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THE REACTION OF 1,2-CYCLONONADIENE WITH PERACETIC ACID[1]

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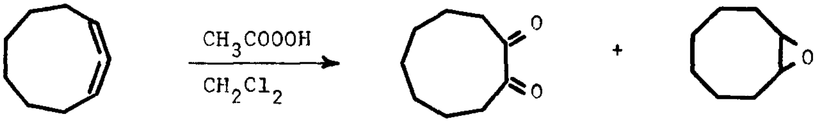
In recent years several papers have appeared describing the peracid oxidation of allenes.[3,4,5,6] However, none of these reports have been concerned with cyclic allenes. We wish to report the reaction of 1,2-cyclononadiene with peracetic acid. Treatment of 1,2-cyclononadiene with three (3) equivalents of acid-free 40% peracetic[7] in methylene chloride for 48 hours resulted in a quantitative conversion into 1,2-cyclononanedione and cyclooctene oxide in a ratio of 60:40.



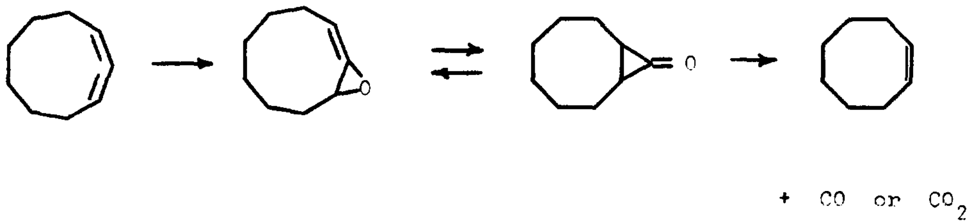
Both products were isolated by preparative gas chromatography using a 20 ft. column of Carbowax 6000 on Chromasorb W.

The structure of cyclooctene oxide was established by comparing infrared, mass spectra, and nmr[8] with an authentic sample prepared by peracid epoxidation of cyclooctene.[9]

The structure of 1,2-cyclononanedione was established by mass spectral analysis (parent peak at m/e 154) and by superimposable infrared and nmr spectra with an authentic sample prepared by selenious acid oxidation of cyclononanone.[10]

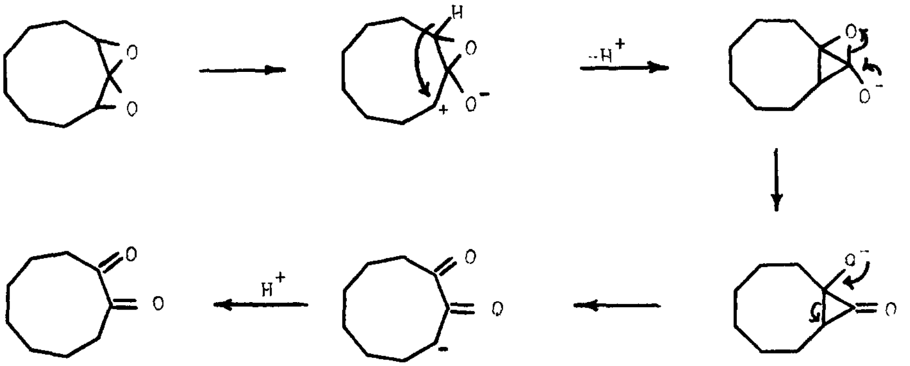
The starting 1,2-cyclononadiene was prepared by treatment of cyclooctene[11] with bromoform and potassium t-butoxide and reaction of the resulting 9,9-dibromobicyclo[6.1.0]nonane with methyl lithium. Since cyclooctene oxide could readily arise from unreacted cyclooctene present in the allene, care was taken to rid the allene of any unreacted cyclooctene.

Mechanistically the cyclooctene oxide could conceivably arise from cyclooctene formed from oxidative decarboxylation of an intermediate cyclopropanone.[12,13]



No attempt has been made to discern if the evolved gas is carbon dioxide or carbon monoxide. However, Baldwin has observed a case where the formal loss of carbon monoxide is actually achieved through removal of a carbon dioxide molecule.[12]

The pathway leading to the 1,2-cyclononanedione has not been elucidated; however, it possibly could arise from rearrangement of the diepoxide of the starting allene.[14]



Attempts to detect this epoxide by spectral and chromatographic techniques have thus far been unsuccessful.

When the reaction was conducted in methanol, cyclooctene oxide (48%) was formed along with several unidentified minor products which tend to polymerize to a dark brown tar upon attempted isolation. Attempts are currently being made to isolate and identify these substances.

Additional studies are being conducted with other cyclic allenes, and the oxidation of 1,2-cyclononadiene is being investigated under a variety of reaction conditions.

REFERENCES

1. Support of this research by the Robert A. Welch Foundation of Houston, Texas is gratefully acknowledged.
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7. Commercial 40% peracetic acid was treated with sodium carbonate (see Ref. 4) to remove acetic acid.
8. The authors wish to express appreciation to Dr. Ben A. Shoulders of The University of Texas at Austin and to Dr. B. L. Shapiro and Mr. John W. Trotter of Texas A & M University for running nmr spectra and to Dr. Manfred Reinecke of Texas Christian University for running the mass spectra.
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14. A referee has suggested an alternative mechanism involving peracetic acid attack on the allene oxide and rearrangement of the resulting α- peroxy ketone to the 1,2-cyclononanedione.