occur? and (b) At what oxidation level (hydroxylamino, nitroso, or nitro) does the oxidized amino group have to attain for ring cleavage to occur? The obvious implication from our result for the cyclobutane ring system is that a similar type of ring cleavage has occurred in the cubane systems. In view of our result, which has been predicted but never verified, the direct oxidation of vicinal primary diamino groups to vicinal dinitro groups in strained polycyclic systems does not appear to be possible. We are attempting to develop alternate synthetic methods for these types of compounds.[9]

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7. A solution of diamine or diamine dihydrosulfate (0.4mmol) was added dropwise to a solution of DMDO in acetone (0.05M, 96mL, 4.8mmol) at 0°C, stirred for 1 hr and the product isolated after careful removal of the solvent. The DMDO solution was prepared according to Adam. Adam, W.; Hadjiarapoglou, L. and Smertz, A. *Chem. Ber.* **1991**, *124*, 227.
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