

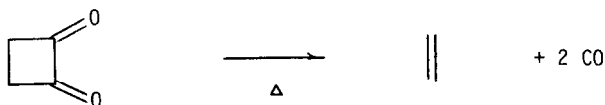
**A STEREOCHEMICAL STUDY OF THE THERMOLYSIS
OF CYCLOBUTANE-1,2-DIONE**

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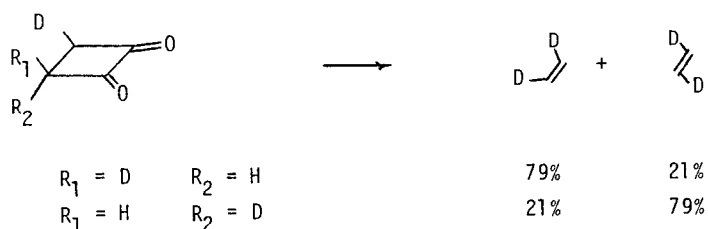
Abstract: The thermolysis of both dl and meso-3,4-dideuterio-cyclobutane-1,2-dione at 250°C yields ethylene and carbon monoxide in which 79% of the stereochemistry of the reactant is retained in the ethylene.

Thermolysis of diketene and cyclobutane-1,3-dione in a flow system produces good yields of ketene.¹ The thermolysis of cyclobutane-1,2-dione under similar conditions has not previously been reported. Using the fragmentation pattern in the mass spectrum particularly at m/e 42, as a guide to thermal fragmentation, suggested that ketene might also be produced upon thermolysis of cyclobutane-1,2-dione. Our interest in a rational synthesis of isotopically pure mono-deuterioketene³ prompted us to investigate the thermal behavior of this diketone. The facile synthesis of this material via the Acyloin condensation of readily available meso and dl-diethyl-2,3-dideuteriosuccinate appeared to be an attractive synthesis of the target molecule.⁴⁻⁶

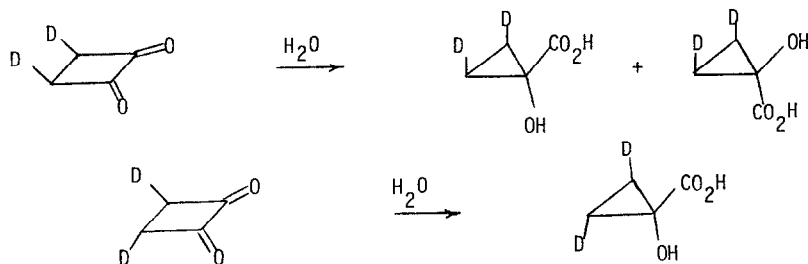
Cyclobutane-1,2-dione was prepared and the thermolysis of this material in a flow system in the temperature range 230-370°C afforded ethylene as the only product condensable at -178°C. The thermolysis was clean as evidenced by mass balance based on the recovery of ethylene and starting material (85%). Polymerization and/or decomposition other than that cited above was not visually apparent on the glass surface. Thermolysis of cyclobutane-1,2-dione in a sealed tube afforded carbon monoxide and ethylene (CO/C₂H₄ = 2.1±.3) and significant amounts of non-volatile decomposition products.⁷ We attribute the clean thermolysis in the flow system to the shorter contact times and the low vapor pressure of cyclobutane-1,2-dione (70 Pa, 25°C), which effectively precludes bimolecular reactions. Examination of the possible routes of fragmentation of cyclobutane-1,2-dione suggested that cyclopropanone, or the corresponding diradical generated by thermolysis of cyclopropanone might be an intermediate in the reaction. Since the chemistry of cyclopropanone has been and continues to be the focus of both experimental⁸ and theoretical studies⁹ we decided to investigate the stereochemical consequences of this thermolysis by examining the thermal behavior of both dl and meso-3,4-dideuteriocyclobutane-1,2-dione.



Thermolysis of samples of *dl* and *meso*-dideuteriocyclobutane-1,2-dione through a 300 x 12mm quartz tube maintained at $250 \pm 20^\circ\text{C}$ using a He flow rate of 1 mL/s for 4 h resulted in the volatilization of approximately 0.9 mmole of solid sample (maintained at 40°C).¹⁰ From the sample, both ethylene (0.68 mmole) and starting material (0.063 mmole) were recovered (mass balance 82%). The stereochemistry of the recovered ethylene was analyzed by infrared spectroscopy. Comparison of the spectra of ethylene isolated from both *dl* and *meso*-3,4-dideuteriocyclobutane-1,2-dione indicated that some loss of stereochemistry had occurred. Analysis of the spectra from both isomers revealed that $79 \pm 4\%$ of the original stereochemistry had been retained in the recovered ethylene.¹¹ This analysis was confirmed by preparing mixtures of authentic samples.¹² At $360 \pm 10^\circ\text{C}$, the amount of retention decreased to $68 \pm 5\%$.

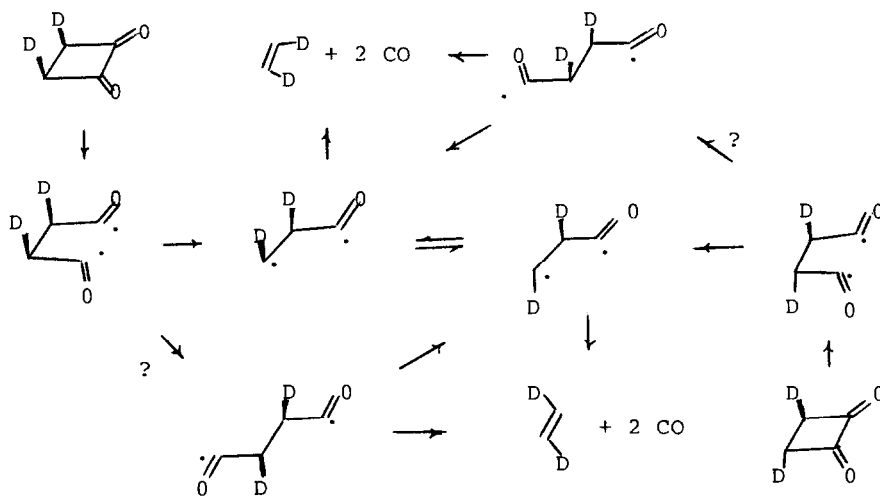


The stereochemistry of recovered 3,4-dideuteriocyclobutane-1,2-dione was determined indirectly by conversion to 1-hydroxy-1-cyclopropanecarboxylic acid. Previous work⁵ had shown that ring contraction of cyclobutane-1,2-dione in D_2O did not lead to deuterium incorporation in the methylene hydrogens of the cyclopropane ring.² Control experiments based on nmr and infrared evidence indicated that the ring contraction is at least stereoselective and the nmr spectra suggest that it occurs with retention of configuration of the migrating group.¹³ A peak at 1025 cm^{-1} , which could partially be resolved in the infrared spectrum of the *dl*-dideuteriocyclopropanecarboxylic acid, served to differentiate between the *dl* and the two *meso* dideuterio-acids isolated from ring contraction of 3,4-dideuteriocyclobutane-1,2-dione. Conversions of the *dl* and *meso*-dideuteriocyclobutane-1,2-dione isolated from 85% thermolysis at 250°C , to the corresponding 1-hydroxycyclopropanecarboxylic acids indicated that little if any scrambling had occurred in the thermolysis step. We conclude from this that the diones do not extensively stereomutate during thermolysis. However it is estimated that as much as 10% of the *meso* acids in *dl*-2,3-dideuterio-1-hydroxycyclopropanecarboxylic acids could have gone undetected in this experiment.



The most likely pathway for fragmentation of cyclobutane-1,2-dione consistent with the lack of significant stereochemical scrambling in recovered starting material and on bond energetics,¹⁴ involves cleavage of the α -diketone to generate a diradical with an extremely short lifetime (Scheme I). If the anti-conformation in this diradical is energetically preferred, as suggested by theoretical calculations on tetramethylene,¹⁵ and experimental results on thermolysis of 7,8-*cis*, *exo*-dideuteriobicyclo[4.2.0]octane,¹⁶ very little initially formed diradical survives long enough to fragment from this conformation. Our experimental results cannot differentiate between sequential and concerted loss of both carbon monoxides. We presently favor loss of CO occurring in two steps. Formation of cyclopropanone or its diradical would be expected to rapidly decarbonylate to yield ethylene.¹⁷ The observed loss of stereochemistry in the recovered ethylene could also occur at this stage as is observed for tetramethylene-d₂,^{6,18} since the pathway proceeding through cyclopropanone and or its diradical should offer the greatest propensity for loss of stereochemistry. The greater amount of scrambling observed at higher temperatures in the recovered ethylene is consistent with an activation energy for methylene torsion in the diradical.

Scheme I



References and Notes

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10. We cannot rigorously exclude the possibility that the thermolysis reaction is a surface catalyzed process. However, indentical results both in terms of the extent of fragmentation, and ethylene isomerization have been obtained in both pyrex and quartz tubes suggesting that the reaction is not extremely sensitive to the nature of the surface.
11. The amount of scrambling could be estimated from the spectra by assuming that the amount of cis ethylene formed from dl-3,4-dideuteriocyclobutane-1,2-dione was equal to the amount of trans ethylene formed from the corresponding meso dione. A value of 79% retention was obtained. The \pm 4% uncertainty was estimated by comparison to mixtures of authentic samples of cis and trans ethylene- d_2 . Both ethylenes were configurationally stable under the reaction conditions used.
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(Received in USA 5 November 1984)