

THE ATTEMPTED SYNTHESIS OF BICYCLO[2.2.0]HEX-2-ENE  
AND CYCLOBUTENE BY THE RAMBERG-BACKLUND REACTION

by

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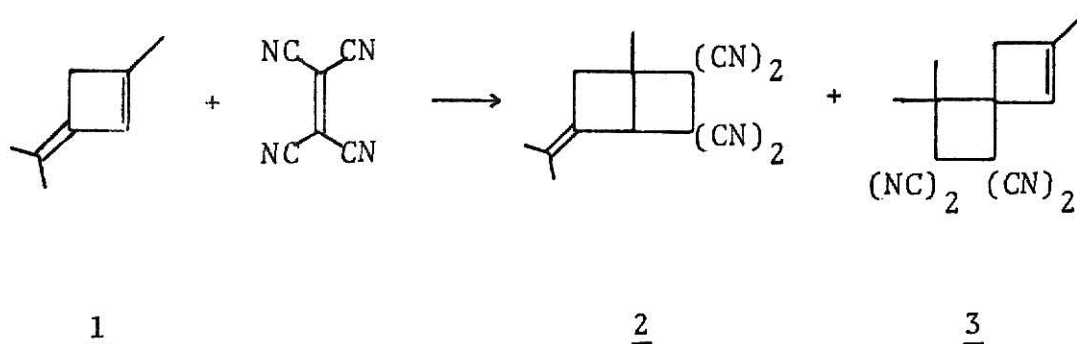
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## INTRODUCTION

Bicyclo[2.2.0]hexane and its derivatives have been synthesized by several different routes. A review of the syntheses and chemistry of bicyclo[2.2.0]hexane systems was completed in 1966 by Reineke<sup>56</sup> and updated by Davis<sup>20</sup> and Sleeter<sup>68</sup> in 1968. The lack of a convenient synthesis of the basic ring system or its simple derivatives has been, in large measure, responsible for the absence of more extensive studies of its chemistry. Only a few synthetic methods lend themselves to the preparation of significant quantities (10 grams or more) of the ring system.

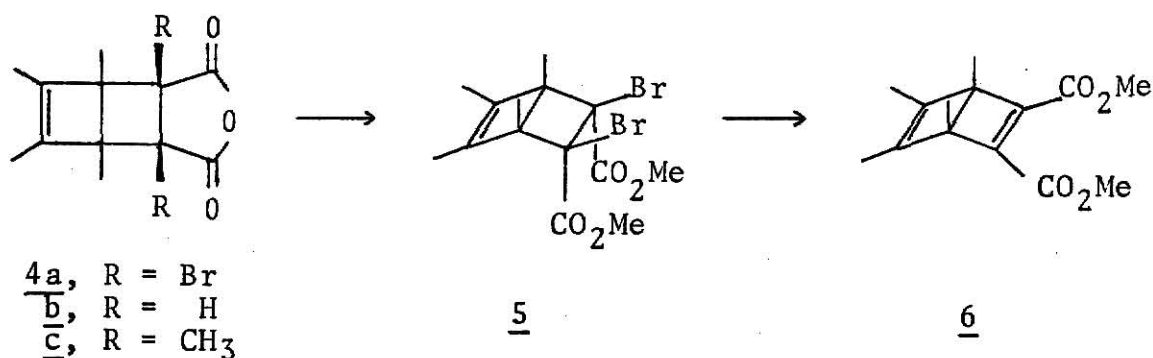
Williams<sup>87</sup> studied the addition of tetracyanoethylene (TCNE) to certain substituted cyclobutenes. He found that when 1-methyl-3-isopropylidenecyclobutene (1) was allowed to react with TCNE, a mixture containing the bicyclic (2) and spiro compounds (3) was formed in 71% yield. The mixture



was estimated to contain 80% of 2 by intensity measurements in the infrared spectrum. Bicyclic 2 was isolated in pure form by recrystallization from dichloromethane-ether. Cyclobutenes similar to 1 in which the exocyclic double bond was not highly substituted gave only spiro adducts. Methylene-

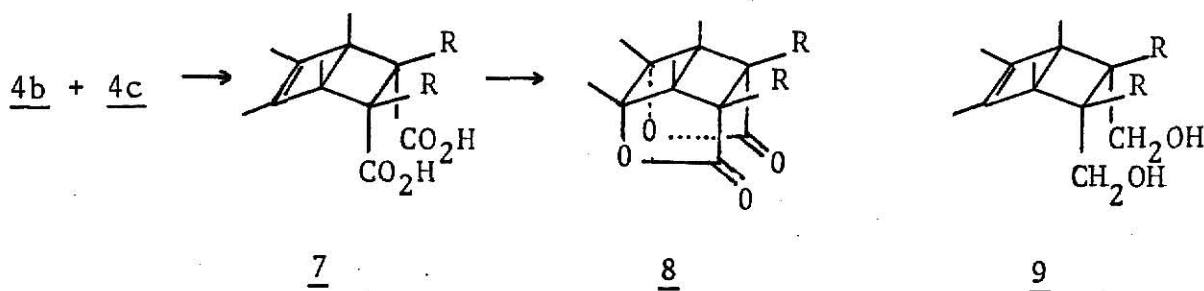
cyclobutane does not react with TCNE.<sup>7</sup>

Criegee and Zanker<sup>18</sup> prepared the tricyclic anhydride 4a in 67% yield by stirring a solution of 2,3-diiodo-1,2,3,4-tetramethylcyclobutene and dibromomaleic anhydride with mercury. Anhydride 4a was converted to dimethyl ester 5 followed by elimination of bromine with copper-zinc couple to give dimethyl "Dewar tetramethylphthalate" (6) in 92% yield. "Decagram quantities" of 6 were reported easy to prepare by this method. Diester 6 was converted quantitatively



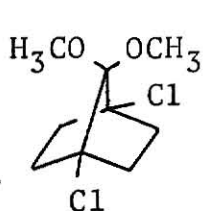
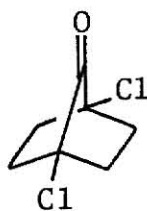
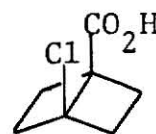
to dimethyl tetramethylphthalate upon heating with a half-life of 4.7 hr at 90.1°C.

By an analogous method Criegee, Kristinsson, Seebach, and Zanker<sup>17</sup> prepared tricyclic anhydrides 4b and 4c from maleic and dimethylmaleic anhydride, respectively. After hydrolysis to the diacids 7b and 7c, treatment with lead tetraacetate in

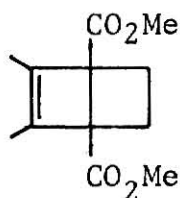
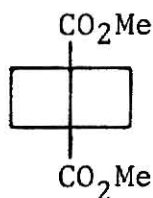
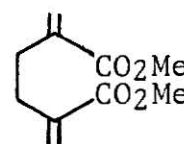


glacial acetic acid gave dilactones 8b and 8c. Diols 9b and 9c were also obtained by reduction of their corresponding anhydrides with lithium aluminum hydride.

Scherer<sup>64</sup> reported that 1,4-dichloro-7,7-dimethoxybicyclo[2.2.1]heptane (10), after acid hydrolysis to the dichloroketone (11), gave 4-chlorobicyclo[2.2.0]hexane-1-carboxylic acid (12) in 93% yield when allowed to react with potassium hydroxide via a Favorski type rearrangement.

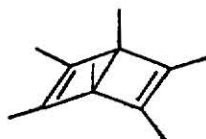
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Photolytic [2 + 2] cycloadditions to cyclobutenes have found success in the synthesis of substituted bicyclo[2.2.0]hexanes. Seebach<sup>65</sup> reported in 1964 that diester 13 could be obtained in 50% yield from the photolysis of dimethyl cyclobutene-1,2-dicarboxylate in 2-butyne as solvent. More recently, Owsley and Bloomfield<sup>43,44</sup> reported that the low temperature photolysis of the same cyclobutene diester in the presence of ethylene gave a quantitative yield of dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate (14). A 9:1 mixture

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of diester 14 and the bicyclopropyl compound 15 was obtained in 63% yield from two consecutive [2 + 2] cycloadditions of ethylene to dimethyl acetylenedicarboxylate. Distillation of the mixture at 75-80°/0.2 mm caused isomerization of 14 to hexadiene 16. Pure 14 was found to rearrange quantitatively to 16 with a first-order rate constant of  $(2.2 \pm 0.4) \times 10^{-4} \text{ sec}^{-1}$  at 75° in chloroform solution. This rate of isomerization was estimated to be approximately  $10^8$  times faster than the rate of isomerization of bicyclo[2.2.0]hexane to 1,5-hexadiene.

A Dewar benzene derivative was first prepared on a "technical scale" by Schafer<sup>60,61</sup> in 1966. He obtained 500 g of hexamethylbicyclo[2.2.0]hexa-2,5-diene (17) by the trimerization reaction of 1 kg of 2-butyne with aluminum chloride. Shortly thereafter, Schafer reviewed<sup>62</sup> the physical properties and chemistry of 17. The ready availability of

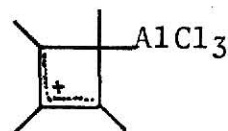
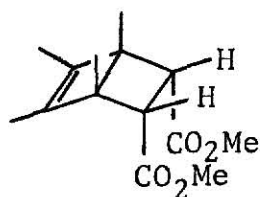
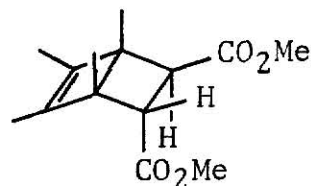


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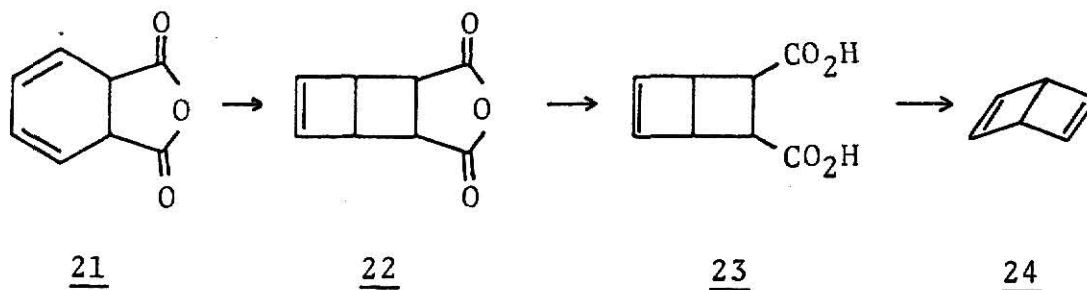
17 (commercially from Aldrich and J.T. Baker chemical companies) spawned a number of recent investigations<sup>2,4,5,15,30,78,86</sup> into its structure and chemistry. Even its carcinogenic activity in mice was studied.<sup>19</sup>

Koster, Timmermans, and van Bekkum<sup>28</sup> reported on the reaction of the tetramethylcyclobutadiene-aluminum chloride complex (18) with dienophilic esters. When 18 was allowed to

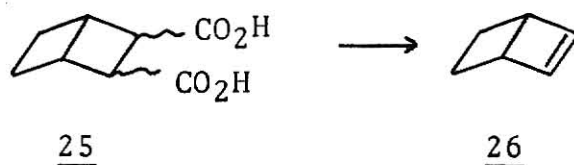
react with dimethyl acetylenedicarboxylate, dimethyl maleate, or dimethyl fumarate, bicyclic diesters 6, 19, and 20, respectively, were obtained in good yields.

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Unsubstituted bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene) (24) was prepared by van Tamelen and Pappas<sup>81,82</sup> in quantities sufficient enough to allow further study of its chemistry.<sup>79,80</sup> Photolysis of cis-1,2-dihydrophthalic anhydride (21) gave bicyclic anhydride 22. Decarboxylation of 22 with lead tetraacetate or hydrolysis to diacid 23 followed by electrolytic decarboxylation gave 24.

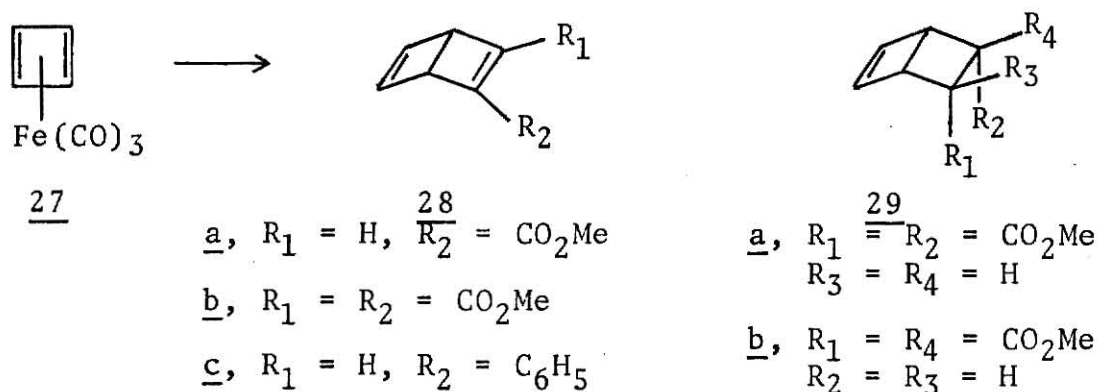
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In an analogous sequence McDonald and Reineke<sup>32,34</sup> were able to prepare bicyclo[2.2.0]hex-2-ene (26) in good yield from anhydride 22 by hydrogenation, hydrolysis, and lead tetraacetate decarboxylation of the resulting bicyclo[2.2.0]-hexane-2,3-dicarboxylic acid (25). From the bicyclic olefin 26,



McDonald and Reineke reported the synthesis and solvolysis of exo-bicyclo[2.2.0]hex-2-yl tosylate<sup>32,34</sup>, and the synthesis of bicyclo[2.2.0]hexan-2-one and endo-bicyclo[2.2.0]hexan-2-ol.<sup>33,35</sup>

Perhaps the most promising and versatile method of preparing substituted bicyclo[2.2.0]hexane ring systems is that involving the decomposition of cyclobutadieneiron tricarbonyl in the presence of olefins or acetylenes. Watts, Fitzpatrick, and Petit<sup>83</sup> showed that when cyclobutadieneiron tricarbonyl (27) was decomposed with ceric ion at 0° in the presence of methyl propiolate, the product was 2-carbomethoxybicyclo[2.2.0]hexa-2,5-diene (28a). Similar decomposition of 27 in the presence of dimethyl acetylenedicarboxylate produced 2,3-dicarbomethoxybicyclo[2.2.0]hexa-2,5-diene (28b). When



27 was decomposed in the presence of dimethyl maleate,<sup>84</sup>



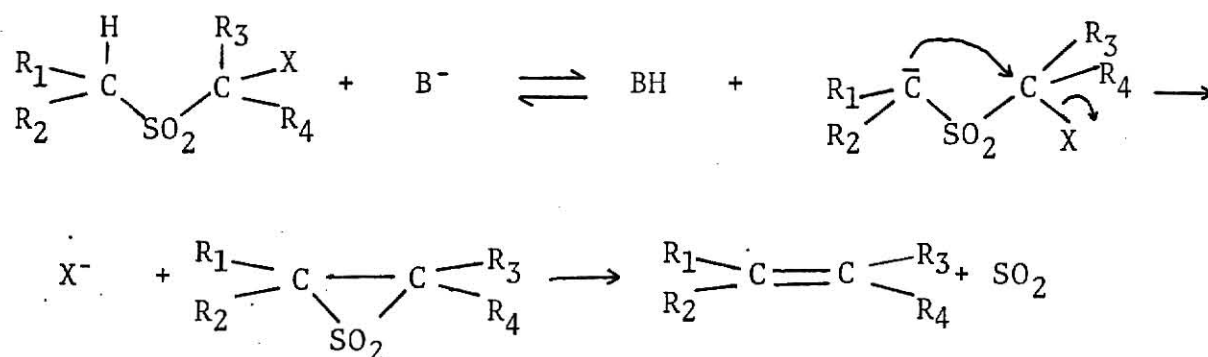
dimethyl fumarate,<sup>84</sup> or phenyl acetylene<sup>14</sup> the products obtained were 29a, 29b, and 28c, respectively. The method becomes even more promising in view of the variety of substituents which may be placed on the four-membered ring of 27.<sup>23,57</sup>

Thus, while there are several methods available for the preparation of substantial quantities of the bicyclo[2.2.0]-hexane ring system, only two have been successfully used for the synthesis of the unsubstituted molecules or their simple derivatives. The first of these routes, that of van Tamelen and Pappas and of McDonald and Reineke, suffers primarily from the tedious nature of the photolysis step. The second method, the cyclobutadieneiron tricarbonyl route, finds its major shortcoming in the synthesis of the iron complex itself. Although the synthesis of the complex has been well worked out,<sup>55</sup> the expense and relative inavailability of the starting materials leaves much to be desired. The complex has been obtained by other methods<sup>25,57,58</sup> but each route suffers from either the expense or lack of available starting materials, low overall yields, or a tedious step in the synthesis.

In considering synthetic methods which might go into the design of a better and more generally applicable synthesis of various structures containing the bicyclo[2.2.0]hexane skeleton, the Ramberg-Backlund reaction of  $\alpha$ -halo sulfones appeared to be a reasonable candidate. The basic reaction conditions would eliminate concerns about acid catalyzed

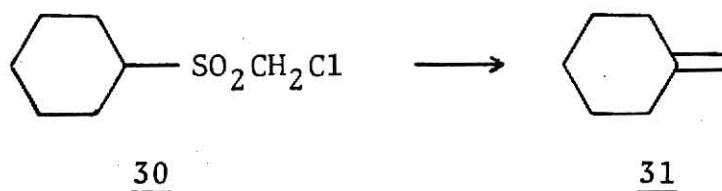
rearrangements which might occur in certain strained ring systems. This reaction had been successfully used to prepare a wide variety of olefins some of which contained a strained cyclobutene moiety. The general utility and mechanism of the Ramberg-Backlund reaction had been discussed in several reviews by Bordwell<sup>9,10</sup> and Paquette.<sup>46,47</sup>

Bordwell,<sup>11</sup> the first worker to study the Ramberg-Backlund reaction in some detail, proposed the following mechanism for the reaction:



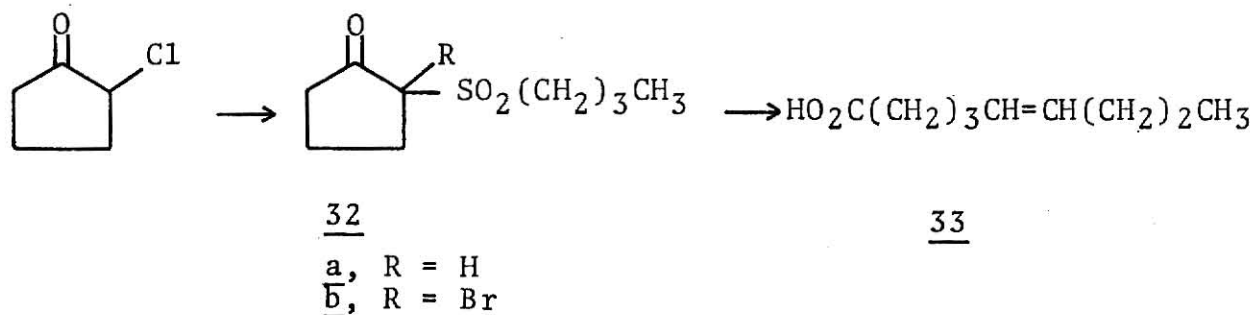
Later work supporting and elaborating upon this general mechanism has been summarized in the reviews by Bordwell and Paquette.<sup>9,10,46,47</sup>

The Ramberg-Backlund reaction has been applied most often to the synthesis of acyclic or unstrained cyclic compounds. Paquette<sup>45</sup> prepared methylenecyclohexane (31) in 80% yield by refluxing chloromethyl cyclohexyl sulfone (30) with aqueous sodium hydroxide. This step represents the final step of a general three-step conversion of



mercaptans to terminal olefins containing one additional carbon atom.

The Ramberg-Bäcklund reaction was employed by Ficini and Stork<sup>21</sup> in a novel sequence for the conversion of cyclic  $\alpha$ -halo ketones to open chain carboxylic acids containing a double bond in a well-defined position. For example, 2-chlorocyclopentanone was converted to 2-(butylsulfonyl)-cyclopentanone (32a) in 70% yield by reaction with sodium butylmercaptide and subsequent oxidation with monoperphthalic acid. Bromo sulfone 32b was obtained by allowing 32a to react with sodium hydride followed by addition of bromine. Treatment with 2N potassium hydroxide gave the olefinic acid 33 in 50% yield from 32a.

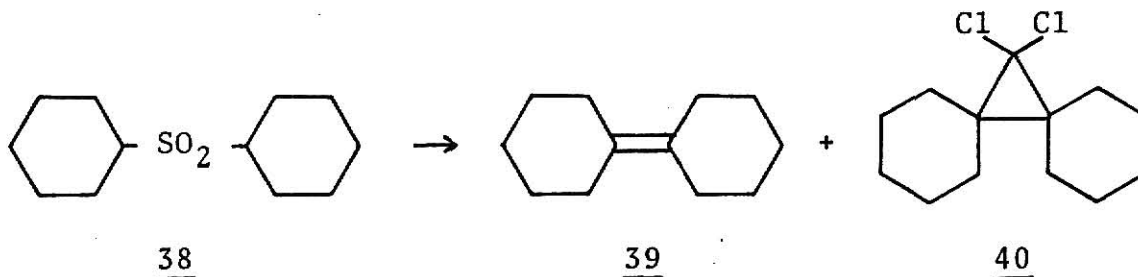
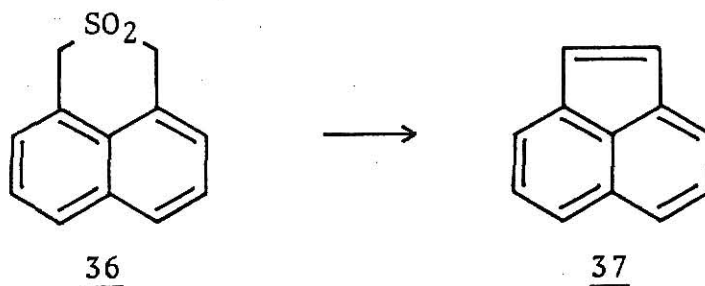


Shahak and Bergman<sup>66</sup> reported the synthesis of a number of  $\alpha,\beta$ -unsaturated ketones and esters from the corresponding  $\alpha$ -bromo- $\beta$ -keto and  $\alpha$ -bromo- $\alpha$ -carbethoxy sulfones. Thus, sulfonyl ester 34 was brominated and treated with sodium

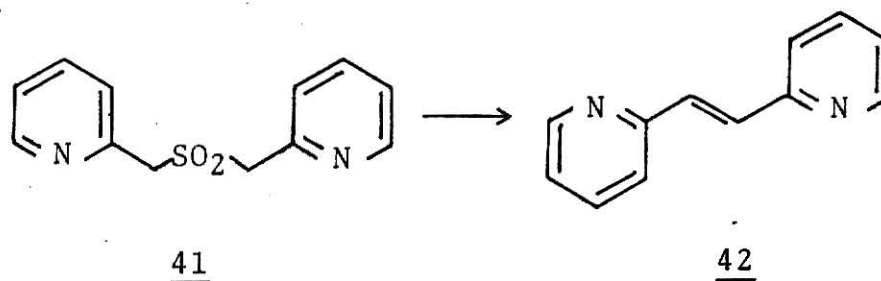
methoxide to give, after ester hydrolysis, 2-methylcinnamic acid (35) in 88% yield.



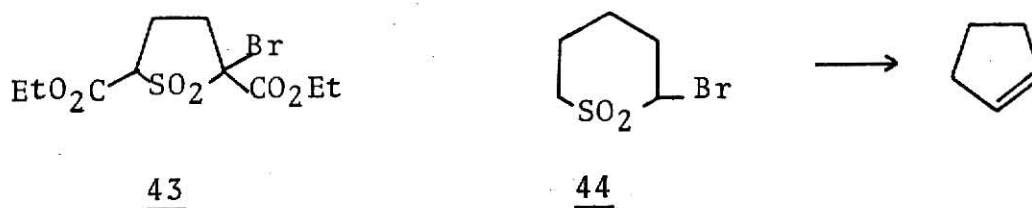
A fascinating one step halogenation-Ramberg-Backlund reaction of dibenzyl and di-sec-alkyl sulfones was reported by Meyers, Malte, and Matthews.<sup>39</sup> In this method, sulfones were allowed to react in a vigorously stirred mixture of carbon tetrachloride, powdered potassium hydroxide, and water. Dibenzyl sulfones gave quantitative yields of stilbenes while di-sec-alkyl sulfones gave mixtures of olefins and their dichlorocarbene adducts. Sulfone 36 gave a 45% yield of acenaphthene (37) while dicyclohexyl sulfone (38) gave 32% of olefin 39 and 60% of the dichlorocarbene adduct 40.



By using the same method, Martel and Rasmussen<sup>31</sup> were able to prepare trans-1,2-di-2-pyridylethene (42) in "excellent yield" from sulfone 41.



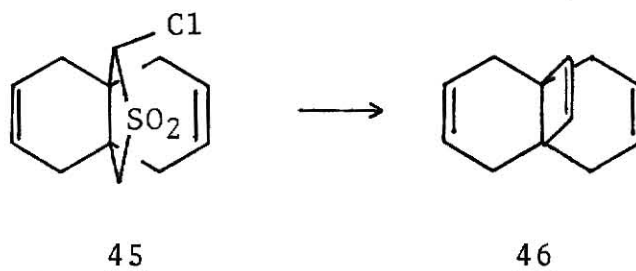
The Ramberg-Backlund reaction has also found success in the synthesis of cyclic olefins. Early attempts at utilizing the reaction in the preparation of cyclic olefins met with little success. Attempted alkaline hydrolysis of 43 to the cyclobutene derivative met with failure<sup>6</sup> and the synthesis of cyclopentene from 2-bromothiacyclohexane-1,1-dioxide (44) was reported to proceed only in poor yield.<sup>40</sup> More recent work,



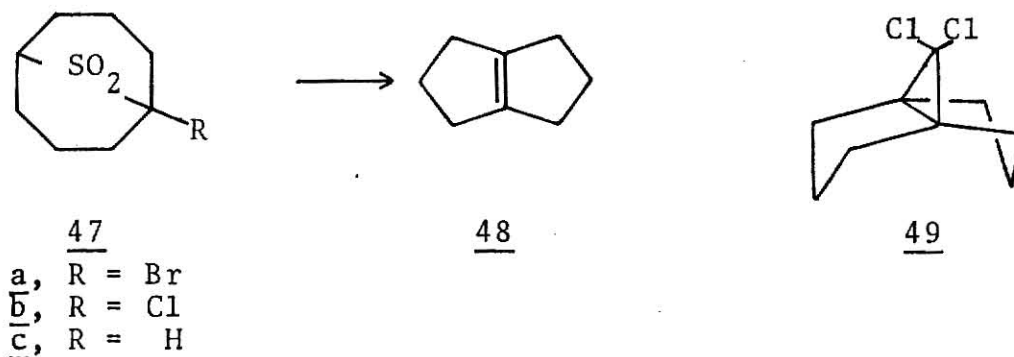
however, has shown that with changes in the nature of the base and solvent the reaction may be successfully applied even to the synthesis of strained cyclic olefins.

Paquette<sup>50,53</sup> reported the first successful synthesis of a cyclobutene derivative via the Ramberg-Backlund reaction. Attempted rearrangement of tricyclic chloro-sulfone 45 by refluxing for four days with 2N sodium hydroxide in aqueous

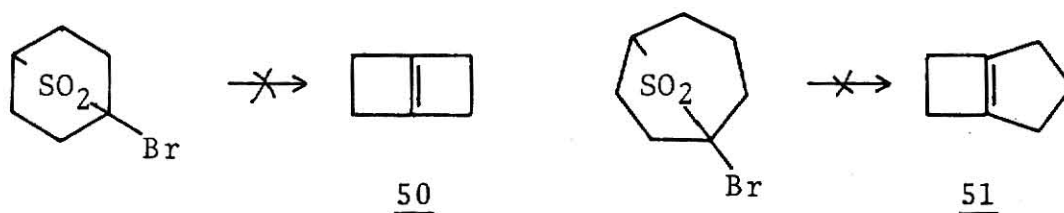
dioxane resulted in near complete recovery of starting material. The failure of the reaction was not due to lack of formation of  $\alpha$ -sulfonyl carbanions since 45-d<sub>3</sub> was isolated in high yield when the reaction was run with sodium deuterio-oxide in deuterium oxide. The lack of rearrangement under these conditions was attributed to "strong aqueous solvation of the carbanionic centers which prevents the attainment of a geometry favorable to the requisite intramolecular S<sub>N</sub>2 process."<sup>50</sup> When such solvation influences were minimized by running the reaction with powdered potassium tert-butoxide in dry tetrahydrofuran, the expected tricyclic olefin 46 was obtained in 50% yield.



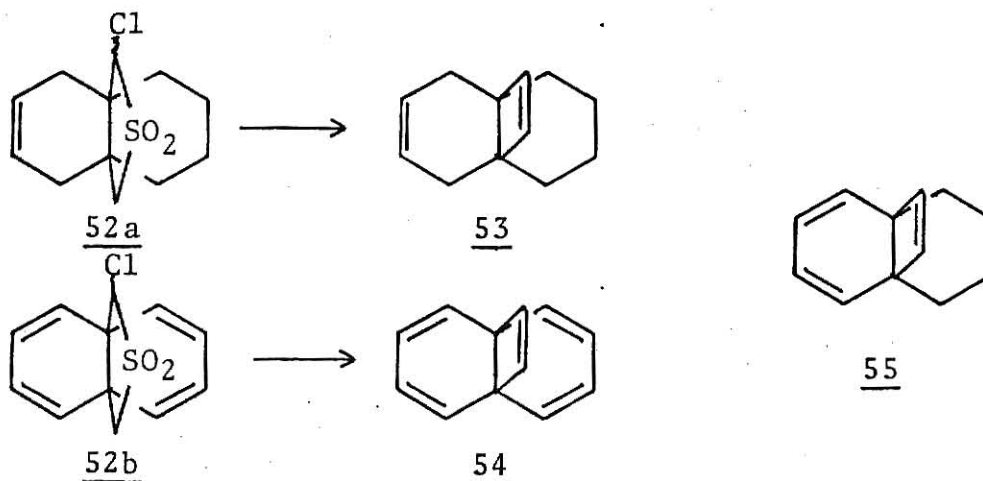
Corey and Block<sup>16</sup> reported the convenient, high yield synthesis of  $\Delta^{1,5}$ -bicyclo[3.3.0]octene (48) by a Ramberg-Backlund rearrangement of 1-bromo-9-thiabicyclo[3.3.1]nonane-9,9-dioxide (47a) with sodium tert-pentoxide in tetraglyme.



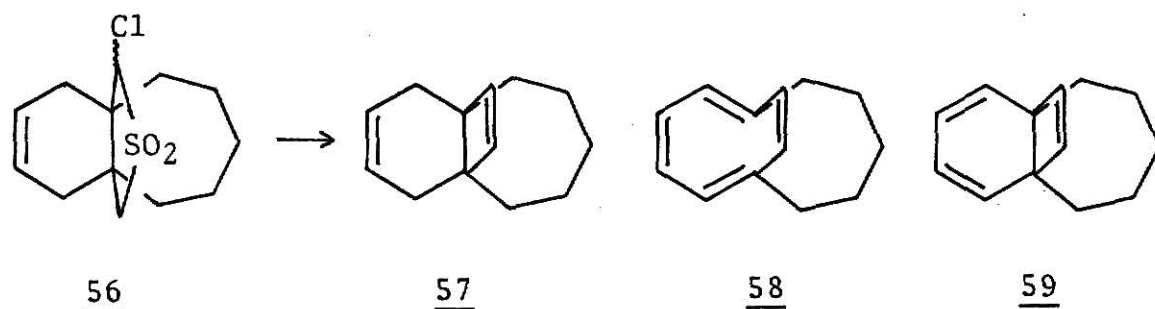
Shortly after Corey and Block's account, Paquette<sup>48</sup> reported a similar synthesis of 48 from 47b in refluxing aqueous potassium hydroxide. Meyers, Malte, and Matthews<sup>39</sup> obtained a 50% yield of 48 and a 45% yield of 49 from 47c by their previously described method. Attempts to produce the more strained transannular olefins 50<sup>16</sup> and 51<sup>48</sup> under a variety a basic conditions met with failure and gave only viscous, water-soluble oils which could not be identified.



Paquette<sup>53</sup> reported the use of the Ramberg-Bäcklund reaction in the synthesis of a number of unsaturated propellanes containing one cyclobutene ring. Tricyclo-[4.4.2.0]dodeca-3,11-diene (53)<sup>51</sup> and tricyclo[4.4.2.0]-dodeca-2,4,7,9,11-pentaene (54)<sup>52</sup> were prepared in 56% and 14% yield, respectively, by treatment of their correspondingly unsaturated chloro sulfones 52a and 52b with potassium tert-butoxide.



Tricyclo[4.4.2.0]dodeca-2,4,11-triene (55) was obtained by allylic bromination-dehydrobromination of 53. Tricyclo-[5.4.2.0]trideca-9,12-diene (57)<sup>53</sup> was prepared in 66% yield by rearrangement of tricyclic chloro sulfone 56 with potassium tert-butoxide in tetrahydrofuran. When 57 was subjected to allylic bromination-dehydrobromination, the ring-opened bicyclo[5.4.2]trideca-7,9,11,12-tetraene (58) was obtained.



The nmr spectrum of 58 was found to be temperature invariant from -80 to +40°C, indicating that 58 does not exist in equilibrium with its valence tautomer 59 over this temperature range.

In view of the success of the Ramberg-Bäcklund reaction in the preparation of olefins, it appeared that the reaction could also make a significant contribution to the synthesis of bicyclo[2.2.0]hex-2-ene and cyclobutene. The work reported in the following section of this thesis was initiated with the hope of establishing this presupposition.



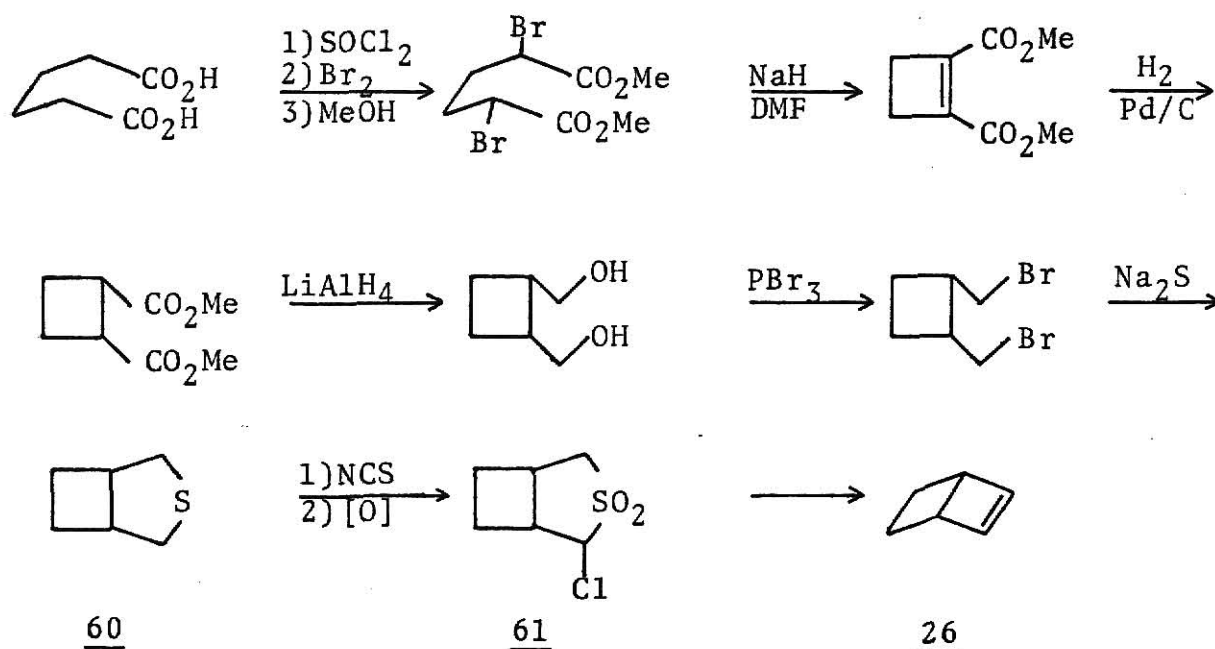
## OBJECTIVES OF THIS INVESTIGATION

The objectives of this investigation were:

1. To synthesize 2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide and examine its utility in the Ramberg-Backlund reaction for the synthesis of bicyclo[2.2.0]hex-2-ene.
2. To synthesize 2-chlorothirolane-1,1-dioxide and examine its utility in the Ramberg-Backlund reaction for the synthesis of cyclobutene.

## DISCUSSION OF EXPERIMENTAL RESULTS

At the time this work began no convenient synthetic method was available for the preparation of the quantities of bicyclo[2.2.0]hex-2-ene (26) desired for other studies. The sequence of reactions outlined below appeared to offer a straightforward route to obtain quantities of 26. Dimethyl  $\alpha,\alpha'$ -dibromoadipate was prepared by an established method<sup>13,26</sup> and subjected to the sodium hydride ring closure reaction of McDonald and Reitz.<sup>36,37</sup> The resultant dimethyl cyclobutene-



1,2-dicarboxylate was hydrogenated in a low pressure Parr hydrogenation apparatus followed by conversion to *cis*-1,2-bis(bromomethyl)cyclobutane by previously published methods.<sup>3,8,38</sup>

Sulfides have been prepared from iodides and bromides most frequently by refluxing the halide with an aqueous or

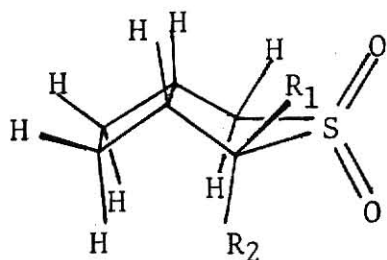
alcoholic solution of sodium or potassium sulfide.<sup>88</sup> Alkyl chlorides may also be used to prepare sulfides provided that an appropriate higher boiling solvent such as dimethylformamide (DMF)<sup>29</sup> or ethylene glycol<sup>69</sup> is used. Using a modification of the method of Lawson, Easley, and Wagner<sup>29</sup> for the synthesis of tetrahydrothiophene (thiolane), 3-thiabicyclo[3.2.0]heptane (60) was prepared by the reaction of cis-1,2-bis(bromomethyl)-cyclobutane with sodium sulfide nonahydrate in DMF (70% yield). Unlike the synthesis of thiolane, it was not found necessary to add the two reactants simultaneously to the hot DMF from separate addition funnels.

Although sulfides containing at least one  $\alpha$ -hydrogen atom have been chlorinated with chlorine or sulfuryl chloride, the use of these reagents often leads to chlorinolysis or mixtures of products, especially with cyclic sulfides and sulfides containing  $\beta$  hydrogens.<sup>12,77</sup> N-Chlorosuccinimide (NCS), however, smoothly converts sulfides into  $\alpha$ -chloro sulfides in good yield.<sup>54,73,74,75,76,77</sup>

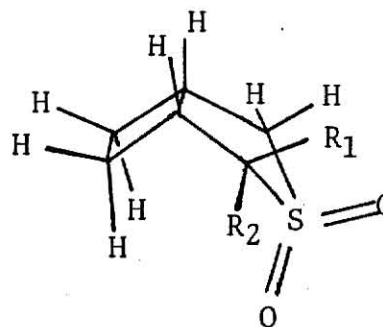
When 60 was chlorinated with NCS in carbon tetrachloride followed by oxidation with m-chloroperbenzoic acid in dichloromethane, a crude mixture of the exo and endo isomers of 2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide (61) was obtained. Separation of the mixture was achieved by chromatography on silica gel using gradually increasing percentages of ether in hexanes as eluent. The predominant isomer of 61 was eluted first in 48% yield with 30-40% ether followed by the minor isomer in 12% yield with 50-60% ether

in hexanes.

Assignment of stereochemistry to 61 was based on examination of molecular models and the magnitude of the nmr coupling constants between the C<sub>2</sub> hydrogen and C<sub>1</sub> bridgehead hydrogen. Two possible conformations of 61 (and of the bicyclo[3.2.0]heptane ring system in general) are shown in structures 62 and 63. Nonbonded interactions present in the exo



62



63

exo, R<sub>1</sub> = Cl, R<sub>2</sub> = H

endo, R<sub>1</sub> = H, R<sub>2</sub> = Cl

and endo isomers of conformation 63 are considerably relieved in going to conformation 62, which especially provides a more favorable steric environment for the chlorine atom of 61. Structure 62 was, therefore, judged to be the preferred conformation of 61.

Further conclusions regarding exo/endo isomerism in 62 were drawn from comparisons of the expected and observed nmr spectra. Molecular models revealed the endo-2-hydrogen (R<sub>2</sub> = H) in exo-62 to be very nearly orthogonal to the 1-position bridgehead hydrogen. The nmr coupling constant (J) would, therefore, be expected to be zero or very small. On the other hand, the exo-2-hydrogen

( $R_1 = H$ ) in endo-62 is only about 30-35° out of alignment with the bridgehead hydrogen. Based on a graph of  $J$  vs. dihedral angle,<sup>67</sup> a dihedral angle of 30-35° would be expected to have a  $J$  of 5.5-6.0 Hz.

An nmr spectrum of the predominant chloro-sulfone isomer formed in the chlorination-oxidation of 60 showed the absorption for the  $C_2$ -hydrogen to be a closely split doublet ( $J = 0.7$  Hz) at  $\tau$ 5.30. The corresponding absorption for the minor isomer appeared as a doublet of doublets ( $J = 8.0$  Hz and  $J = 1.0$  Hz) centered at  $\tau$ 5.10. Thus, the major isomer was assigned the exo configuration and the minor isomer the endo. These assignments have been summarized in Table I. The small additional coupling constant in endo-62 is probably due to long range coupling of the 2-hydrogen ( $R_1 = H$ ) with the exo-7 hydrogen.

TABLE I

PREDICTED AND OBSERVED  $J$  FOR THE  $C_2$ -HYDROGEN OF  
2-CHLORO-3-THIABICYCLO[3.2.0]HEPTANE-3,3-DIOXIDE

	<u>Predicted</u>	<u>Observed</u>
<u>exo-62</u>	$J = 0$	$J = 0.7$ Hz
<u>endo-62</u>	$J = 5.5-6.0$ Hz	$J = 8.0$ and $1.0$ Hz

Since exo- and endo-62 were found to have an appreciable solubility in water, a known quantity of exo-62 was subjected to the work-up conditions (several washes with saturated aqueous sodium carbonate) of the chlorination-oxidation reaction to determine possible loss of product. A quantitative

recovery of the chloro sulfone was obtained. The necessity of using saturated aqueous washes was indicated by the very low yields obtained from initial attempts at work-up using 10% aqueous sodium carbonate.

In a purification of bicyclo[2.2.0]hex-2-ene (26) by spinning-band distillation, Reineke<sup>56</sup> found the boiling point to be 43-48° at a pressure of 277 torr. By using this value for the boiling point, a nomograph of boiling point vs. pressure indicated that 26 should distill at about room temperature at a pressure of 100 torr. It was then decided to modify the conditions of the Ramberg-Backlund reaction so that 26 could be removed from the reaction mixture by simple vacuum distillation with a minimum of handling and work-up.

An initial small scale attempt at the Ramberg-Backlund rearrangement of exo-62 was a modification of the method of Paquette.<sup>53</sup> Treatment of exo-62 with powdered potassium tert-butoxide in diglyme at 0° followed by an attempted vacuum distillation produced no volatile products. Work-up of the reaction mixture gave only brown, water-soluble materials which were not identified.

A procedure analogous to that of Corey and Block<sup>16</sup> was then attempted using larger quantities of exo-62. Sodium tert-pentoxide was produced in tetraglyme by the reaction of excess sodium hydride with tert-amyl alcohol. After removing small amounts of unreacted alcohol by short-path distillation, exo-62 was added and the mixture heated to 55° while still

at atmospheric pressure. In so doing, tert-amyl alcohol formed in the reaction was reconverted to alkoxide by reaction with the excess sodium hydride present. Volatile materials formed in the reaction were removed by short-path distillation at 0.4 torr. An nmr spectrum of the small amount of distillate collected revealed the presence of the desired bicyclic olefin 26 as well as a quantity of tert-amyl alcohol and an unidentified material. Due to overlapping absorptions it was not possible to determine the relative amounts of each material present by integration of the nmr peak heights. However, even by considering the amount of alcohol and unidentified material present as being negligible, the weight of distillate obtained would still only correspond to a yield of 1.3% of 26 for the reaction. The nmr spectrum of the olefin produced agreed with that reported by Reineke.<sup>56</sup> However, expansion of the olefinic region showed the absorption at  $\tau$ 3.74 to be a three line pattern (apparent  $J = 1.2$  Hz) rather than a closely split doublet. The three line pattern is due to virtual coupling<sup>67</sup> of the vinylic hydrogens with the two bridgehead hydrogens. Work-up of the reaction mixture gave only brown water-soluble products in the aqueous layer and mineral oil from the sodium hydride in the ether layer.

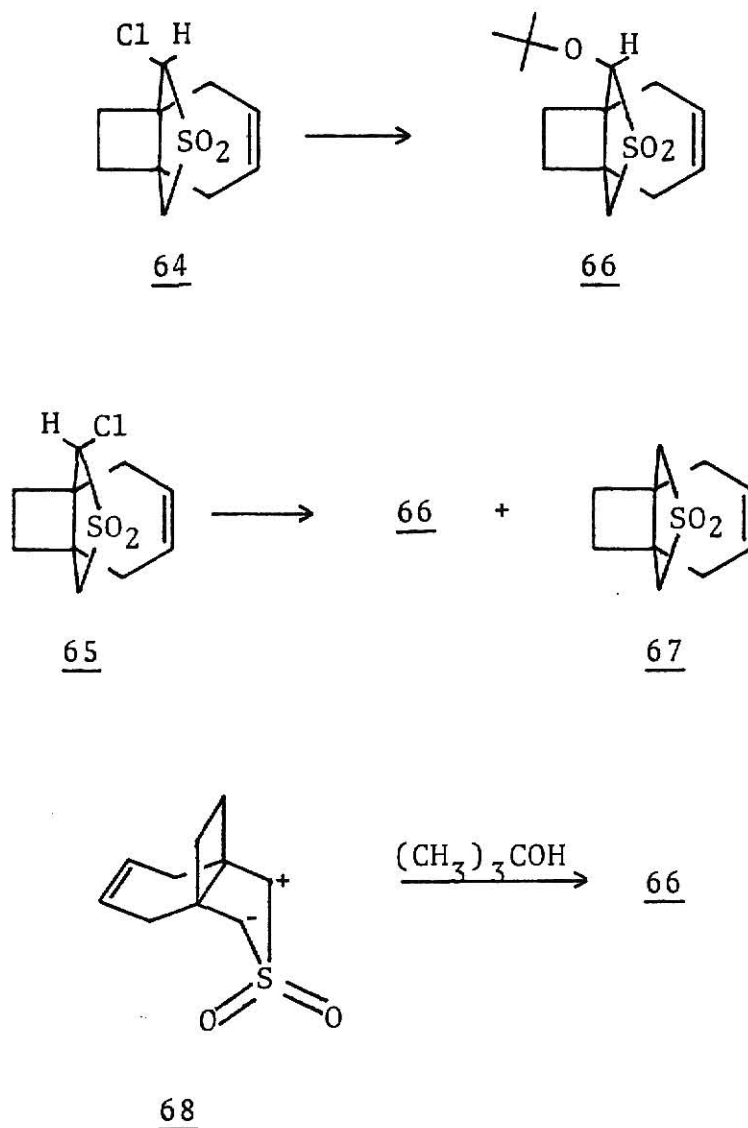
The reaction was repeated again at 0° and 70°. In these reactions the pressure was reduced to 14 torr and 9 torr, respectively, as soon as the chloro sulfone was added in an attempt to remove 26 from the reaction mixture as soon as it was formed. At 0° the reaction mixture remained brick-red

until it was allowed to warm to room temperature, whereupon it turned to the dark brown color of the reactions run at warmer temperatures. The only volatile material obtained was tert-amyl alcohol. The results at 70° were much like those at 55° with the exception that the unidentified material collected with the olefin comprised a much greater percentage of the distillate.

In order to determine whether sodium hydride or sodium tert-pentoxide was initiating the Ramberg-Backlund reaction, exo-62 was added to a stirred slurry of sodium hydride in diglyme at 0° and allowed to stir for 3.5 hours. During this time no color change was observed. Work-up of the mixture gave only recovered starting material. Thus, sodium tert-pentoxide was probably the base which initiated the Ramberg-Backlund reaction of the chloro sulfone.

Paquette and Houser<sup>49</sup> reported that treatment of chloro sulfones 64 and 65 with potassium tert-butoxide led, not to the expected tricyclic olefin but, to the tert-butyl ether 66 in the case of 64 and to a mixture of 66 and sulfone 67 in the case of 65. They reasoned that 64 and 65 gave rise initially to their corresponding episulfones. The episulfones, due to the magnitude of the energy barrier leading to formation of the new severely strained double bond, did not undergo sulfur dioxide expulsion but, rather interconverted with one another via dipolar intermediate 68. Product 66 then arose from the reaction of tert-butyl alcohol with 68. In addition, the geometry of 65 in its preferred conformation is such that it did not allow for

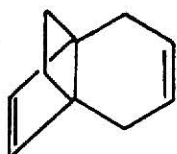
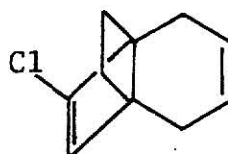




facile intramolecular elimination of hydrogen chloride to form the episulfone. In this case, base abstraction of chlorine to form 67 then became competitive with episulfone formation from a higher energy conformer of 65.

Paquette and Houser<sup>49</sup> reasoned that in the absence of protic substances such as tert-butyl alcohol, the episulfones could not be trapped as tert-butyl ethers via 68 and should, therefore, stand a greater chance of forming the desired

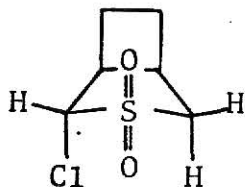
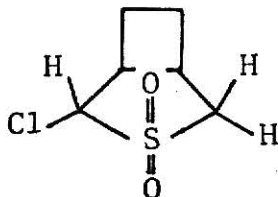
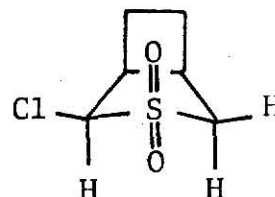
olefin. To substantiate this 65 was allowed to react with n-butyllithium in ether at  $-78^{\circ}$  and diene 69 was obtained in low yield (2.6%) along with a smaller amount of 70. Under the same conditions, 64 gave 69 in 1.4% yield and a trace of 70. In each case the major product was an unidentifiable water-soluble polymer.

6970

Since many of the arguments of Paquette and Houser<sup>49</sup> could be applied to the reaction of 61 with base, it was decided to attempt the reaction of exo-62 with n-butyllithium. Treatment of a diglyme solution of exo-62 with n-butyllithium in ether at  $-78^{\circ}$  gave only a trace of 26 upon work-up. When the reaction was run at  $33^{\circ}$ , the yield of 26, although still low, was qualitatively seen to improve considerably.

The detrimental effect of low temperature upon the Ramberg-Backlund reaction of exo-62 with either sodium tert-pentoxide or n-butyllithium may be due to the presence of a sizeable energy barrier leading to a conformation of exo-62 from which facile 1,3-elimination of hydrogen chloride can occur. Structure 71, another view of exo-62, shows that the chlorine atom is not properly arranged for elimination to take place via the necessary semi-W transition state.<sup>41</sup> In order to attain the required geometry the sulfone ring of 71 must

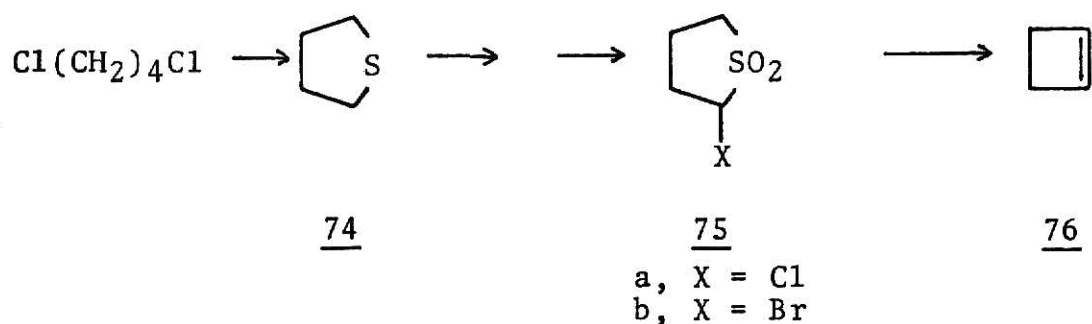
pucker to the higher energy conformer 72 (same conformation

717273

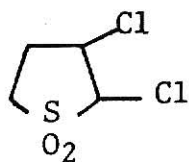
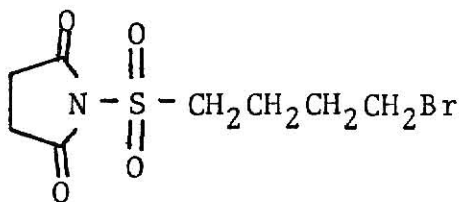
as exo-63). At low reaction temperatures 71 may greatly predominate in its equilibrium with 72, thus allowing a greater proportion of the reaction to be diverted into undesirable products. This possibility was not examined further.

The results of the reaction of endo-62 with sodium tert-pentoxide at 55° were very similar to those of exo-62 under the same conditions. The yield of 26 from endo-62 was at least as large as from the exo-isomer. The elimination of hydrogen chloride from endo-62 might have been expected to be more facile than from exo-62 since the geometry required for the elimination was already present in the preferred conformation (73).

It was also desired to examine the Ramberg-Backlund reaction as a possible route to cyclobutene (76). In analogy to the mode of synthesis of 26 the following route to 76 seemed plausible.

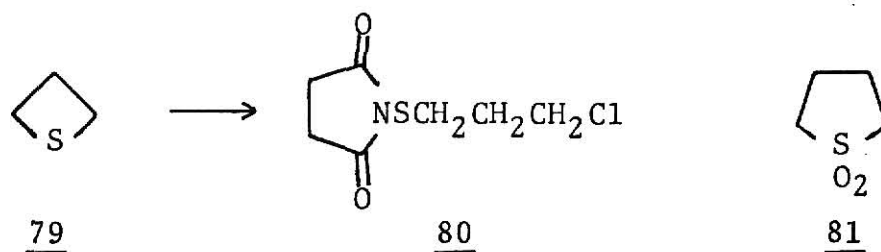


Difficulty was encountered in attempting the halogenation-oxidation of thiolane (74) to  $\alpha$ -halo sulfone 75. When 74 was treated with N-chlorosuccinimide in dichloromethane at room temperature or in carbon tetrachloride under gentle reflux, the major product obtained upon oxidation with *m*-chloroperbenzoic acid was not the expected 2-chlorothiolane-1,1-dioxide (75a). Instead, work-up followed by chromatography on silica gel gave a 65% yield of 2,3-dichlorothiolane-1,1-dioxide (77) as a fluffy white solid. The desired 75a was obtained as an oil in 25% yield. Dichlorosulfone 77 might have arisen from dehydrohalogenation of the intermediate chloro-sulfide followed by readdition of chlorine.

7778

Bromination of 74 with N-bromosuccinimide in refluxing dichloromethane followed by oxidation with *m*-chloroperbenzoic acid led not to 2-bromothiolane-1,1-dioxide (75b), but to

N-(4-bromobutylsulfonyl)succinimide (78) in 22% yield. A small amount of material postulated to be 2,3-dibromothiolane-1,1-dioxide from its nmr spectrum was also obtained. The formation of the unusual ring-opened product is not without precedent. Groebel<sup>24</sup> found that the reaction of N-bromo-succinimide with certain alkyl aryl sulfides led to cleavage of the alkyl carbon-sulfur bond and the production of N-phenyl-mercaptosuccinimide derivatives. Tuleen and Stephens<sup>76</sup> also reported that attempted chlorination of the strained cyclic sulfide 79 gave only the ring-opened product 80.

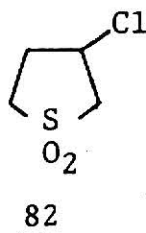


Due to the lack of success with the attempted  $\alpha$ -halogenation of thiolane, it was decided to try to obtain 75 directly by halogenation of the readily available thiolane-1,1-dioxide (81). However, attempted halogenation using either N-chlorosuccinimide or N-bromosuccinimide in refluxing carbon tetrachloride met with failure. In particular, the reaction with NBS could not be made to commence even with extended heating, addition of benzoyl peroxide or bromine, or external irradiation with a sunlamp.

Two recent reports have shown that sulfoxides may be readily  $\alpha$ -chlorinated with sulfuryl chloride. Tin and Durst<sup>71</sup> reported that sulfuryl chloride reacts rapidly with dialkyl

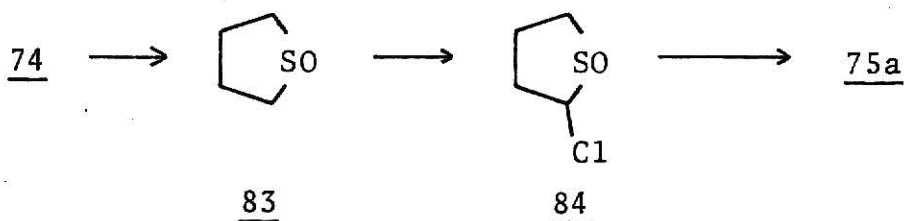
sulfoxides in dichloromethane at  $-78^{\circ}$  in the presence of dry calcium oxide to produce the corresponding  $\alpha$ -chloro sulfoxides in good yield. Tsuchihashi, Ogura, and Iriuchijima<sup>72</sup> also reported that in the presence of pyridine, sulfoxides were  $\alpha$ -chlorinated in good yield with sulfuryl chloride in dichloromethane at  $0^{\circ}$ .

The extension of sulfoxide chlorination to the chlorination of sulfones, however, evidently cannot be made. Attempted chlorination of 81 with sulfuryl chloride using either of the previous conditions for the chlorination of sulfoxides led only to recovery of starting material. On the other hand, when a solution of 81 in benzene was refluxed with sulfuryl chloride in the presence of either benzoyl peroxide or azobisisobutyronitrile (free radical initiators), 3-chloro-thiolane-1,1-dioxide (82) was obtained in 78% yield (57% conversion) along with recovered starting material. At this point, attempts to  $\alpha$ -halogenate 81 were abandoned.



Shortly thereafter Tabushi, Tamura, and Yoshida<sup>70</sup> reported that the reaction of 81 with sulfuryl chloride at  $60^{\circ}$  gave only the  $\beta$ -chlorinated product 82 in 46% conversion. When the reaction was initiated by di-tert-butyl peroxide, the product mixture was composed of 2.6%  $\alpha$ -chloro and 97.4%  $\beta$ -chloro-thiolane-1,1-dioxide.

It was then decided to attempt the sequence below to obtain 75a. Oxidation of 74 to the corresponding sulfoxide 83 with hydrogen peroxide in acetone proceeded in 86% yield.



Chlorination of 83 by the method of Tsuchihashi, Ogura, and Iriuchijima,<sup>72</sup> immediately followed by oxidation with hydrogen peroxide in glacial acetic acid, gave the desired  $\alpha$ -chloro sulfone 75a in 56% yield.

The Ramberg-Bäcklund reaction of 75a with sodium *tert*-pentoxide in tetraglyme at 44° gave rise to the isolation of a small amount of liquid in a liquid nitrogen trap. Difficulties were encountered in handling this liquid due to its extreme volatility. Bromine in dichloromethane was added in an attempt to convert any cyclobutene present to its higher boiling dibromo derivative. However, an nmr spectrum showed the major product to be not 1,2-dibromocyclobutane but, rather 1,4-dibromo-2-butene. None of the expected dibromocyclobutane was obtained. Since sulfur dioxide should have also been isolated, it is possible that any moisture present may have reacted to form sulfurous acid which then permitted an acid catalyzed isomerization of cyclobutene to 1,3-butadiene to take place.

In a subsequent reaction an attempt was made to remove

the sulfur dioxide by passing the gases evolved through a dilute sodium hydroxide solution and a column of 4A molecular sieves using nitrogen as a carrier gas. However, no volatile materials were collected in the liquid nitrogen trap. It is possible that the amount of cyclobutene produced in the reaction was so small that losses in the apparatus prevented its isolation. Another possible alternative would be that the gas evolved was actually 1,4-butadiene which was absorbed by the molecular sieves.

A previous reaction of 75a with sodium tert-pentoxide at 0-5° gave no evident reaction while kept cold. Upon warming slightly above ice-bath temperatures the reaction mixture foamed so severely that the reaction had to be discontinued.

At this point the supply of  $\alpha$ -chloro sulfone precursor was exhausted and the investigation was terminated.



### SUMMARY

This work was initiated with the hope of establishing the Ramberg-Backlund reaction as a convenient synthetic route to large quantities of bicyclo[2.2.0]hex-2-ene (26) and cyclobutene.

Dimethyl  $\alpha,\alpha'$ -dibromoadipate was converted to dimethyl  $\Delta^1$ -cyclobutene-1,2-dicarboxylate by reaction with sodium hydride in DMF. 3-Thiabicyclo[3.2.0]heptane (60) was then prepared by a standard sequence of reactions. Chlorination of 60 with N-chlorosuccinimide and subsequent oxidation with *m*-chloroperbenzoic acid gave a 4:1 mixture of *exo*- and *endo*-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide (62) in 60% yield. Separation was achieved by chromatography on silica gel. Stereochemistry was assigned on the basis of examination of molecular models and nmr coupling constants.

Several modifications of the Ramberg-Backlund reaction on 62 were attempted, each of which should have allowed 26 to be isolated from the reaction mixture by simple distillation at reduced pressure. An initial attempt using potassium *tert*-butoxide as base gave only unidentified, brown, water-soluble materials. An attempted reaction with sodium hydride gave no apparent reaction and recovery of 62. Reaction of 62 with sodium *tert*-pentoxide at 55° led to the isolation of a very small quantity of a mixture of *tert*-amyl alcohol, 26, and unidentified material. A crude estimate of 1.3% yield for the reaction was obtained by assuming the mixture to be pure 26. At 0° the reaction would not commence and no 26 was obtained. At a reaction

temperature of  $70^{\circ}$ , the isolated product mixture was comprised of a greater percentage of the unidentified material. Treatment of 62 with *n*-butyllithium at  $-78^{\circ}$  gave only a trace of 26. At  $33^{\circ}$ , an improved but still very low yield of 26 was obtained.

Several approaches to a 2-halothiolane-1,1-dioxide were also attempted. A quantity of this material was required to test the feasibility of the Ramberg-Bäcklund reaction for the synthesis of cyclobutene. When thiolane (74) was treated with NCS and subsequently oxidized, the major product obtained was 2,3-dichlorothiolane-1,1-dioxide (77) in 65% yield. The expected 2-chlorothiolane-1,1-dioxide (75a) was obtained in 25% yield. Similarly, bromination of 74 with N-bromosuccinimide followed by oxidation led not to 2-bromothiolane-1,1-dioxide but, rather to a 22% yield of the ring-opened N-(4-bromobutylsulfonyl)succinimide (78). A trace of material postulated to be 2,3-dibromothiolane-1,1-dioxide was also obtained.

Several  $\alpha$ -halogenations of thiolane-1,1-dioxide (81) were attempted. Treatment of 81 with NCS or NBS gave only recovered starting material as did low temperature treatment with sulfuryl chloride. Reaction of 81 with sulfuryl chloride in refluxing benzene, however, led to a 78% yield of 3-chlorothiolane-1,1-dioxide.

Success in the synthesis of 75a was achieved by conversion of 74 to the corresponding sulfoxide followed by sulfuryl chloride chlorination and hydrogen peroxide oxidation in 48% overall yield.

The Ramberg-Backlund reaction of 75a with sodium tert-pentoxide gave rise to a very small quantity of volatile material. Addition of bromine to this product gave 1,4-dibromo-2-butene and none of the expected 1,2-dibromocyclobutane. Several attempts to repeat a modified version of this reaction met with failure.

## INFRARED SPECTRA

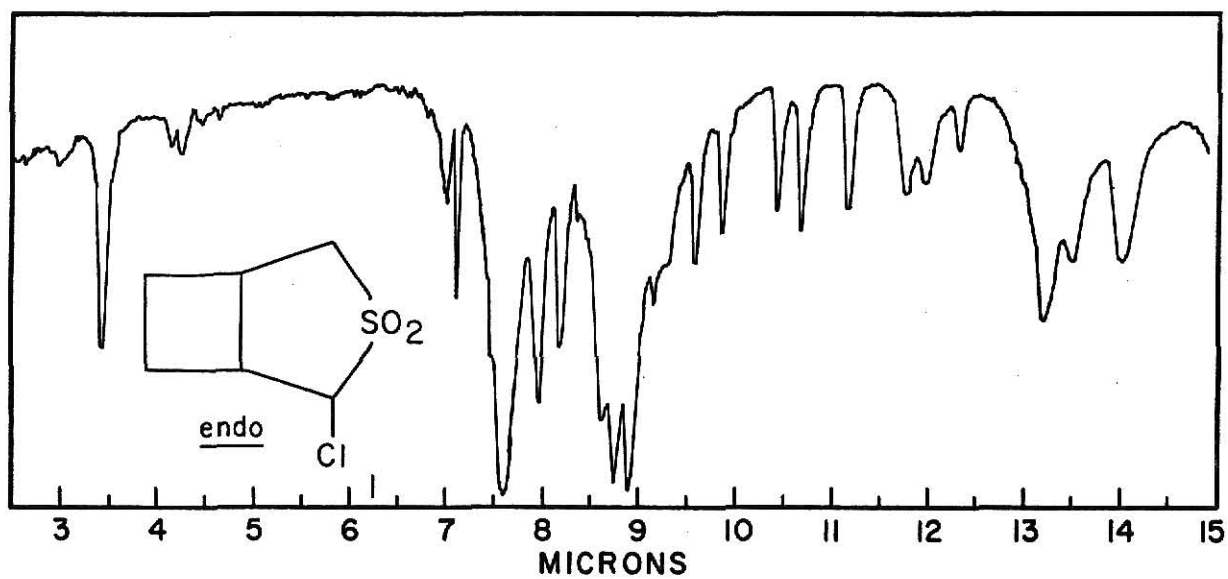
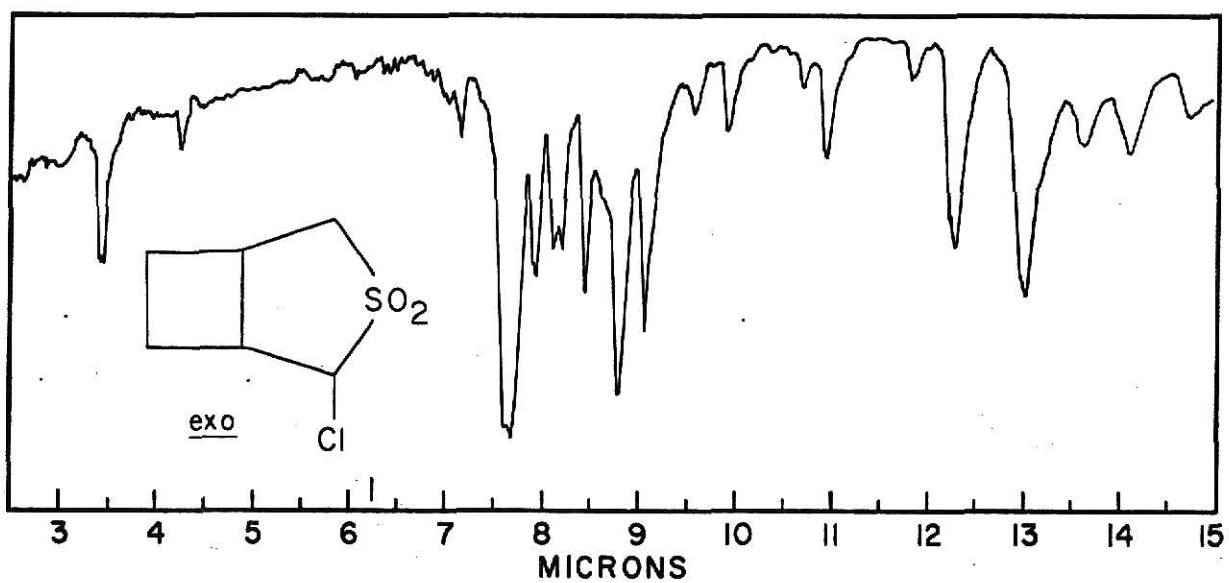
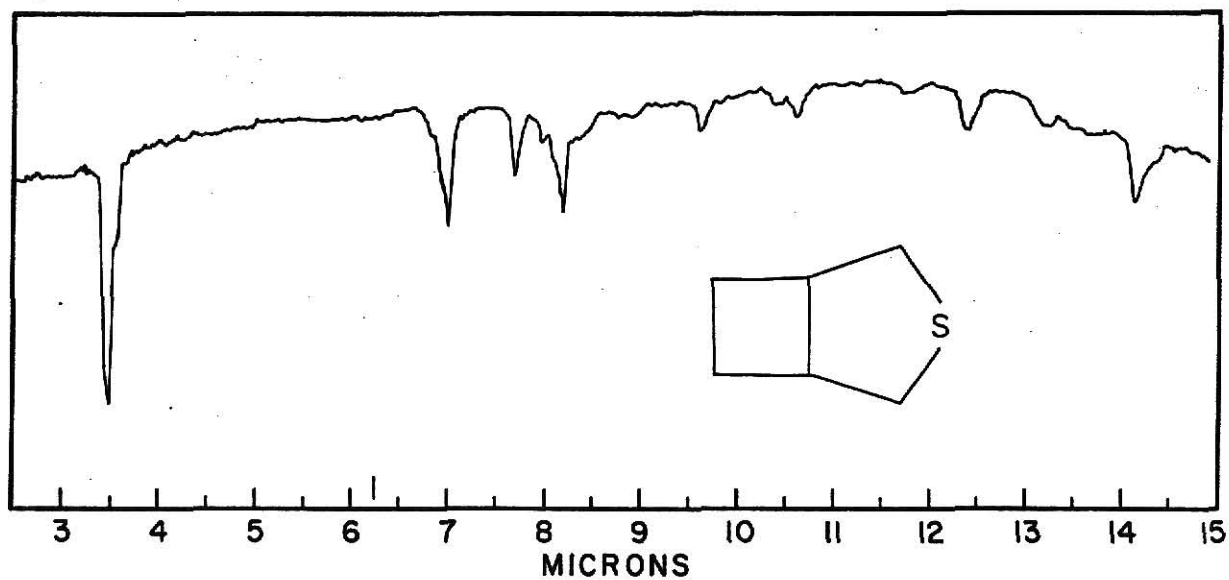
3-Thiabicyclo[3.2.0]heptane  
(neat)

exo-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide  
(KBr)

endo-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide  
(KBr)

**THIS BOOK  
CONTAINS  
NUMEROUS PAGES  
WITH DIAGRAMS  
THAT ARE CROOKED  
COMPARED TO THE  
REST OF THE  
INFORMATION ON  
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## INFRARED SPECTRA

2,3-Dichlorothiolane-1,1-dioxide

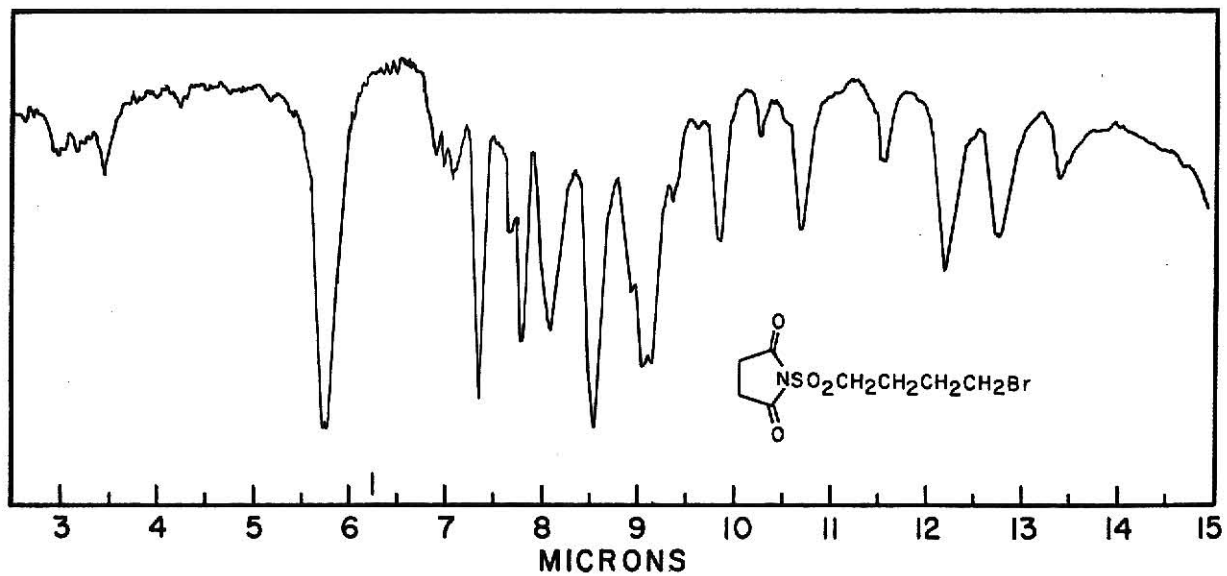
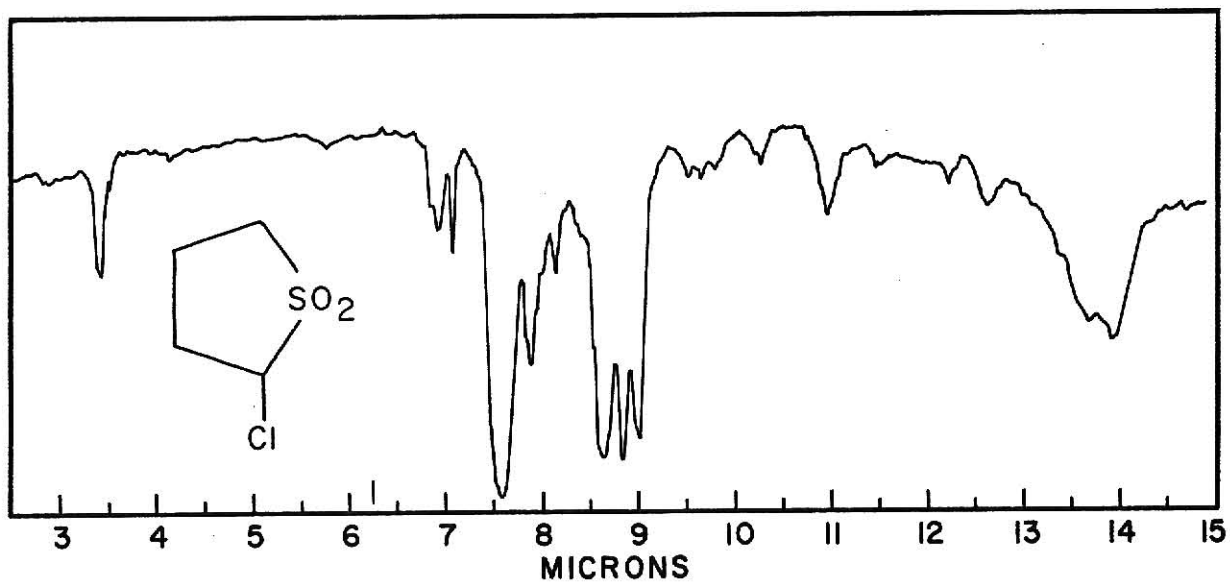
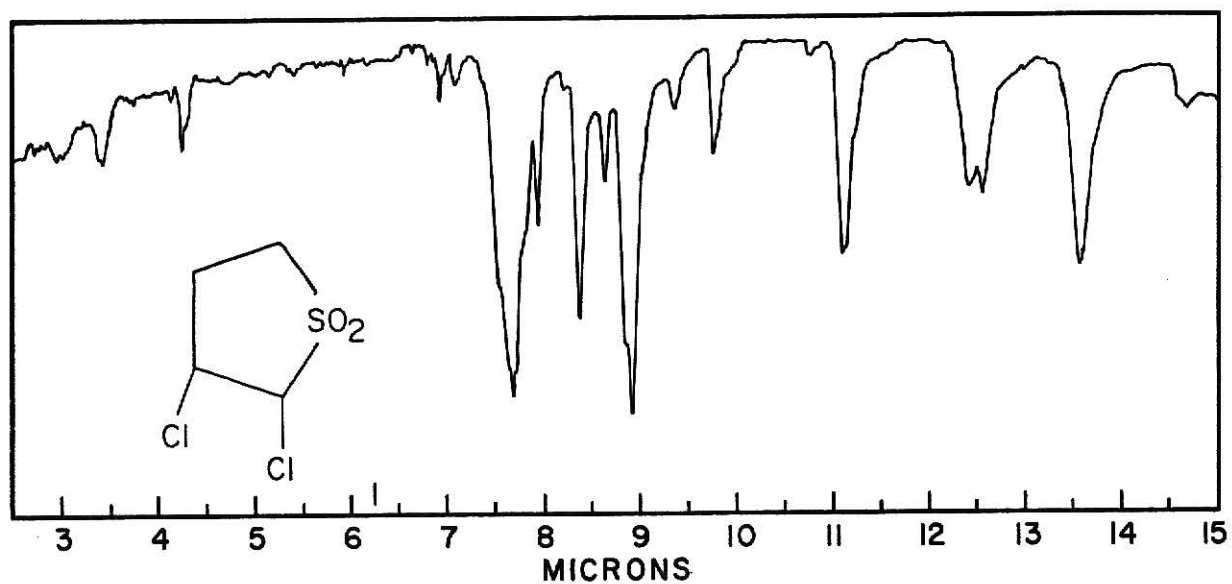
(KBr)

2-Chlorothiolane-1,1-dioxide

(neat)

N-(4-Bromobutylsulfonyl)succinimide

(KBr)





## N.M.R. SPECTRA

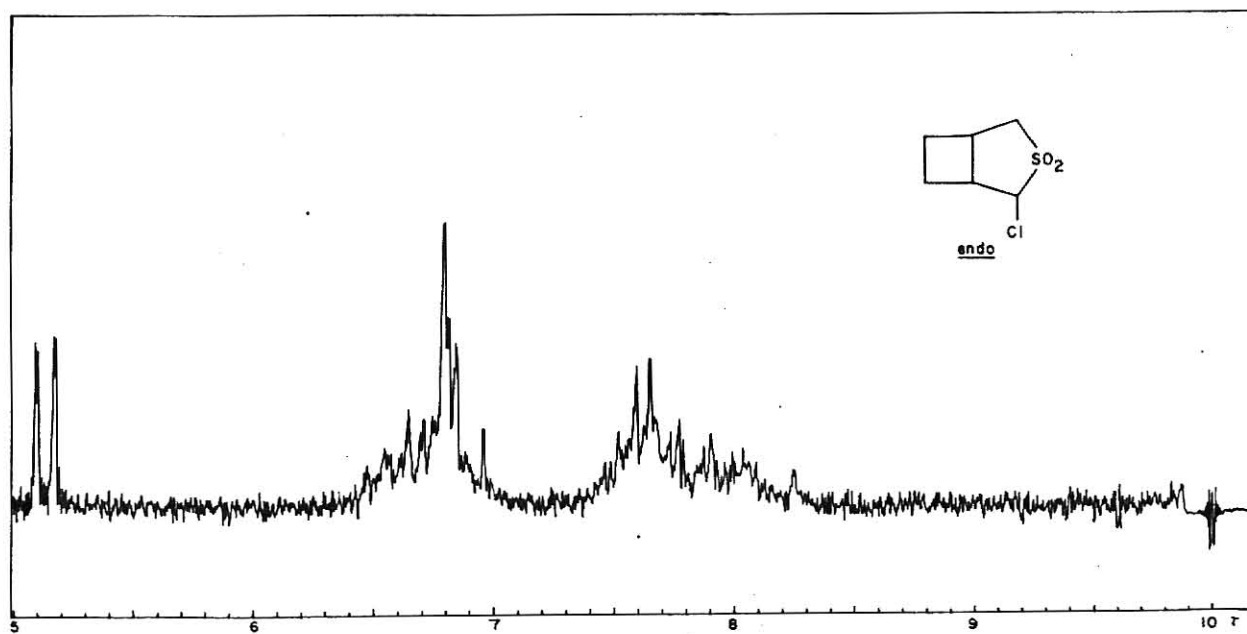
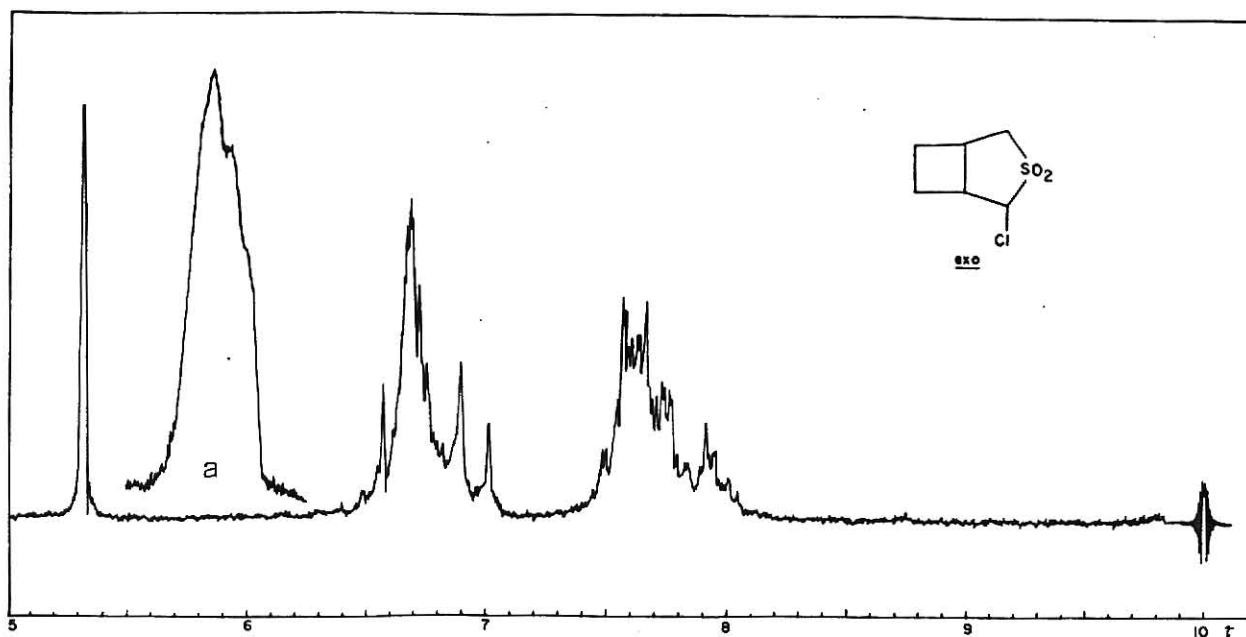
exo-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide

(CDCl<sub>3</sub>, internal TMS standard)

a) Sweepwidth = 50 Hz

endo-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide

(CDCl<sub>3</sub>, internal TMS standard)



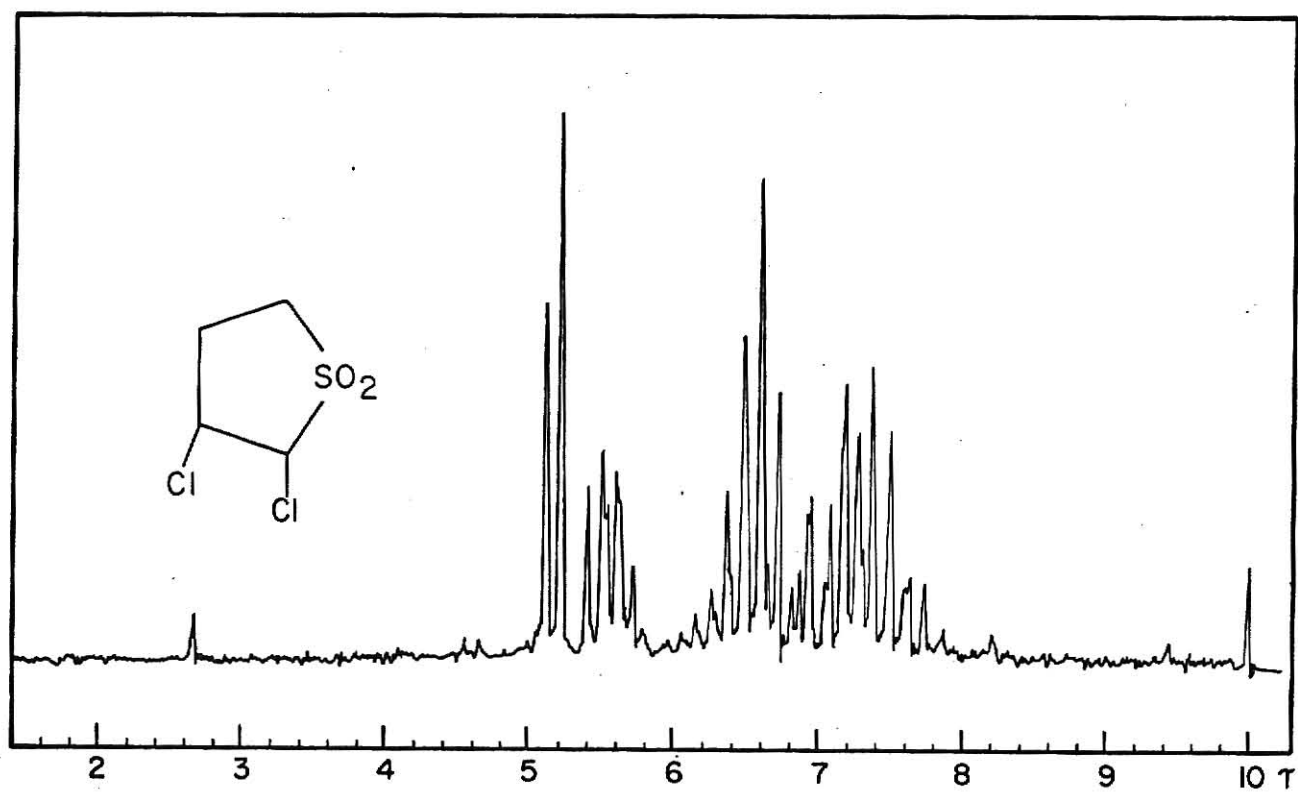
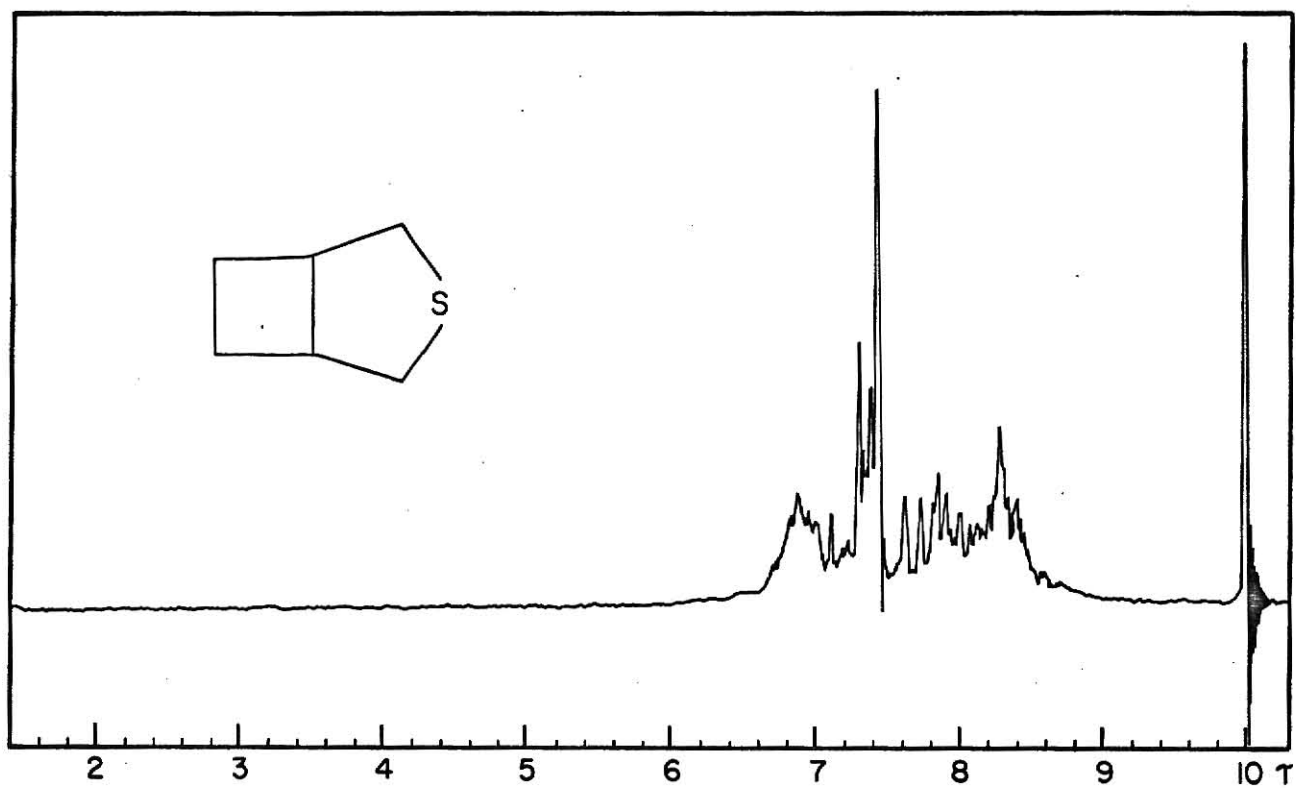
## N.M.R. SPECTRA

3-Thiabicyclo[3.2.0]heptane

(CCl<sub>4</sub>, internal TMS standard)

2,3-Dichlorothiolane-1,1-dioxide

(CDCl<sub>3</sub>, internal TMS standard)



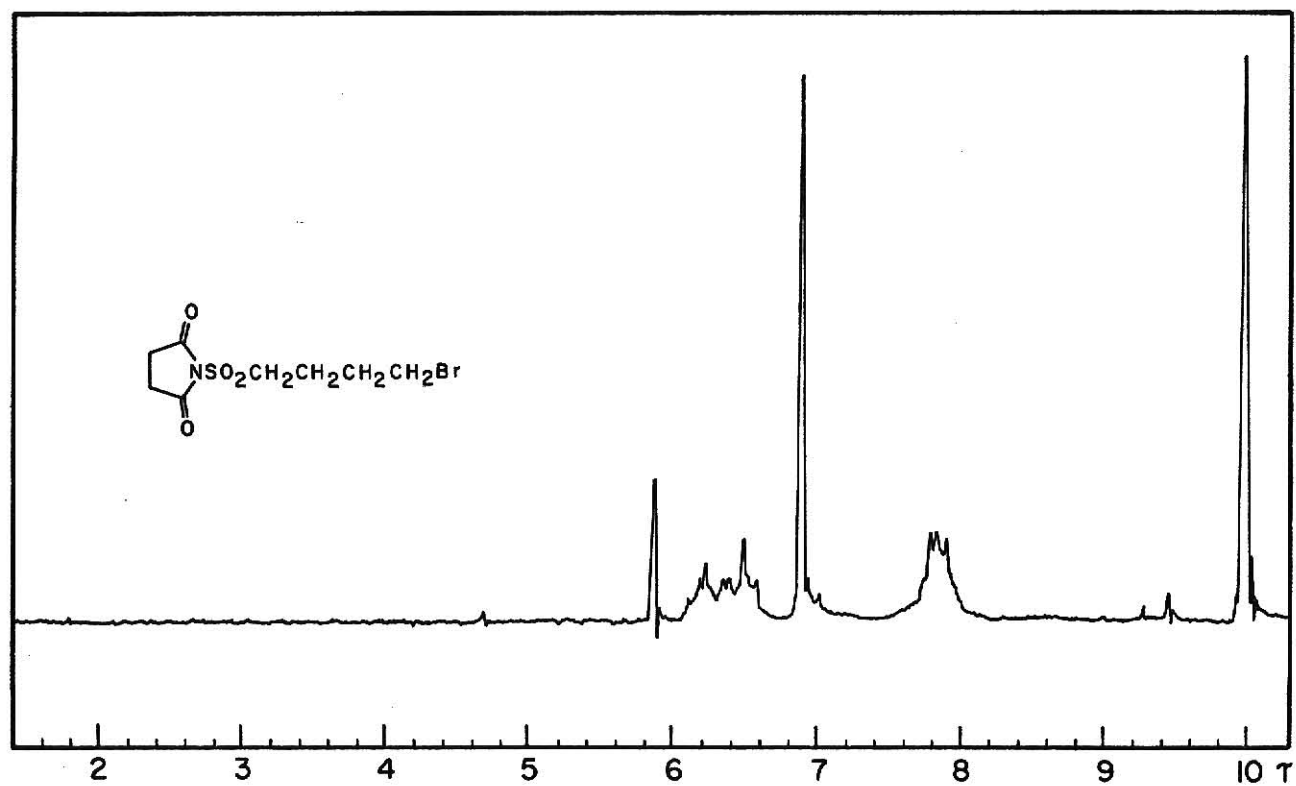
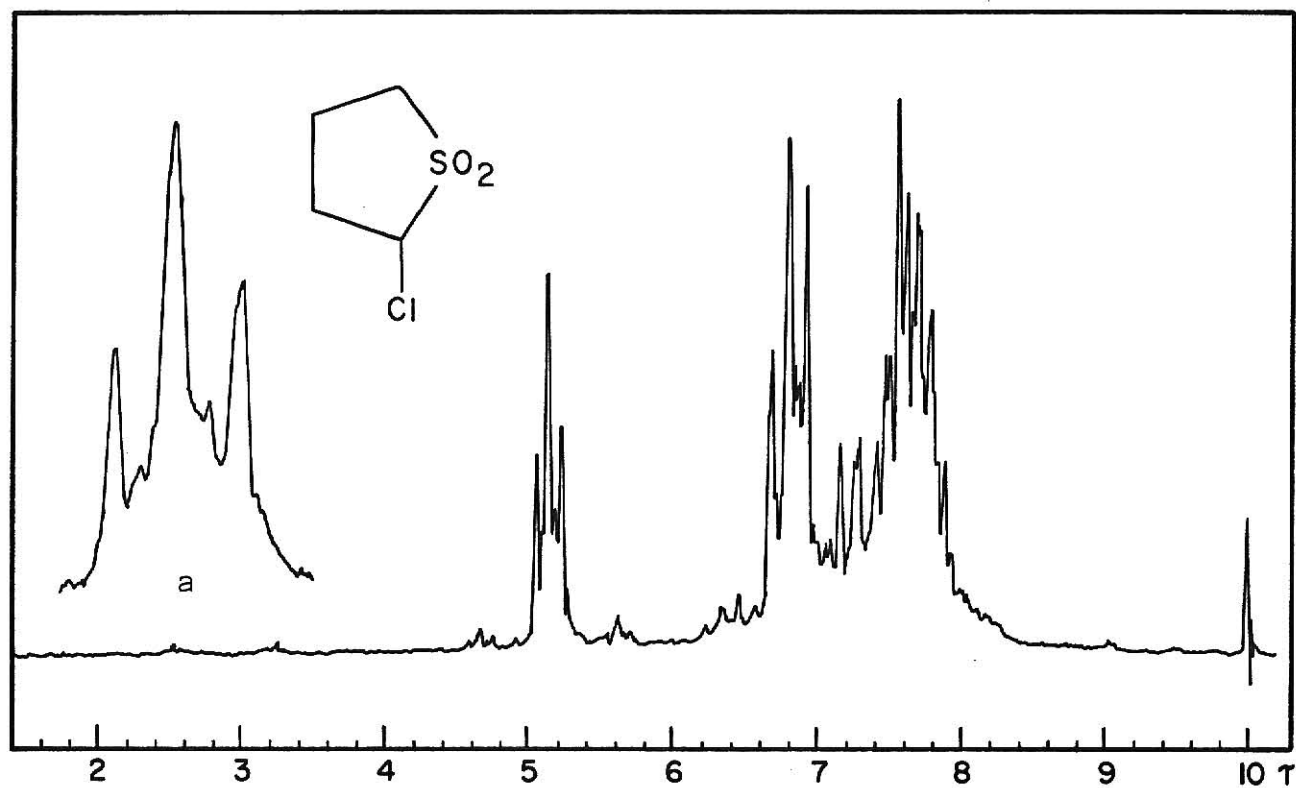
## N.M.R. SPECTRA

2-Chlorothiolane-1,1-dioxide  
(CDCl<sub>3</sub>, internal TMS standard)

a) Sweepwidth = 100 Hz

N-(4-Bromobutylsulfonyl)succinimide  
(CF<sub>3</sub>CO<sub>2</sub>H, internal TMS standard)

a) Solvent Impurity



EXPERIMENTAL<sup>90</sup>

Dimethyl  $\alpha,\alpha'$ -Dibromoadipate. This diester was prepared from adipic acid by the stepwise reaction with thionyl chloride, bromine, and methanol according to the method of Buchman, Reims, Skei, and Schlatter,<sup>13</sup> and of Guha and Sankaran.<sup>26</sup> A mixture of solid and liquid isomers was obtained from two runs in an average yield of 73% (lit.<sup>13</sup> 93%).

The nmr spectrum ( $\text{CCl}_4$ , internal TMS) showed absorptions at  $\tau$  5.75 (m, CH, 2), 6.20 (s,  $\text{OCH}_3$ , 6), and 7.85 (m,  $\text{CH}_2$ , 4).

Dimethyl  $\Delta^1$ -Cyclobutene-1,2-dicarboxylate. The method used for the preparation of this material was that of McDonald and Reitz.<sup>36,37</sup> To 13.2 g (314 mmol) of sodium hydride (57% in mineral oil) in 350 ml of dry DMF was added 50.0 g (150 mmol) of dimethyl  $\alpha,\alpha'$ -dibromoadipate while cooling in an ice bath. After a few minutes of vigorous stirring the ice bath was removed and the stirring was continued until the evolution of hydrogen had ceased (about 4 hr). To this, 600 ml of ether was added, and the precipitate of sodium bromide and unreacted sodium hydride was filtered off. The filtrate was washed with four 150-ml portions of brine to remove the DMF. The aqueous layers were extracted several times with additional ether. The ether layers were combined and dried ( $\text{MgSO}_4$ ). The ether was removed with an aspirator to yield a reddish-brown liquid which was fractionated through an 8 in. Vigreux column with the major portion distilling at 65-71°/0.4 mm. The product was composed mainly of a white solid. Analysis of the

distillate by glpc on a 6 ft x 0.25 in. 5% QF-1 on Anachrom ABS column (column temperature, 135°; He flow rate 60 ml/min; injection port 190°) showed one main component with a retention time of 5.1 minutes. Much smaller peaks due to impurities had retention times of 3.0, 5.9, and 7.3 minutes. The average yield from 12 runs (after correcting for impurities) was 57% (range 46-69%). The nmr spectrum (CCl<sub>4</sub>, external TMS) showed two singlets at  $\tau$ 6.25 (OCH<sub>3</sub>, 6) and 7.36 (CH<sub>2</sub>, 4) in agreement with those reported.<sup>37,65</sup>

Dimethyl cis-Cyclobutane-1,2-dicarboxylate. This compound was prepared in an average yield of 92% from 16 runs. In a typical reaction, 12.042 g (70.8 mmol) of dimethyl  $\Delta^1$ -cyclobutene-1,2-dicarboxylate was dissolved in 200 ml of methanol and hydrogenated over 5% palladium on carbon at room temperature in a Parr hydrogenation apparatus at an initial pressure of 55-60 psi of hydrogen. The reaction was allowed to continue until hydrogen uptake had ceased (12-24 hr). The catalyst was removed by filtration through filter-cel and the methanol removed at reduced pressure to give a light yellow liquid as the crude product. Distillation of this liquid through an 8 in. Vigreux column at 53-63°/0.4 mm (lit.<sup>63</sup> 96-97°/8mm) yielded 11.12 g of a colorless, sweet-smelling liquid. Glpc of the distillate on an 8 ft x 0.25 in. 10% Carbowax on Anachrom ABS column (column temperature, 205°; He flow rate 80 ml/min; injection port, 190°) gave only two peaks with retention times of 4.3 minutes and 5.4 minutes. These peaks were integrated to 5.1% and 94.9% and were assumed to



represent the trans and cis isomers, respectively, of dimethyl cyclobutane-1,2-dicarboxylate. The infrared spectrum (thin film) showed absorptions at 3.42 (m), 5.74 (s), 6.97 (m), 7.37 (m), 7.49 (m), 7.81 (m), 8.01 (m), 8.27 (s), 8.54 (s), 9.18 (m), 9.44 (m), 9.79 (w), 10.35 (w), 10.84 (w), 11.85 (w), and 12.58 (w)  $\mu$ . The nmr spectrum ( $\text{CCl}_4$ , internal TMS) showed absorptions at  $\tau$  6.35 (s,  $\text{OCH}_3$ , 6), 6.65 (m, CH, 2), and 7.70 (m,  $\text{CH}_2$ , 4).

cis-1,2-Bis(hydroxymethyl)cyclobutane. This diol was prepared in an average yield of 86% on seven runs by a modification of the method of Blomquist and Verdol.<sup>8</sup> In a typical reaction, a solution of 66.75 g (0.388 mole) of dimethyl cyclobutane-1,2-dicarboxylate in 200 ml of anhydrous ether was added dropwise to an ice bath cooled, mechanically stirred slurry of 40.4 g (1.06 mole) of lithium aluminum hydride in 1.0-1.5 l of anhydrous ether. When the addition was complete (about 3 hr), the mixture was allowed to stir at room temperature overnight. Excess lithium aluminum hydride was destroyed by the cautious dropwise addition of water and the resulting salts dissolved with 10% hydrochloric acid. Sodium chloride was added to near saturation and the two phase mixture continuously extracted with ether for three days. The ether was dried ( $\text{MgSO}_4$ ) and removed at the aspirator to leave a viscous sweet-smelling residue. Distillation of the residue through an 8 in. Vigreux column at 87-89°/0.4 mm gave 36.9 g (82%) of product as a clear, colorless, viscous liquid (lit.<sup>3</sup> 90% yield, b.p. 111-113°/2.7 mm). The infrared spectrum (thin film)

showed absorptions at 3.0 (s), 3.43 (s), 6.75-7.15 (m), 8.82 (w), 9.28 (m), and 9.77 (s)  $\mu$ , in agreement with that reported.<sup>56</sup> The nmr spectrum ( $\text{CCl}_4$ , internal TMS) of the cis-diol exhibited absorptions at  $\tau$ 5.15 (s, OH, 2, position concentration dependent), 6.45 (m,  $\text{OCH}_2$ , 4), 7.35 (m, CH, 2), and 7.8-8.6 (m,  $\text{CH}_2$ , 4), similar to that reported<sup>38</sup> for the trans-diol.

cis-1,2-Bis(bromomethyl)cyclobutane. The dibromide was prepared according to the method of Blomquist and Verdol<sup>8</sup> in an average yield of 68% (lit.<sup>3</sup> 71%) on five runs. The crude dibromide was distilled through an 8 in. Vigreux column at 56-59°/0.4 mm (lit.<sup>3</sup> 92°/4.5 mm) to give a clear liquid which slowly darkened upon exposure to light. The infrared spectrum (thin film) agreed with that reported<sup>56</sup> and exhibited absorptions at 3.43 (m), 3.54 (w), 6.94 (m), 7.98 (m), and 8.18 (m)  $\mu$ . The nmr spectrum ( $\text{CCl}_4$ , internal TMS) of the cis-dibromide exhibited three broad multiplets at  $\tau$ 6.5, 7.1, and 7.9, similar to that reported<sup>38</sup> for the trans-dibromide.

3-Thiabicyclo[3.2.0]heptane. This bicyclic sulfide was prepared by a method similar to that described by Lawson, Easley, and Wagner<sup>29</sup> for the preparation of thiolane. To a stirred solution of 59.5 g (0.248 mole) of cis-1,2-bis(bromomethyl)cyclobutane in 200 ml of DMF was added 61.2 g (0.255 mole) of sodium sulfide nonahydrate in 200 ml of water. The addition caused the solution to become warm and turn to a brilliant aqua in color. The initial color gradually faded.

The reaction mixture was heated to a gentle reflux for 5 hrs and then allowed to stir overnight at room temperature. The sulfide was distilled out as an azeotrope at atmospheric pressure until the distillate was clear. The distillate was made alkaline by adding 30 ml of 10% sodium hydroxide and then extracted three times with ether. The combined ether extracts were washed with two portions of saturated sodium chloride solution and dried ( $\text{MgSO}_4$ ). The ether was removed by distillation through an 8 in. Vigreux column followed by distillation of the sulfide to give 20.8 g (74% yield) of clear, foul-smelling liquid (b.p.  $65-67^\circ/26$  mm). The average yield on five runs was 70%. The sulfide could be analyzed by glpc on a 12 ft x 0.25 in. Silicon Gum Rubber column (column temperature,  $175^\circ$ ; He flow rate, 60 ml/min; injection port,  $275^\circ$ ). Analysis following individual reactions either showed the material to be pure (retention time 4.0 min) or contaminated with a small amount of DMF (retention time 2.4 min). The infrared (page 35), nmr (page 41), and mass spectra (page 70) were recorded from material collected from the glpc.

Anal. Calcd. for  $\text{C}_6\text{H}_{10}\text{S}$ : C, 63.10; H, 8.83.

Found: C, 62.90; H, 9.35.

exo- and endo-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide.

To a magnetically stirred solution of 9.013 g (79.0 mmol) of 3-thiabicyclo[3.2.0]heptane in 150 ml of carbon tetrachloride was added 10.573 g (79.2 mmol) of N-chlorosuccinimide and the mixture refluxed gently under nitrogen for 1.5 hr. The reaction mixture was cooled and succinimide removed by filtration

under a blanket of nitrogen. The carbon tetrachloride was removed by distillation at reduced pressure to leave a yellow-brown liquid residue. To a magnetically stirred solution of this residue in 400 ml of dichloromethane at 0° was added portion-wise 37.8 g (166 mmol) of 76% m-chloroperbenzoic acid. After stirring for 3-4 days at room temperature the mixture was cooled and m-chlorobenzoic acid removed by filtration. The filtrate was washed with 100 ml of saturated sodium carbonate, 100 ml of saturated sodium bisulfite, 100 ml of saturated sodium carbonate, and finally with 100 ml of saturated sodium chloride. The dichloromethane was dried (MgSO<sub>4</sub>) and evaporated to give 12.9 g of a clear viscous oil which slowly solidified. An nmr spectrum (CDCl<sub>3</sub>, internal TMS) of this crude product showed absorptions at  $\tau$ 1.9-2.6 (m), 5.1 (d), 5.33 (s), 6.1-6.9, 7.1 (s), and 7.4-8.2. Integration of the 5.1  $\tau$  doublet relative to the singlet at 5.33  $\tau$  indicated a ratio of approximately 1:4, respectively, for the two  $\alpha$ -chloro sulfone isomers.

It was found that attempting to remove residual m-chlorobenzoic acid from the dichloromethane solution by extraction using nonsaturated aqueous washes inevitably led to greatly decreased yields. Also, the crude product could be recrystallized with difficulty from chloroform-hexanes, but at the expense of the overall yield.

The crude product mixture was separated into its components by chromatography on 400 g of silica gel with gradually increasing percentages of ether in hexanes. The first eluted

(10% ether) material showed only nmr absorptions at  $\tau$  1.9-2.6 (m) and was discarded. The second eluted material (30-40% ether) gave 6.86 g (48.1%) of exo-2-chloro-3-thiabicyclo-[3.2.0]heptane-3,3-dioxide as the major isomer. The material could be further purified by recrystallization from chloroform-hexanes, m.p. 84.5-86° (sealed capillary). The infrared spectrum (page 35) showed characteristic absorptions at 7.66 and 8.79  $\mu$  (SO<sub>2</sub>). The nmr spectrum<sup>89</sup> (page 39) showed a closely split doublet ( $J = 0.7$  Hz) at  $\tau$  5.30 (1, CHCl), two complex multiplets centered at  $\tau$  6.70 (4, CH<sub>2</sub>SO<sub>2</sub> and methine), and 7.70 (4, cyclobutane methylene). The mass spectrum (page 71) showed a very weak molecular ion at  $m/e$  180 and 182 and the 100% peak at  $m/e$  81 corresponding to C<sub>6</sub>H<sub>9</sub><sup>+</sup>.

Anal. Calcd. for C<sub>6</sub>H<sub>9</sub>SO<sub>2</sub>Cl: C, 39.89; H, 5.02.

Found: C, 39.86; H, 4.99.

The last eluted (50-60% ether) material gave 1.70 g (11.9%) of endo-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide as the minor isomer. This material could also be purified by recrystallization from chloroform-hexanes to give white needles, m.p. 90-91° (sealed capillary). The infrared spectrum (page 35) showed distinctive absorptions at 7.60, 8.79, and 8.88  $\mu$  (SO<sub>2</sub>). The nmr spectrum<sup>89</sup> (page 39) showed a doublet of doublets at  $\tau$  5.10 (1, CHCl) corresponding to the X portion of an ABX pattern ( $J_{BX} = 8$  Hz,  $J_{AX} = 1$  Hz). Other absorptions were observed as complex multiplets at  $\tau$  6.35-7.15 (4, CH<sub>2</sub>SO<sub>2</sub>, and methine, characteristic peak at  $\tau$  6.75) and 7.35-8.25 (4, cyclobutane methylene). The mass spectrum (page 72) was

very similar to that of the exo isomer exhibiting a very weak molecular ion at  $m/e$  180 and 182 and the 100% peak at  $m/e$  81 corresponding to  $C_6H_9^+$ .

Anal. Calcd. for  $C_6H_9SO_2Cl$ : C, 39.89; H, 5.02.

Found: C, 39.90; H, 5.10.

Solubility-Stability Check of *exo*-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide. A mixture of 0.300 g of the title chloro sulfone and 0.600 g of m-chlorobenzoic acid in 20 ml of dichloromethane was stirred briefly and chilled in an ice bath. The m-chlorobenzoic acid was filtered off and washed with a few milliliters of dichloromethane. The combined filtrate and washings were then extracted with three 5 ml portions of saturated sodium carbonate solution and once with 7 ml of saturated sodium chloride solution. After drying ( $MgSO_4$ ) the dichloromethane solution was passed through a short basic alumina column. The solvent was then removed at the aspirator and finally at the vacuum pump to give a quantitative recovery of the chloro sulfone. An nmr spectrum of the recovered material did not show the presence of m-chlorobenzoic acid.

Reaction of *exo*-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide with Potassium *tert*-Butoxide. To an ice bath cooled solution of 1.742 g (15.5 mmol) of powdered potassium tert-butoxide in 50 ml of dry diglyme (distilled from lithium aluminum hydride) was added 0.700 g (3.88 mmol) of exo-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide while stirring magnetically. The mixture became a dark yellow-brown in

color immediately upon addition of the chloro sulfone. After stirring for 2 hr at 0-5° the reaction mixture was allowed to warm to room temperature. A short-path distillation was attempted at 29°/48 mm but, no volatile material was collected in the dry ice trap. The diglyme was removed by adding 50 ml of ether to the reaction mixture followed by extraction with five 40 ml portions of 20% aqueous sodium chloride. Most of the dark color was removed in the aqueous washes. After drying (MgSO<sub>4</sub>) the ether was distilled leaving a clear liquid. An nmr spectrum of this liquid showed the presence of only diglyme and a small amount of ether.

Reaction of *exo*-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide with Sodium Hydride. While working in a glove-bag under dry nitrogen, 0.600 g (14.2 mmol) of 57% sodium hydride in mineral oil was weighed into a 100 ml three-necked flask and washed with 5 ml of dry diglyme (distilled from lithium aluminum hydride). A vial containing 0.600 g (3.32 mmol) of *exo*-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide was connected to the center neck of the flask with a piece of gooch tubing. After adding 30 ml of dry diglyme the flask was equipped with a gas inlet and a drying tube.

The flask was transferred to an ice bath and the gas inlet connected to a source of dry nitrogen. The chloro sulfone was then added in small portions to the sodium hydride slurry. After stirring for 3.5 hrs, 20 ml of ether was added and unreacted sodium hydride filtered off. The filtrate was washed with nine 20-ml portions of 10% sodium chloride,



dried ( $\text{MgSO}_4$ ), and concentrated to 5 ml by careful distillation through a 30 cm Vigreux column. The only product obtained from this ethereal residue was 384 mg of starting material (64% recovery).

Reaction of *exo*-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide with Sodium *tert*-Pentoxide. The procedure of Corey and Block<sup>16</sup> was used for the preparation of the sodium *tert*-pentoxide solutions. While working in a glove-bag under a dry nitrogen atmosphere, 8.325 g (190 mmol) of sodium hydride (54.8% in mineral oil) was added to a flamed 250 ml three-necked flask and washed several times with dry pentane. After adding 60 ml of tetraglyme (distilled from calcium hydride) and 9.0 ml of *tert*-amyl alcohol (83.3 mmol, distilled from calcium hydride), the flask was equipped with a stirring bar, a stopcock, and two stoppers. The flask was removed from the glove-bag and the stopcock connected to a source of dry nitrogen. One of the stoppers was replaced with a short-path distillation apparatus leading to a liquid nitrogen cooled receiving flask, a dry ice trap, and finally to a vacuum pump via a manostat and manometer. The suspension was warmed to 70° (oil bath temperature) while stirring vigorously and, when hydrogen evolution had ceased, evacuated to 0.4 mm for 1 hr. The reaction mixture was cooled to 30° and the vacuum broken with nitrogen.

1. At 55° and Atmospheric Pressure. To the prepared solution of sodium *tert*-pentoxide at 30° was added 6.00 g (33.2 mmol) of *exo*-2-chloro-3-thiabicyclo[3.2.0]heptane-



3,3-dioxide in one portion. The temperature was then raised to 55° while stirring vigorously. The initial gray color gave way briefly to a light yellow which rapidly turned to brown and finally to a dark olive-green. The reaction mixture bubbled vigorously during the first 15 min after the chloro sulfone addition. After one hour at 55°, the pressure was gradually lowered to 0.4 mm for 1.75 hr. The vacuum was broken with nitrogen and the receiving flask allowed to warm to room temperature. The small amount of liquid in the receiving flask was short-path distilled in two fractions. The first fraction (22°/35 mm) gave approximately 35 mg of a sweet-smelling material, an nmr spectrum of which showed the presence of desired bicyclo[2.2.0]hex-2-ene, tert-amyl alcohol, and an unidentified material. The portion of the spectrum corresponding to the bicyclic olefin agreed with that previously obtained by Reineke,<sup>56</sup> with the exception that expansion of the olefinic region showed the absorption at  $\tau$  3.74 to be a three line pattern (apparent  $J = 1.2$  Hz) rather than a finely split doublet. Since the nmr absorptions of the alcohol and the unidentified material overlapped, it was not possible to determine the relative amounts of alcohol and olefin present. The second fraction (22°/4 mm) gave only tert-amyl alcohol and none of the bicyclic olefin.

Water and ether were added to the reaction mixture and the ether layer washed with several portions each of water and 20% sodium chloride, and once with saturated sodium chloride. Almost all the dark color was removed in the

aqueous washes. The ether was dried ( $\text{MgSO}_4$ ) and removed at the aspirator to give a light brown oil. This oil was chromatographed on silica-gel (ether-hexanes) to give a faint yellow oil. An nmr spectrum showed it to be mineral oil from the sodium hydride.

2. At 0° and 14 mm Pressure. To a prepared solution of 69.4 mmol of sodium tert-pentoxide at 0° under nitrogen was added 5.00 g (27.7 mmol) of exo-2-chloro-3-thiabicyclo[3.2.0]-heptane-3,3-dioxide while stirring vigorously. The reaction mixture turned an intense brick-red within five minutes after adding the chloro sulfone. The system was slowly evacuated to 14 mm and held at this pressure for 13 hrs while attempting to trap volatile materials in a dry ice-alcohol trap. The reaction mixture was then allowed to warm to room temperature which caused the brick-red color to turn dark brown. After an additional two hours at 14 mm, the vacuum was broken with nitrogen and the contents of the dry ice-alcohol trap examined by nmr spectroscopy. None of the bicyclo[2.2.0]hex-2-ene was present.

3. At 70° and 9 mm Pressure. A three-necked flask containing a prepared solution of 66.4 mmol of sodium tert-pentoxide was fitted with a short-path distillation apparatus leading to a liquid nitrogen trap, a stopcock connected to a source of nitrogen, and a constant pressure addition funnel containing 3.00 g (16.6 mmol) of exo-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide in 15 ml of dry tetraglyme. While at an oil bath temperature of 70° and a pressure of 9 mm, the

chloro sulfone solution was added dropwise over a period of 2 hr. The reaction mixture turned to an intense olive-green upon addition of the chloro sulfone solution. After breaking the vacuum with nitrogen, the material collected in the liquid nitrogen trap was short-path distilled in two fractions. An nmr spectrum of the first fraction (106 mg, 27°/89 mm) showed the presence of bicyclo[2.2.0]hex-2-ene and tert-amyl alcohol as minor components along with unidentified material exhibiting complex absorptions centered at  $\tau$  8.73 and 9.10. The second fraction (46 mg, 27°/3 mm) contained only tert-amyl alcohol and a small percentage of bicyclo[2.2.0]hex-2-ene. It was not possible to reasonably estimate the weight of bicyclic olefin in each fraction.

Reaction of exo-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide with n-Butyllithium.

1. At -78° in Diglyme. To a solution of 3.00 g (16.6 mmol) of exo-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide in 80 ml of dry diglyme (distilled from lithium aluminum hydride) cooled in a dry ice-alcohol bath was added 23.5 ml (37.4 mmol) of 1.59 M n-butyllithium in ether while stirring under nitrogen. The reaction mixture initially turned a light yellow and rapidly changed to a creamy brown. It was stirred for 15 min at dry ice bath temperature, stored overnight at -26°, and then at 4° for 3 hrs. After warming to room temperature, ether and other volatile materials were short-path distilled from the reaction mixture at 30°/15 mm. Ether was carefully removed from the distillate by subsequent distillation through

a semi-micro spinning band column. An nmr spectrum of the residue revealed the presence of only ether, diglyme, and a trace of bicyclo[2.2.0]hex-2-ene.

Water was added to the reaction mixture and the resulting solution extracted twice with 150 ml of ether. The combined ether extracts were washed with six 50-ml portions of water and once with 50 ml of saturated sodium chloride solution. The dark brown color of the reaction mixture was removed in the aqueous washes. The ether was dried ( $\text{Na}_2\text{SO}_4$ ) and removed by distillation through a 30 cm Vigreux column. An nmr spectrum of the residue revealed the presence of only diglyme and ether.

2. At 33° in Tetraglyme. To a solution of 3.00 g (16.6 mmol) of exo-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide in 30 ml of dry tetraglyme in an oil bath at 32-34° was added 23 ml (36.6 mmol) of 1.59 M n-butyllithium in ether while stirring under nitrogen. The reaction mixture became brown-red during the addition which later gave way to dark brown. The pressure was reduced to 97 mm for 1 hr and volatile materials collected in a dry ice-alcohol trap via a short-path distillation apparatus. During this period a considerable amount of solid brown material was deposited on the inside of the flask just above the level of the solution. The volatile material collected in the dry ice trap was carefully concentrated to approximately 2 ml by distillation on a semi-micro spinning band column. An nmr spectrum of the pot residue showed it to be composed mainly of ether with a small

amount of the desired bicyclo[2.2.0]hex-2-ene.

Reaction of endo-2-Chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide with Sodium tert-Pentoxide. The title chloro sulfone (4.017 g, 22.3 mmol) was added to a prepared solution of 67 mmol of sodium tert-pentoxide at 35° and the temperature raised to 55° while stirring under nitrogen. The reaction briefly became light yellow and rapidly changed to intense brown-green. The reaction mixture was allowed to stir for one hour at 55° while passing a slow stream of nitrogen through the flask and into a liquid nitrogen cooled trap via a short-path distillation apparatus. The pressure was gradually lowered to 0.4 mm for 2 hr, the vacuum broken with nitrogen, and the liquid nitrogen trap allowed to warm to room temperature. The liquid collected in the trap was short-path distilled and collected in two fractions. The first fraction (26°/73 mm) gave 115 mg of a sweet smelling liquid which contained bicyclo[2.2.0]hex-2-ene, tert-amyl alcohol, and unidentified material having complex nmr absorptions centered at  $\tau$  8.73 and 9.13. The olefin was a minor component compared to the unidentified material. The second fraction (26°/0.4 mm) gave 30 mg of tert-amyl alcohol containing a trace of the bicyclic olefin.

1,4-Dichlorobutane. This material was prepared by the standard reaction of 1,4-butanediol with excess thionyl chloride.<sup>27</sup> Distillation at 153-155° gave the dichloride in 64% yield. (lit. b.p.<sup>27</sup> 150-155°, b.p.<sup>85</sup> 161-163°).

Thiolane. The method of Lawson, Easley, and Wagner<sup>29</sup> was used

to prepare the title compound in 69% yield, b.p. 119-121° (lit.<sup>29</sup> 73-78% yield, b.p. 119-121°). The nmr spectrum was in agreement with that published.<sup>42</sup>

#### Halogenation-Oxidation of Thiolane.

##### 1. N-Chlorosuccinimide-m-Chloroperbenzoic Acid.

To 10.00 g (113.8 mmol) of thiolane in 100 ml of dichloromethane cooled in an ice bath was added 15.21 g (114.1 mmol) of N-chlorosuccinimide in small portions while stirring magnetically. The addition quickly caused the reaction mixture to set to a thick mass. This was loosened by briefly allowing the mixture to stir while out of the ice bath. The reaction mixture was allowed to stir until a test with moist potassium iodide starch paper was negative. Then while stirring in the ice bath, 36.7 g of 71% and 17.5 g of 74% (total peracid 226 mmol) m-chloroperbenzoic acid was added in small portions along with additional dichloromethane. After stirring for two days at room temperature, the flask was cooled in an ice bath and m-chlorobenzoic acid filtered off. The filtrate was washed with three portions of saturated sodium carbonate solution, dried (MgSO<sub>4</sub>), and the dichloromethane removed at the aspirator to leave 18.5 g of an off-white semi-solid as crude product. This crude product was chromatographed on 280 g of silica gel using 20% ether in hexanes. The first eluted material showed only nmr absorptions in the aromatic region and was discarded. Continued elution gave 7.0 g (64.8% yield based on NCS) of 2,3-dichlorothiolane-1,1-dioxide as a fluffy white solid which was further purified by

recrystallization from chloroform-hexanes, m.p. 80-81.5°. The infrared spectrum (page 37) showed characteristic absorptions at 7.69 and 8.91  $\mu$  (both strong, SO<sub>2</sub>) with other distinctive absorptions appearing at 7.93 (m), 8.39 (s), 8.62 (w), 9.79 (w), 11.11 (m), 12.41 (m), 12.57 (m), and 13.59 (m)  $\mu$ . The nmr spectrum (page 41) showed absorptions at  $\tau$  5.17 (d, J = 6.4 Hz, SO<sub>2</sub>CHCl, 1), 5.59 (m, CHCl, 1), and 6.15-7.83 (m, CH<sub>2</sub>CH<sub>2</sub>, 4). The mass spectrum (page 73) showed a weak molecular ion at m/e 188, 190, and 192 and a 100% peak at m/e 96 corresponding to C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub><sup>+</sup>.

Anal. Calcd. for C<sub>4</sub>H<sub>6</sub>SO<sub>2</sub>Cl<sub>2</sub>: C, 25.40; H, 3.19.

Found: C, 25.25; H, 3.00.

In another reaction, 7.125 g (81 mmol) of the sulfide was chlorinated with 10.90 g (81.6 mmol) of N-chlorosuccinimide in carbon tetrachloride under gentle reflux. The NCS and solvent were removed and the residue oxidized with m-chloroperbenzoic acid in dichloromethane. Work-up followed by chromatography of the crude product (10.7 g) gave 3.109 g (24.6% yield) of 2-chlorothiolane-1,1-dioxide as an oil. This chloro sulfone was eluted from the column with 100% ether after the dichloro sulfone has been eluted. The oil was short-path distilled at 125°(pot)/0.4 mm. Although 2-chlorothiolane-1,1-dioxide has been prepared previously,<sup>72</sup> no physical data were reported. The infrared spectrum (page 37) showed distinctive absorptions at 7.59, 8.63, 8.83, 9.01  $\mu$  (all strong, SO<sub>2</sub>) as well as absorptions at 3.43 (w), 6.92 (w), 7.09 (w), 7.89 (m), 8.16 (w), 10.98 (w), 13.69 (m), and 13.92 (m)  $\mu$ .



The nmr spectrum (page 43) showed absorptions at  $\tau$ 5.15 (t,  $J = 5.3$  Hz,  $\text{CHCl}_3$ , 1) and 6.66-8.15 (m,  $\text{CH}_2$ 's, 6, characteristic peaks at  $\tau$ 6.70, 6.83, 6.95, 7.59, and 7.65).

## 2. N-Bromosuccinimide-m-Chloroperbenzoic Acid.

To a stirred, ice bath cooled solution of 10 g (113.8 mmol) of thiolane in 100 ml of dichloromethane was added 20.23 g (113.8 mmol) of N-bromosuccinimide. After stirring for 4 hrs in the ice bath, the presence of unreacted N-bromosuccinimide was indicated by a positive test with moist potassium iodide starch paper. The reaction mixture was then heated to reflux until the moist potassium iodide starch paper test was negative. After cooling to  $0^\circ$ , 31.4 g of 74% and 21.7 g of 76% (230 mmol total) m-chloroperbenzoic acid was added in small portions, along with additional solvent, and the mixture allowed to stir at room temperature for two days. The mixture was again cooled and m-chlorobenzoic acid filtered off and washed with solvent. The filtrate was washed with three portions of 10% sodium carbonate which had been nearly saturated with sodium chloride. The solution was dried ( $\text{MgSO}_4$ ) and the solvent removed at the aspirator to leave a brownish-red waxy material. Recrystallization twice from dichloromethane-hexanes gave 7.5 g (22.2% yield) of N-(4-bromobutylsulfonyl)succinimide, m.p.  $122-123^\circ$ . The infrared spectrum (page 37) showed distinctive absorptions at 5.77 (s,  $\text{C=O}$ ) and 7.34 and  $8.53 \mu$  (both strong,  $\text{SO}_2$ ). The nmr spectrum ( $\text{CF}_3\text{CO}_2\text{H}$ , internal TMS; page 43) showed absorptions at  $\tau$ 6.07-6.59 (m,  $\text{SO}_2\text{CH}_2$  and  $\text{CH}_2\text{Br}$ , 4), 6.90 (s, succinimide



CH<sub>2</sub>, 4), and 7.66-8.00 (m, middle CH<sub>2</sub>CH<sub>2</sub> of chain, 4). The mass spectrum (page 75) gave a molecular ion at m/e 297 and 299 with the 100% peak at m/e 55.

Anal. Calcd. for C<sub>8</sub>H<sub>12</sub>NSO<sub>4</sub>Br: C, 32.23; H, 4.06; N, 4.70. Found: C, 32.14; H, 3.96; N, 4.44.

The mother liquor was chromatographed on silica gel with gradually increasing amounts of dichloromethane in benzene. The only material obtained for which a reasonable structure could be postulated was 2,3-dibromothiolane-1,1-dioxide. It gave an nmr spectrum almost identical to that of 2,3-dichlorothiolane-1,1-dioxide.

#### Halogenation of Thiolane-1,1-dioxide.

1. N-Chlorosuccinimide. To a stirred solution of 1.00 g (8.33 mmol) of thiolane-1,1-dioxide in 10 ml of carbon tetrachloride at 0° was added 1.11 g (8.35 mmol) of N-chlorosuccinimide and a few grains of benzoyl peroxide. The reaction did not commence after one hour as evidenced by the absence of succinimide floating on the surface of the solution. The reaction mixture was then heated to near reflux and stirred for an additional two hours. The N-chlorosuccinimide was filtered off and the reaction mixture concentrated. An nmr spectrum showed the presence of only starting material.

2. N-Bromosuccinimide. To a stirred solution of 2.00 g (16.7 mmol) of thiolane-1,1-dioxide in 20 ml of carbon tetrachloride was added 3.005 g (16.9 mmol) of N-bromosuccinimide and a few grains of benzoyl peroxide and the mixture heated to reflux. The reaction could not be made to commence even

with continued heating, addition of more peroxide, addition of a small amount of bromine, or external irradiation. Again an nmr spectrum indicated the presence of only starting material.

3. Sulfuryl Chloride at  $-78^{\circ}$ . A two-necked flask containing a solution of 0.944 g (7.85 mmol) of thiolane-1,1-dioxide in 12 ml of dichloromethane was equipped with a drying tube and a rubber serum cap and cooled in a dry ice-alcohol bath. A solution of 0.81 ml (10 mmol) of sulfuryl chloride in 5 ml of dichloromethane was added slowly through the serum cap by means of a syringe and the reaction mixture allowed to stir for one hour. After warming to room temperature the solvent was removed at the aspirator and finally at the vacuum pump. An nmr spectrum of the residue revealed only the presence of starting material.

4. Sulfuryl Chloride and Pyridine at  $0^{\circ}$ . To a magnetically stirred solution of 1.224 g (10.2 mmol) of thiolane-1,1-dioxide and 1.70 ml of pyridine in 15 ml of dichloromethane at  $0^{\circ}$  was added 0.91 ml (11.2 mmol) of sulfuryl chloride in 15 ml of dichloromethane. After stirring for 70 min the solvent and unreacted sulfuryl chloride were removed at the aspirator. The residue was redissolved in 30 ml of dichloromethane and washed with 15 ml of 10% hydrochloric acid and 20 ml of water. The solution was dried over anhydrous magnesium sulfate and the solvent removed at the aspirator. An nmr spectrum of the residue showed only the presence of starting thiolane-

1,1-dioxide.

5. Sulfuryl Chloride and a Free Radical Initiator.

A solution of 4.00 g (33.3 mmol) of thiolane-1,1-dioxide, 2.85 ml (35.0 mmol) of sulfuryl chloride, and a catalytic amount of a free radical initiator (either benzoyl peroxide or azobisisobutyronitrile) in 15 ml of benzene was heated at reflux for 45 min. The reaction commenced when reflux temperature was reached as evidenced by the rapid increase in the rate of reflux and the evolution of sulfur dioxide and hydrogen chloride through a drying tube at the top of the condenser. The solvent was removed at reduced pressure to leave 4.01 g of a white semi-solid. An nmr spectrum of this crude product revealed the presence of starting material and 3-chlorothiolane-1,1-dioxide. Analysis of the semi-solid by glpc on a 12 ft x 0.25 in. Silicon Gum Rubber column (column temperature, 175°; He flow rate, 52 ml/min; injection port temperature, 265°) showed the semi-solid to be composed of 26.8% starting material (retention time, 7.9 min) and 73.2% of the  $\beta$ -chloro sulfone (retention time 11.0 min). Correcting for the unreacted starting material gave a yield of 78% (57% conversion). Most of the starting material was removed by distillation through an 8 in. Vigreux column. The first fraction (85-109°/0.4 mm) was primarily thiolane-1,1-dioxide while the second fraction (110-119°/0.4 mm) was primarily 3-chlorothiolane-1,1-dioxide. The second fraction could be further purified by recrystallization from ether-hexanes or benzene-hexanes, m.p. 58.0-

59.0° (lit.<sup>70</sup> b.p. 128-130°/2.0-2.5 mm; m.p. 54.2-54.4°; 46% conversion). The nmr spectrum agreed with that reported.<sup>70</sup> The mass spectrum (page 76) showed a molecular ion at m/e 154 and 156 with the 100% peak at m/e 55.

Anal. Calcd. for C<sub>4</sub>H<sub>7</sub>SO<sub>2</sub>Cl: C, 31.06; H, 4.56.

Found: C, 30.90; H, 4.72.

Thiolane-1-oxide. To a stirred solution of 20.00 g (227 mmol) of thiolane in 60 ml of acetone at 0° was added 25 ml (291 mmol) of 30% hydrogen peroxide dropwise from an addition funnel. The reaction mixture was allowed to sit in the refrigerator (-4°) for two days and then overnight at room temperature. The solvent was removed by short-path distillation, Linde 13X molecular sieves added, and the sulfoxide distilled (105°/25-30 mm) to give 20.32 g (86.0% yield) of colorless product (lit.<sup>22</sup> 45°/3 mm). The infrared spectrum showed a strong absorption at 9.75  $\mu$  (SO). The material appeared to be contaminated by a small amount of water as evidenced by a weak absorption at 2.95  $\mu$ .

2-Chlorothiolane-1,1-dioxide. The method of Tsuchihashi, Ogura, and Iriuchijima<sup>72</sup> was used to chlorinate 28.4 g of thiolane-1-oxide. The crude  $\alpha$ -chloro sulfoxide was not isolated and purified, but was immediately oxidized with 30% hydrogen peroxide in glacial acetic acid. After stirring the oxidation reaction mixture for several days, the acetic acid was removed by short-path distillation. The residue was dissolved in chloroform and dried with 4A molecular sieves overnight. The molecular sieves were removed by

filtration and the solvent was removed at the aspirator. The residue was then distilled over an 8 in. Vigreux column in two fractions. The first fraction (92.5-101°/0.4 mm, 3.7 g) had an nmr spectrum almost identical to that of 2-chloro-thiolane-1,1-dioxide with additional peaks at  $\tau$ 6.98, 7.10, and 7.78. The second fraction (101-108°/0.4 mm, 23.5 g, 55.6% yield) gave an nmr and infrared spectrum identical in all respects to the 2-chlorothiolane-1,1-dioxide prepared previously. The mass spectrum (page 74) gave a molecular ion at  $m/e$  154 and 156 and a 100% peak at  $m/e$  62 corresponding to  $C_2H_3Cl^+$ .

Anal. Calcd. for  $C_4H_7SO_2Cl$ : C, 31.06; H, 4.56.

Found: C, 31.04; H, 4.48.

Reaction of 2-Chlorothiolane-1,1-dioxide with Sodium tert-Pentoxide. The procedure of Corey and Block<sup>16</sup> was used to prepare a 194 mmol solution of sodium tert-pentoxide in tetraglyme. To the base solution heated in an oil bath at 44° was added 10.00 g (64.7 mmol) of 2-chlorothiolane-1,1-dioxide in 15 ml of dry tetraglyme over a period of 1.25 hr. During the addition a slow stream of dry nitrogen was passed through the flask and then through a trap cooled in liquid nitrogen. The initial addition of the chloro sulfone caused the reaction mixture to become grey-red in color which then gave way to grey-brown. The evolution of gas caused the reaction mixture to froth severely. When the addition was complete, the nitrogen flow was stopped and the pressure reduced to 200 mm for 30 min. The vacuum was broken with

nitrogen and the liquid nitrogen cooled trap transferred to a dry ice bath. This caused the trap contents to melt to a colorless liquid. A portion of the trap contents was then short-path distilled into an nmr tube containing  $\text{CDCl}_3$  and TMS by removing the trap from the dry ice bath while cooling the nmr tube in a liquid nitrogen bath. The nmr tube was tightly capped and removed from the liquid nitrogen. This caused the cap to be blown off with explosive force.

The tube was quickly reimmersed in the liquid nitrogen and bromine in dichloromethane added to the nmr tube and the remainder of the trap contents. After combining the two, the solvent was removed at the aspirator and an nmr spectrum taken of the residue. The spectrum ( $\text{CCl}_4$ , internal TMS) indicated the presence of several components. The main component was judged to be trans-1,4-dibromo-2-butene (multiplets at  $\tau$ 4.07 and 6.08) based on a comparison with the published spectrum.<sup>59</sup> Other absorptions were observed at  $\tau$ 5.10-5.85 (complex multiplet), 7.95-8.30 (m), and 8.70-9.25 (m). There did not appear to be any of the desired 1,2-dibromocyclobutane present based on a description of its nmr spectrum.<sup>1</sup>

The reaction was repeated at 0-5°. The reaction mixture became an intense grey-red to lavender which persisted for as long as the flask was kept in the ice bath. When the reaction was allowed to warm slightly above ice bath temperatures, foaming became so severe that the reaction had to be discontinued.

In a subsequent reaction using the same quantities of reactants, the stream of nitrogen passed over the reaction mixture was bubbled into a 1 N solution of sodium hydroxide. From there the gas was passed through a condenser, a tube containing 80 g of 4A molecular sieves, and finally into a liquid nitrogen cooled trap. At the end of the reaction period no volatile materials had collected in the cold trap.

## APPENDIX



TABLE 1

## MASS SPECTRUM OF 3-THIABICYCLO[3.2.0]HEPTANE

<u>m/e</u>	<u>Relative Abundance, (%)</u>	<u>m/e</u>	<u>Relative Abundance, (%)</u>
116	4.3	67	30.4
115	74.1	66	4.7
114	100.0	65	5.2
113	5.4	60	7.8
99	28.8	59	5.9
87	4.9	58	5.8
86	32.6	55	2.6
85	66.0	54	2.9
84	2.4	53	7.8
81	24.2	51	4.0
80	32.1	47	4.8
79	14.4	46	4.6
77	3.8	45	21.8
73	20.4	41	12.9
72	9.2	40	3.0
71	7.1	39	28.4
68	8.7	38	2.5

TABLE 2

MASS SPECTRUM OF *exo*-2-CHLORO-  
3-THIABICYCLO[3.2.0]HEPTANE-3,3-DIOXIDE

<u>m/e</u>	<u>Relative Abundance, (%)</u>	<u>m/e</u>	<u>Relative Abundance, (%)</u>
90	3.6	55	2.7
88	10.2	54	25.4
82	6.2	53	16.4
81	100.0	52	3.8
80	30.4	51	8.9
79	16.6	50	2.5
78	2.5	49	5.1
77	32.4	44	4.6
76	3.3	42	2.0
75	93.5	41	47.0
68	4.0	40	3.6
67	69.8	39	37.8
65	4.8	38	2.4

TABLE 3

MASS SPECTRUM OF endo-2-CHLORO-  
3-THIABICYCLO[3.2.0]HEPTANE-3,3-DIOXIDE

<u>m/e</u>	<u>Relative Abundance, (%)</u>	<u>m/e</u>	<u>Relative Abundance, (%)</u>
90	3.0	64	2.9
88	10.3	55	4.3
82	6.5	54	33.0
81	100.0	53	20.8
80	32.4	52	5.1
79	17.5	51	12.0
78	3.4	50	3.2
77	34.6	49	6.7
76	3.5	48	2.1
75	92.9	42	3.1
69	2.0	41	72.6
68	4.5	40	5.5
67	79.8	39	59.5
66	2.1	38	3.0
65	5.8	36	2.0

TABLE 4

## MASS SPECTRUM OF 2,3-DICHLOROTHIOLANE-1,1-DIOXIDE

<u>m/e</u>	<u>Relative Abundance, (%)</u>	<u>m/e</u>	<u>Relative Abundance, (%)</u>
152	3.3	73	5.4
125	11.8	65	2.9
124	6.6	64	18.1
123	18.8	63	12.7
111	3.1	62	47.5
109	4.9	61	25.3
105	9.1	60	5.4
100	10.2	54	6.5
98	64.6	53	87.9
97	3.0	52	8.2
96	100.0	51	27.9
91	15.8	50	11.5
89	61.3	49	8.8
88	33.9	48	9.4
87	6.3	47	2.0
85	3.6	45	5.3
83	4.1	41	26.3
77	13.4	39	32.7
76	2.3	38	4.8
75	39.6	36	4.1

TABLE 5

## MASS SPECTRUM OF 2-CHLOROTHIOLANE-1,1-DIOXIDE

<u>m/e</u>	<u>Relative Abundance, (%)</u>
120	4.2
91	19.8
90	5.1
89	62.0
75	5.2
65	2.5
64	32.9
63	4.9
62	100.0
56	8.9
55	57.5
54	6.5
53	12.9
51	4.1
48	2.1
44	24.6
43	3.0
42	3.0
41	18.1
39	12.4
32	27.0

TABLE 6

MASS SPECTRUM OF N-(4-BROMO-  
BUTYLSULFONYL) SUCCINIMIDE

<u>m/e</u>	<u>Relative Abundance, (%)</u>	<u>m/e</u>	<u>Relative Abundance, (%)</u>
299	3.3	106	4.6
297	3.4	101	5.5
256	3.6	100	76.9
254	3.4	99	21.7
218	8.0	98	3.0
201	15.8	84	3.8
200	8.6	82	9.8
199	15.6	80	2.3
198	7.8	72	3.9
154	5.6	70	9.1
137	18.4	57	7.0
136	4.2	56	78.1
135	20.6	55	100.0
134	2.1	54	5.3
127	2.7	53	5.1
126	11.7	44	3.6
119	15.1	43	2.7
112	6.3	42	2.7
109	5.7	41	7.4
108	4.4	39	6.4
107	6.2		

TABLE 7

## MASS SPECTRUM OF 3-CHLOROTHIOLANE-1,1-DIOXIDE

<u>m/e</u>	<u>Relative Abundance, (%)</u>	<u>m/e</u>	<u>Relative Abundance, (%)</u>
156	2.4	55	100.0
154	6.7	54	29.0
126	2.0	53	15.8
105	4.9	52	2.2
92	2.4	51	6.0
91	5.7	50	3.4
90	7.2	49	2.5
89	18.2	48	3.6
77	3.7	45	2.3
75	9.5	43	2.3
64	18.4	41	14.3
63	3.3	40	19.0
62	45.0	39	27.2
61	2.3	38	2.3
56	4.6		

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90. All melting points were taken on a Kofler hot stage and are uncorrected; boiling points are also uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double beam recording spectrophotometer. N.m.r. spectra were obtained using a Varian T-60 or XL-100 recording spectrophotometer. Mass spectra were recorded using an AEI MS-9 recording spectrophotometer by Mr. Michael Rennekamp. Glpc analyses were performed using an F & M Model 500 temperature programmed gas chromatograph or a Hewlett-Packard 5750 gas chromatograph. Microanalyses were determined by Mr. Moon Kim, Department of Chemistry, Kansas State University, Manhattan, Kansas.

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## VITA

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THE ATTEMPTED SYNTHESIS OF BICYCLO[2.2.0]HEX-2-ENE  
AND CYCLOBUTENE BY THE RAMBERG-BACKLUND REACTION

by

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## ABSTRACT

A synthetic route from adipic acid to 3-thiabicyclo[3.2.0]-heptane (60) was developed using a series of well-known reactions. Treatment of 60 with N-chlorosuccinimide followed by immediate oxidation gave a 4:1 mixture of exo- and endo-2-chloro-3-thiabicyclo[3.2.0]heptane-3,3-dioxide (62).

Several attempts at subjecting 62 to modifications of the Ramberg-Backlund reaction met with little success. Using either diglyme or tetraglyme as solvent, reaction of 62 with potassium tert-butoxide gave only brown decomposition products while reaction with sodium hydride led to recovery of starting material. Bicyclo[2.2.0]hex-2-ene was obtained in less than 1% yield from the reaction of 62 with sodium tert-pentoxide at temperatures above 20°C. Similar results were obtained using n-butyllithium as base.

Difficulty was encountered in the synthesis of a 2-halothiolane-1,1-dioxide. Treatment of thiolane (74) with N-chlorosuccinimide followed by immediate oxidation gave 2,3-dichlorothiolane-1,1-dioxide in 65% yield and 2-chlorothiolane-1,1-dioxide (75a) in 25% yield. Bromination of 74 with N-bromosuccinimide followed by oxidation gave N-(4-bromobutylsulfonyl)succinimide (78). Treatment of thiolane-1,1-dioxide (81) with NCS or NBS or at low temperatures with sulfuryl chloride led only to the recovery of starting material. Reaction of 81 with sulfuryl chloride in refluxing benzene gave 3-chlorothiolane-1,1-dioxide. Synthesis of 75a was finally achieved

by oxidation of 74 to thiolane-1-oxide, chlorination with sulfonyl chloride, and oxidation again to the sulfone.

Subjection of 75a to the Ramberg-Bäcklund reaction using sodium tert-pentoxide as base led to the isolation of an extremely volatile material. Treatment of this material with bromine gave 1,4-dibromo-2-butene as the major product. An explanation of this reaction sequence was postulated, but attempts to investigate it further met with failure.