Fused small ring compounds
by Shi-Kuang Yao

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University

Abstract:
Bicyclo(3.1.0)hexane-6-carboxylic acid [diagram not captured by OCR] has been synthesized by reaction of cyclopentene with ethyl diazoacetate in the presence of copper powder followed by alkaline hydrolysis. It has been observed that this compound does not undergo the Hell-Volhard-Zelinsky reaction.

Rearrangement of 6,6-dichlorobicyclo(3.1.0)hexane was found to occur on heating. Both the original dichloride and the rearrangement product gave the same l-chloro-6-acetoxy-l-cyclohexene when refluxed with potassium acetate and acetic anhydride.

The structure of the rearrangement product, 1,6-dichloro-l-cyclohex-ene, was proved by degradation and by preparing an authentic compound. The unknown and the authentic compound were found identical by both infrared and vapor phase chromatography analyses.

The following mechanisms are proposed: 1. 6,6-DichlorobicycIo(3,1.0)hexane* is heated at 150°C.: [diagrams not captured by OCR] 2. 6,6-Dichlorobicyclo(3.1.0)hexane reacts with potassium acetate in acetic anhydride: [diagrams not captured by OCR] * The number of members in the ring to the right exclusive of the members linking the two rings togethere are indicated by a number. Similarly the members of the smaller ring are designated. Lastly the members of the link (bridge) exclusive of the linking members are designated by number also. viz. bicyclo(3.1.0)hexane [diagram not captured by OCR] For the numbering of the compound, start numbering 1 at one of the carbons in the bridge as illustrated above.

FUSED SMALL RING COMPOUNDS

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Shi-Kuang Yao

A THESIS

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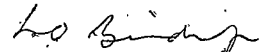
Approved:

Head, Major Department



Chairman, Examining Committee

Dean, Graduate Division

Bozeman, Montana
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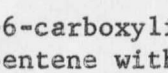
ABSTRACT

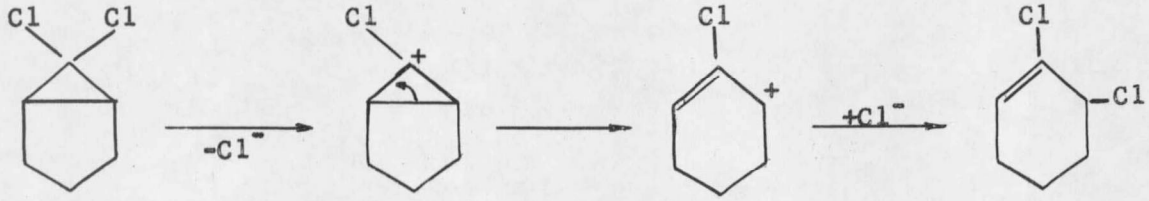
Bicyclo(3.1.0)hexane-6-carboxylic acid () has been synthesized by reaction of cyclopentene with ethyl diazoacetate in the presence of copper powder followed by alkaline hydrolysis. It has been observed that this compound does not undergo the Hell-Volhard-Zelinsky reaction.

Rearrangement of 6,6-dichlorobicyclo(3.1.0)hexane was found to occur on heating. Both the original dichloride and the rearrangement product gave the same 1-chloro-6-acetoxy-1-cyclohexene when refluxed with potassium acetate and acetic anhydride.

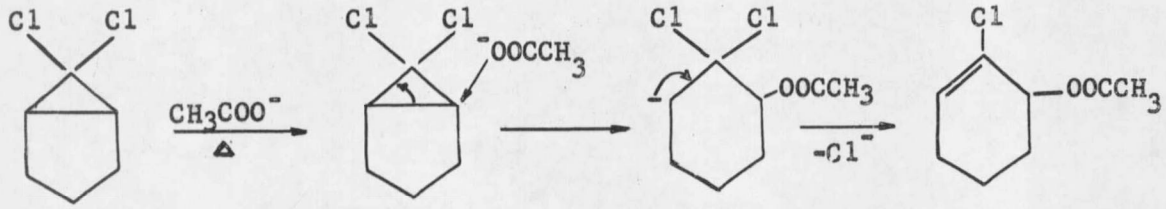
The structure of the rearrangement product, 1,6-dichloro-1-cyclohexene, was proved by degradation and by preparing an authentic compound. The unknown and the authentic compound were found identical by both infrared and vapor phase chromatography analyses.

The following mechanisms are proposed:

1. 6,6-Dichlorobicyclo(3.1.0)hexane* is heated at 150°C.:



2. 6,6-Dichlorobicyclo(3.1.0)hexane reacts with potassium acetate in acetic anhydride:



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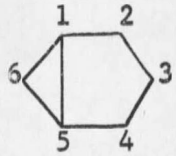
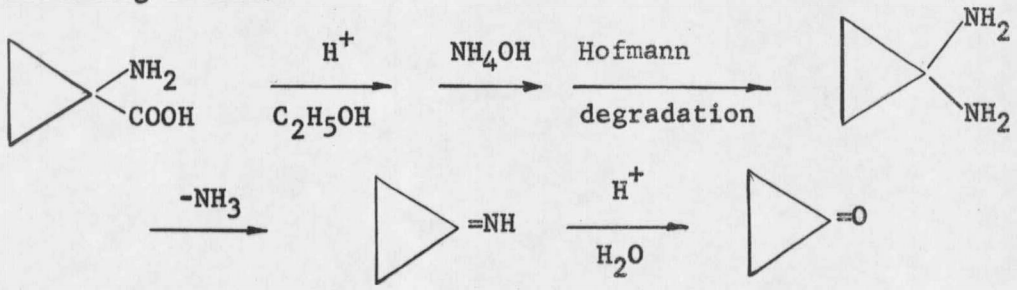


For the numbering of the compound, start numbering 1 at one of the carbons in the bridge as illustrated above.

INTRODUCTION

There have been attempts to synthesize cyclopropanone for the past 40 years; however all these attempts have met with failure. This is undoubtedly due to the great strain on a three-membered ring.

In 1922, Ingold (1) reported the synthesis of cyclopropanone by the following method:



Demyanov and Feofilaktov (2) attempted to repeat Ingold's (1) work very carefully by the following scheme: