

STUDY OF THE SYNTHESIS OF
DIMETHYL 1,3-BUTADIENE-1,3-DICARBOXYLATE
AND 1,3-BUTADIENE-1,3-DICARBONITRILE

by

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vii
ABSTRACT	viii
CHAPTER	
1 INTRODUCTION	1
2 RESULTS	4
Attempted Synthesis of Dimethyl 1,3-butadiene-1,3-dicarboxylate	4
Preparation of 2-chloro-4-methylene-glutaronitrile 2 and Derivatives	4
Via Cracking of the Cyclopentadiene Adduct of Dimethyl-1,3-butadiene-1,3-dicarboxylate 7	9
Attempted Synthesis of Dimethyl 2-Acetoxy or 2-Benzoyl-4-Methyleneglutarate 9,10	12
Attempted Synthesis of 1,3-Butadiene-1,3-dicarbonitrile 22	15
Attempted Synthesis of Cyclopentadiene Adduct of 1,3-butadiene-1,3-dicarbonitrile 22	15
Dehalogenation of 2-Halo-4-methylene-glutaronitrile	15
Attempted Synthesis of 2-Acetoxy or 2-benzoyloxy-4-methyleneglutaronitrile 12, 13	17
Attempted Synthesis of 4-Methylenepyran-2,6-dione 17	19
Synthesis of 4-Methylene-2-hydroxy-glutaric Acid 14	19
Synthesis of 2-Acetoxy-4-methylene-glutaric Anhydride 16	19
Attempts to Crack 2-Acetoxy-4-methylene-glutaric Anhydride 16	20
Polymerization of 2-Acetoxy-4-methylene-glutaric Anhydride 16	20

TABLE OF CONTENTS (Continued)

	Page
Other Results	21
Attempted Synthesis of 1,3-butadiene- dicarboxylic Acid 24	21
Preparation of Lactones	22
3 DISCUSSION	25
Conclusions	30
4 EXPERIMENTAL	31
Dimethyl-2-chloro-4-methyleneglutarate 4	32
Dimethyl 2-Iodo-4-methyleneglutarate 5	33
2-Iodo-4-methyleneglutaronitrile 5	34
Cyclopentadiene Adduct of 1,3-Butadiene-1,3- Dimethyl ester 7	35
Dimethyl 1,3-Butadiene-1,3-dicarboxylate Dimer 8	36
Dimethyl 2-Acetoxy-4-methylene-glutarate 9 . . .	37
2-Hydroxy-4-methyleneglutaric Acid 14	38
2-Acetoxy-4-methyleneglutaric Anhydride 16 . . .	38
Pyrolysis of 2-Acetoxy-4-methyleneglutaric Anhydride 16	39
Disodium 2-Hydroxy-4-methyleneglutarate 15 . . .	40
3-Chloro-tetrahydropyran-2-on-5-carboxylic Acid 18	41
3-Methylenetetrahydrofuran-2-on-5-carboxylic Acid 19	41
2-Chloro-4-(chloromethyl) glutaric Acid 25	42
2-Chloro-4-(chloromethyl) glutaric Anhydride 20 .	43
REFERENCES	44

LIST OF TABLES

Table		Page
1	List of Compounds	5

ABSTRACT

The synthesis of 1,3-butadiene-1,3-dicarbonitrile and dimethyl 1,3-butadiene-1,3-dicarboxylate for use as new monomers was studied. Evidence for the formation of dimethyl 1,3-butadiene-1,3-dicarboxylate 6, followed by its rapid trapping or dimerization, was obtained. A new monomer, 2-methylene-4-acetoxyglutaric anhydride 16, was synthesized. During this work a variety of interesting new compounds was also made.

Treatment of 2-chloro-4-methyleneglutaronitrile 2 with various bases did not give the desired 1,3-butadiene-1,3-dicarbonitrile 22, only oligomers being formed.

Conversion to the corresponding acetate also failed, owing to oligomerization.

Finally, treatment of 2 with triethylamine and cyclopentadiene or furan failed to yield the adducts of the diene 22.

The dimethyl 2-chloro-4-methyleneglutarate 4 was hydrolyzed by base or using tetraisopropyl titanate as catalyst to 2-hydroxy-4-methyleneglutaric acid 14. Dehydration using acetic anhydride or acetyl chloride gave 2-acetoxy-4-methyleneglutaric anhydride 16. This polymerized too readily to undergo thermal cracking of acetic acid. Thermal

dehydration of 2-hydroxy-4-methyleneglutaric acid 14 gave
3-methylenetetrahydrofuran-2-one-5-carboxylic acid 19.

CHAPTER I

INTRODUCTION

The search for new monomers continues in order to synthesize new polymers which may have unusual properties as plastics or fibers.

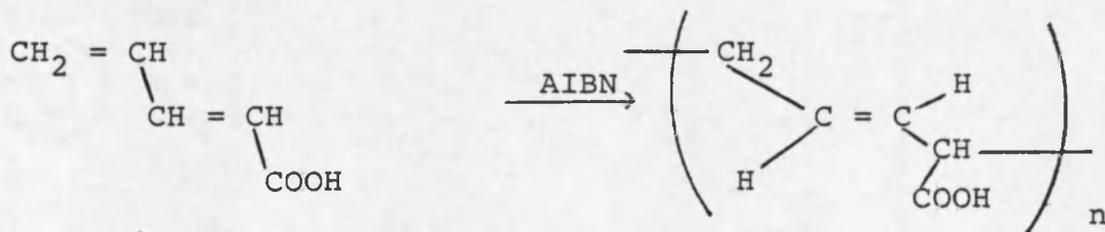
Acrylate esters and acrylonitrile have been popular mono-olefinic vinyl monomers. It was of interest to synthesize analogous diolefinic monomers.

The mono-substituted derivatives of 1,3-butadiene have been investigated to some extent.

1,3-Butadiene-1-carbonitrile (α -cyanoprene) was synthesized and polymerized (1,2). The polymers of α -cyanoprene are the result of 1,4 enchainment (cis and trans) and are amorphous. This polymer is thermoplastic.

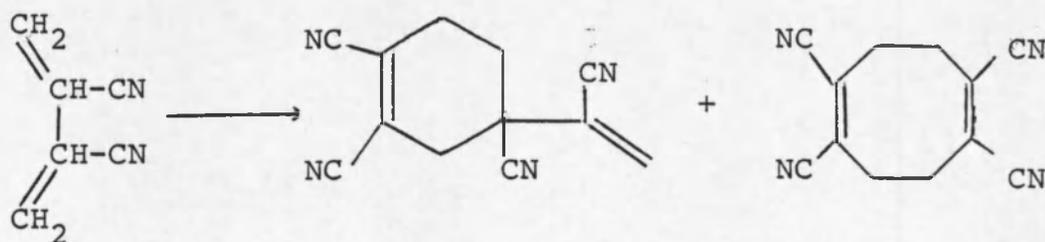
1,3-Butadiene-2-carbonitrile (β -cyanoprene) was also reported by Wei and Milliman (2) and by Muller, Mayer-Mader, and Huellstrung (3). This polymer involves 1,4 enchainment but is partially crystalline. It is also thermoplastic.

1,3-Butadiene-1-carboxylic acid was also found to undergo radical polymerization (4,5,6) through a trans 1,4 addition with free radical initiator in the manner shown:

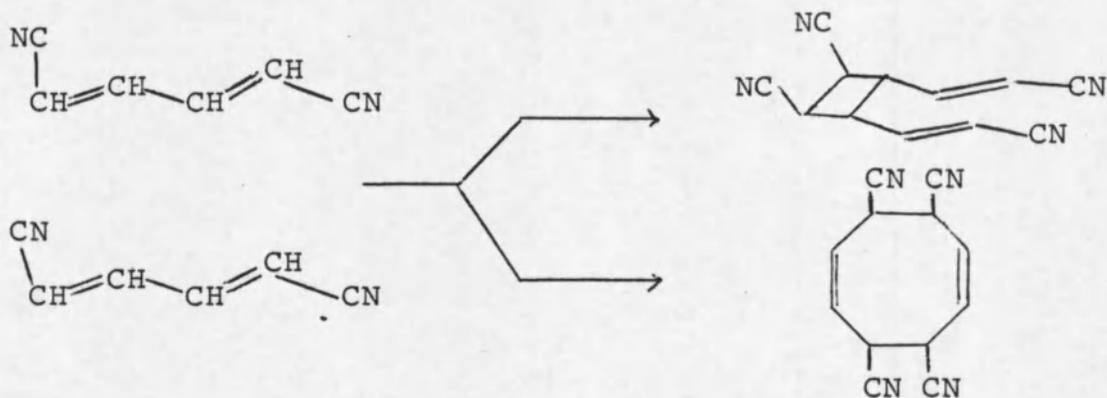


The esters of 1,3-butadiene-1-carboxylic acid, namely the methyl, ethyl, n-butyl, and t-butyl esters were polymerized anionically by Tsunetsugu, Fueno, and Fuzukawa (7). Some of these polymers were tough rubbers and some were brittle solids or pastes.

Electronegatively disubstituted butadienes have been also of interest as monomers 1,3-butadiene-2,3-dicarbonitrile was synthesized recently (8). Its dimerization is known:



Butadiene-1,4-dicarbonitrile is also known to dimerize readily (9) in the solid state in the manner shown:



No polymerization of either butadiene-1,4-or 2,3-dicyano has been reported.

1,3-Butadiene-1,4-dicarboxylic acid and its ethyl ester have been reported to polymerize anionically and by free radicals by Bando, Dodou, and Minoura (10). The diacid and diester units were composed of 1,4 bonds in the homopolymers or copolymers.

Our literature search showed that no 1,3-electro-negatively disubstituted butadiene was ever synthesized. Our interest in their synthesis is enhanced since they should copolymerize readily to give polymers which might have potentially useful properties.

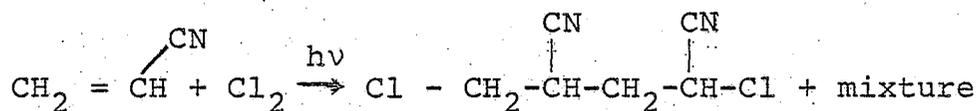
CHAPTER 2

RESULTS

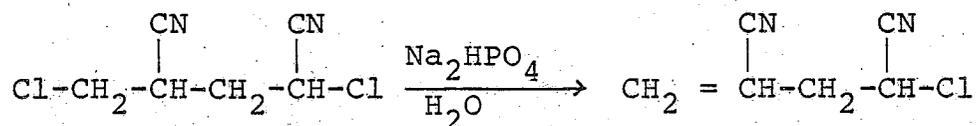
Attempted Synthesis of Dimethyl 1,3-butadiene-1,3-dicarboxylate

Preparation of 2-chloro-4-methyleneglutaronitrile 1 and Derivatives

The chlorination of acrylonitrile using ultraviolet light yields a mixture of products from which 2-chloro-4-(chloromethyl)-glutaronitrile 1 (see Table 1) was isolated by distillation (11). This compound was treated with sodium phosphate (dibasic) to yield 2-chloro-4-methyleneglutaronitrile 2:



1



1

2

Table 1. List of Compounds

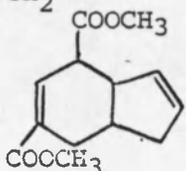
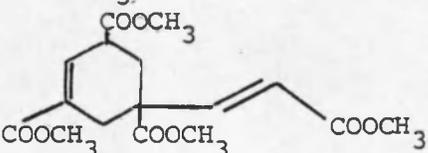
Number	Structure	Name
1	$\text{CH}_2 = \begin{array}{c} \text{CN} \\ \\ \text{CH} \end{array} - \text{CH}_2 - \begin{array}{c} \text{CN} \\ \\ \text{CH} \end{array} - \text{Cl}$	2-Chloro-4-(chloromethyl)-glutaronitrile
2	$\text{CH}_2 = \begin{array}{c} \text{CN} \\ \\ \text{C} \end{array} - \text{CH}_2 - \begin{array}{c} \text{CN} \\ \\ \text{CH} \end{array} - \text{Cl}$	2-Chloro-4-methyleneglutaronitrile
3	$\text{CH}_2 = \begin{array}{c} \text{CN} \\ \\ \text{C} \end{array} - \text{CH}_2 - \begin{array}{c} \text{CN} \\ \\ \text{CH} \end{array} - \text{I}$	2-Iodo-4-methyleneglutaronitrile
4	$\text{CH}_2 = \begin{array}{c} \text{COOCH}_3 \\ \\ \text{C} \end{array} - \text{CH}_2 - \begin{array}{c} \text{COOCH}_3 \\ \\ \text{CH} \end{array} - \text{Cl}$	Dimethyl 2-chloro-4-methyleneglutarate
5	$\text{CH}_2 = \begin{array}{c} \text{COOCH}_3 \\ \\ \text{C} \end{array} - \text{CH}_2 - \begin{array}{c} \text{COOCH}_3 \\ \\ \text{CH} \end{array} - \text{I}$	Dimethyl 2-iodo-4-methyleneglutarate
6	$\text{CH}_2 = \begin{array}{c} \text{COOCH}_3 \\ \\ \text{C} \end{array} - \text{CH} = \begin{array}{c} \text{H} \\ \\ \text{C} \end{array} - \text{COOCH}_3$	Dimethyl 1,3-butadiene 1,3-dicarboxylate
7		Cyclopentadiene adduct of dimethyl 1,3-butadiene-1,3-dicarboxylate
8		Dimethyl 1,3-butadiene-1,3-dicarboxylate dimer
9	$\text{CH}_2 = \begin{array}{c} \text{COOCH}_3 \\ \\ \text{C} \end{array} - \text{CH}_2 - \begin{array}{c} \text{COOCH}_3 \\ \\ \text{CH} \end{array} - \text{OC}(=\text{O})\text{CH}_3$	Dimethyl 2-acetoxy-4-methyleneglutarate

Table 1 (Continued)

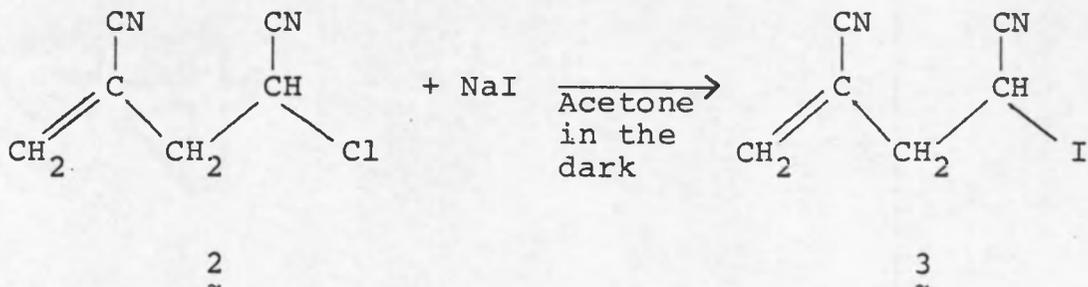
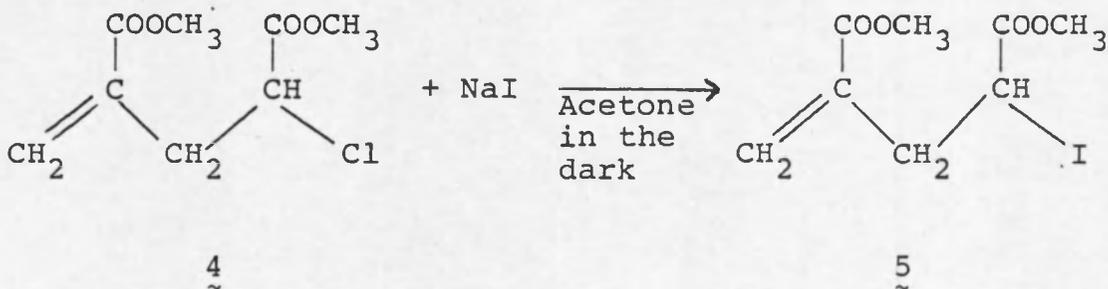
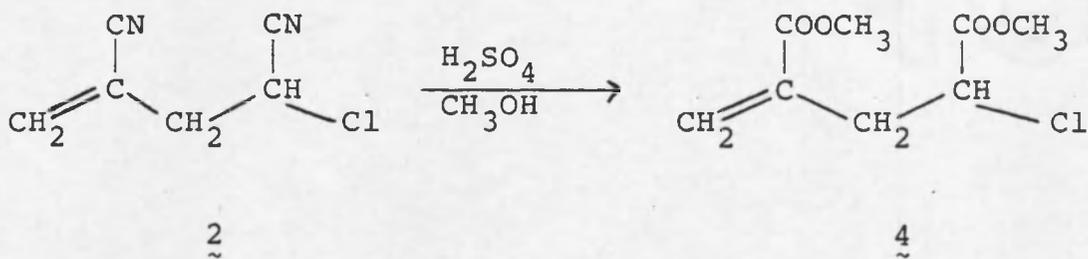
Number	Structure	Name
10		Dimethyl 2-benzoyloxy-4-methylene-glutarate
11		Cyclopentadiene adduct of 1,3-butadiene-1,3-dicarbonitrile
12		2-Acetoxy-4-methyleneglutaronitrile
13		2-Benzoyloxy-4-methyleneglutaronitrile
14		2-Hydroxy-4-methyleneglutaric acid
15		Sodium 2-hydroxy-4-methyleneglutarate
16		2-Acetoxy-4-methyleneglutaric anhydride
17		4-Methylenepyran-2,6-dione
18		3-Chloro-tetrahydropyran-2-on-5-carboxylic acid

Table 1 (Continued)

Number	Structure	Name
19		3-Methylenetetrahydrofuran-2(1H)-one-5-carboxylic acid
20		2-Chloro-4-(chloromethyl)glutaric anhydride
21		2-Chloro-4-methyleneglutaric anhydride
22		1,3-Butadiene-1,3-dicarbonitrile
23		2-Chloro-4-(chloromethyl)glutaric acid
24		1,3-Butadiene-1,3-dicarboxylic acid
25		2-Chloro-4-methyleneglutaric acid

Dimethyl-2-chloro-4-methyleneglutarate 4 was prepared by direct esterification of 2-chloro-4-methylene glutaronitrile 2 in methanol and sulfuric acid (8-10 days).

Dimethyl 2-iodo-4-methyleneglutarate 5 was prepared by allowing dimethyl 2-chloro-4-methylene glutarate 4 to react with sodium iodide in acetone (12). This reaction took 3 to 4 days to go to completion:

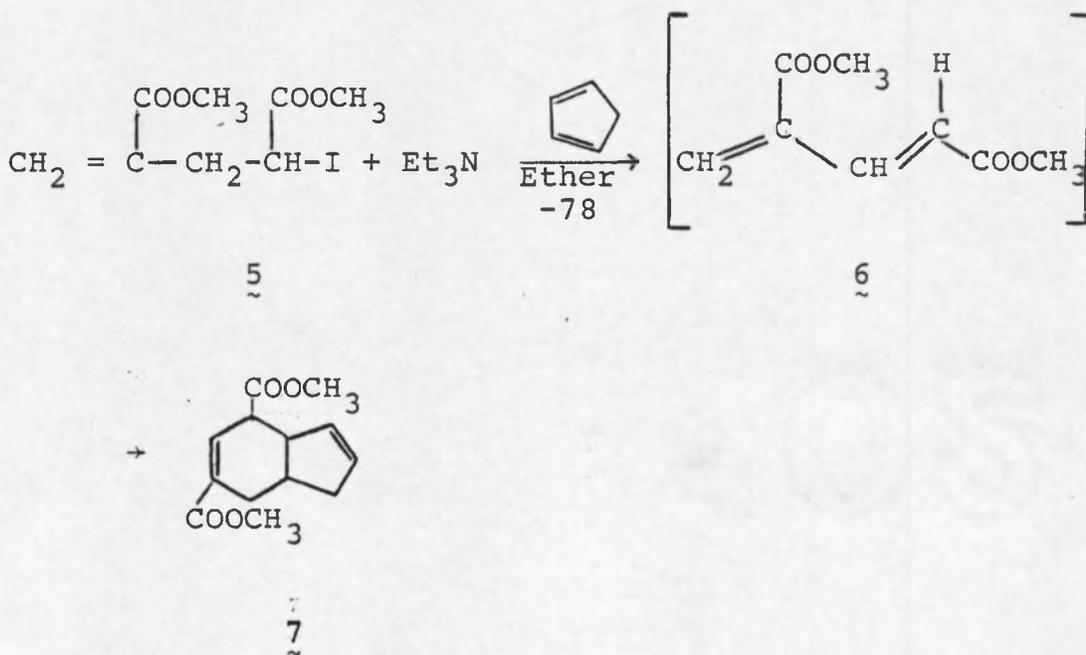


The same reaction was done to obtain 2-iodo-4-methylene glutaronitrile 3 but gave a much lower yield.

Via Cracking of the Cyclopentadiene
Adduct of Dimethyl-1,3-butadiene-1,
3-dicarboxylate 7

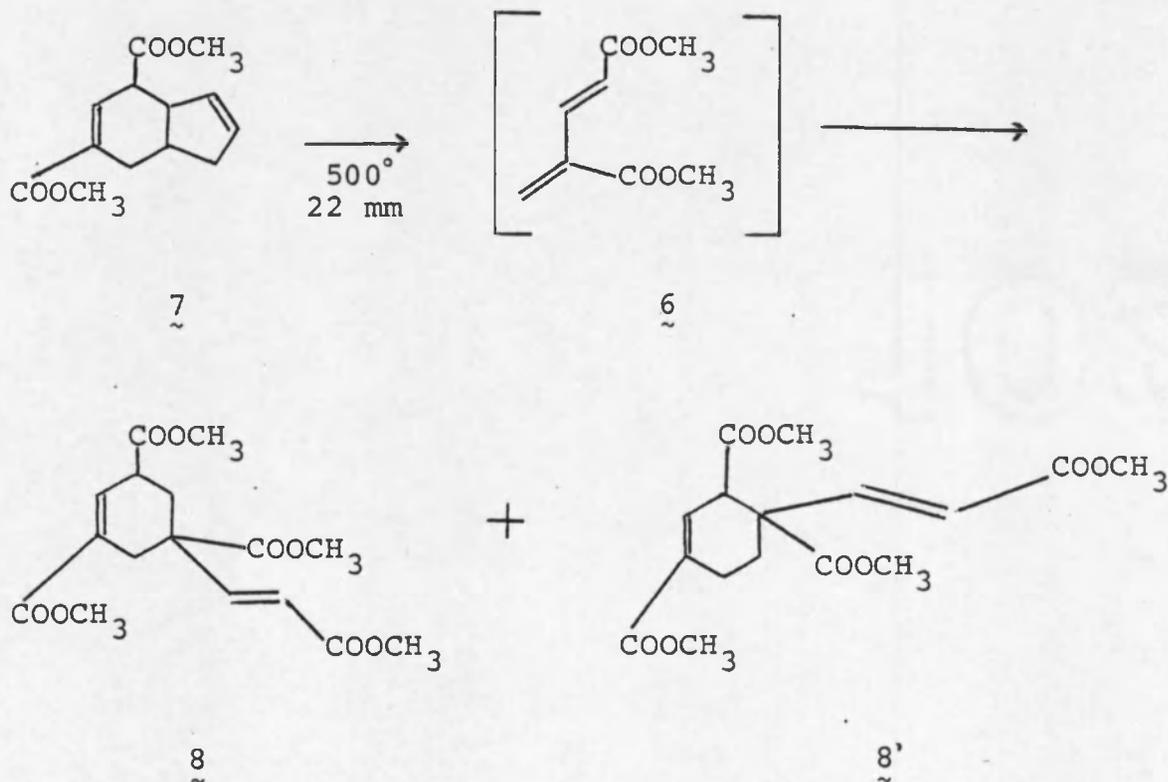
Synthesis of Cyclopentadiene Adduct 7. 1,3-Disubstituted butadienes were suspected to be very reactive compounds. Trapping these molecules would be our first attempt to isolate them.

Triethylamine was used to eliminate hydrogen iodide from dimethyl 2-iodo-4-methyleneglutarate 5 to form the desired diene 6 which would then be trapped with cyclopentadiene.



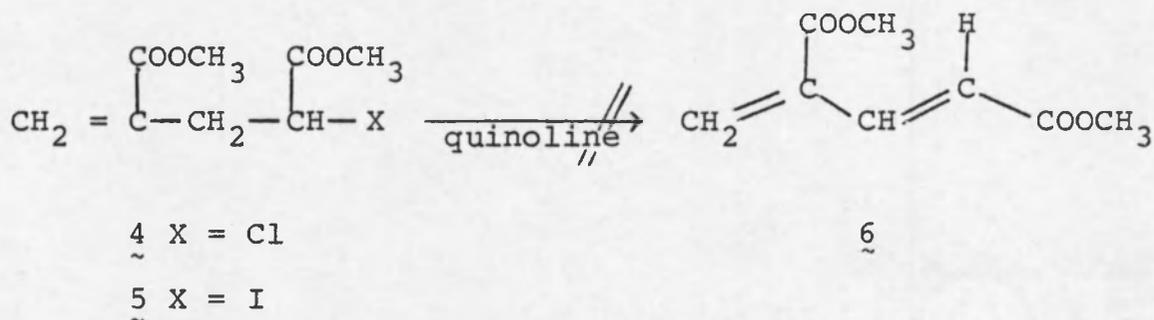
This reaction was carried out at -78° and left to warm up to room temperature for 18 hours. Triethylammonium iodide was identified and the cyclopentadiene adduct was isolated by distillation in 77% yield.

Cracking of Cyclopentadiene Adduct 7. The cyclopentadiene adduct was cracked (13) in a quartz tube packed with quartz chips at 500° C under 20 mm Hg. The product was collected in a liquid nitrogen cooled flask. The cyclopentadiene was pumped off while the flask was still cold and collected in a liquid nitrogen cooled trap in approximately 75% yield, and identified by nmr. The product that remained in the flask was not diester 6 but its dimers 8:



Dehydrohalogenation of Dimethyl 2-Halo-4-methylene-
glutarate. Dimethyl 2-halo-4-methyleneglutarate (either the iodo or the chloro) were heated under 25 mm Hg in the presence of quinoline without solvent. These attempts failed

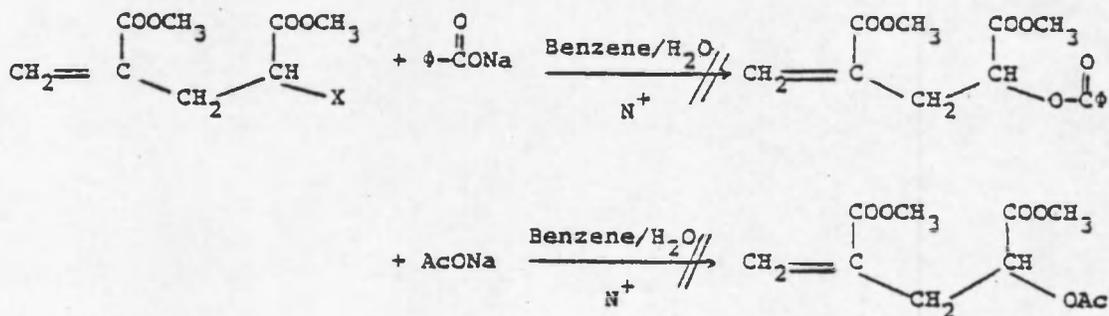
to give the desired diene 6. In all cases there was essentially no reaction even with heating to 120° C. The starting material distilled before dehalogenation.



Extensive attempts were done with stronger amine bases such as triethylamine, DABCO, N,N-diethylcyclohexylamine in solvents such as ether and THF, at various temperatures. In most cases the ammonium salts were identified but no traces of the diolefin were seen. It might have been formed, then homopolymerized under these conditions.

Attention was then switched to less nucleophilic bases such as sodium hydride, potassium hydride, and sodium triphenylmethide with various temperature and solvents. The expected by-products were found; sodium and potassium halides were characterized. Triphenylmethane was identified by nmr. In the case of potassium and sodium hydride, the expected volume of hydrogen was collected.

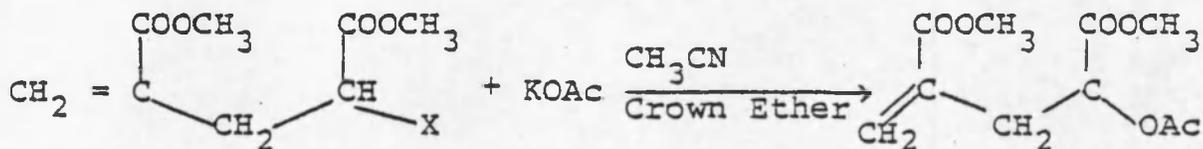
benzoic acid or acetic acid, the starting materials, and some oligomers.



4 X = Cl

5 X = I

Use of Crown Ether. The 2-halo compounds 4 and 5 were allowed to react with potassium acetate in acetonitrile in the presence of crown ether. These attempts also failed.

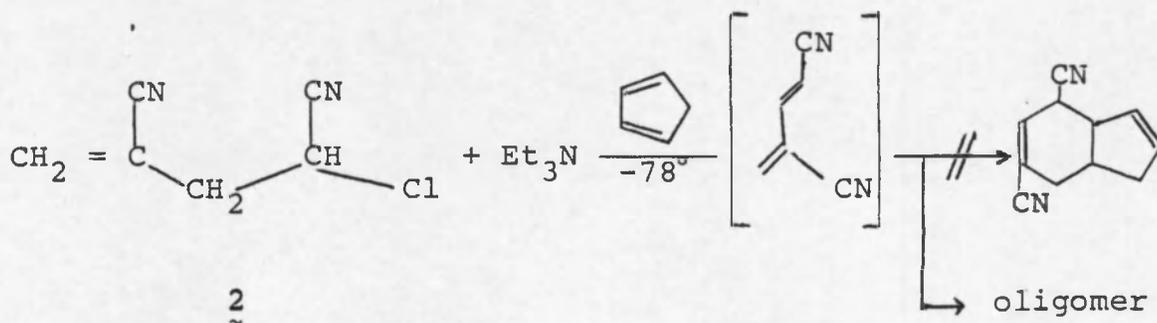


In one experiment in which the reaction mixture was heated to reflux for 7 days the 2-iodo-4-methyleneglutarate 5

Attempted Synthesis of
1,3-Butadiene-1,3-dicarbonitrile

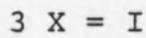
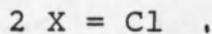
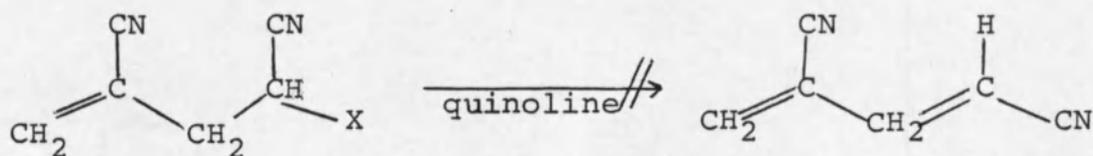
Attempted Synthesis of
Cyclopentadiene Adduct of
1,3-butadiene-1,3-dicarbonitrile 22

2-Chloro-4-methyleneglutaronitrile 2 was allowed to react with triethylamine in the presence of cyclopentadiene and in a similar attempt with furan in order to trap the diolefin. In both cases the ammonium salt was formed and identified but instead of cyclopentadiene or furan adduct we obtained only oligomers. This was an indication that 1,3-butadiene-1,3-dicarbonitrile 22 was far more reactive than the 1,3-butadiene-1,3 diester 6. This indicates that reactions with nucleophilic bases will yield oligomers rather than the diene itself.



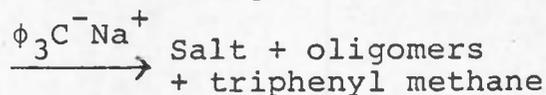
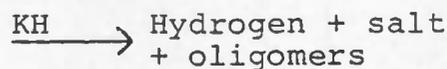
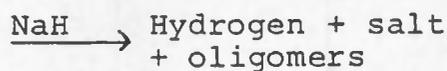
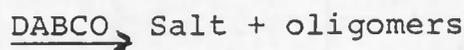
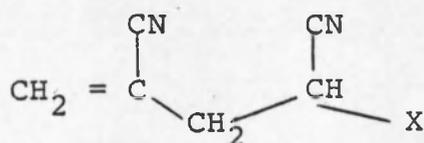
Dehalogenation of 2-Halo-4-methyleneglutaronitrile

Nitrile 2 and 3 were heated under 25 mm Hg in the presence of quinoline without solvent. These attempts failed to give any desired diolefin 22. No reaction occurred and only the starting material distilled at 130°C (25 mm).

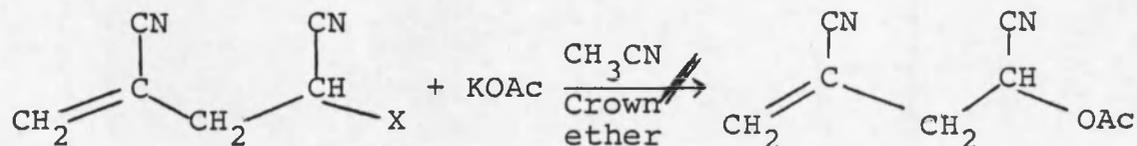


We already had an indication that nucleophilic bases such as triethylamine and DABCO were not suitable for such dehydrohalogenation and further experiments done in this area confirmed it. Even at temperatures as low as -95°C the oligomers were formed.

Attention was switched to non-nucleophilic bases such as sodium or potassium hydride and triphenylmethylenesodium salt under various temperatures and solvent conditions. In these experiments the expected amount of hydrogen or triphenylmethane was identified and the metal halides were always characterized but no diolefin 22 was isolated and always insoluble oligomers were isolated.



derivative was isolated. The loss of some of the starting material was accounted for by the presence of oligomers.

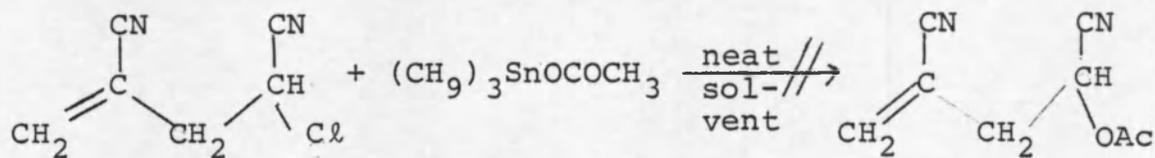


12

2 : X = Cl

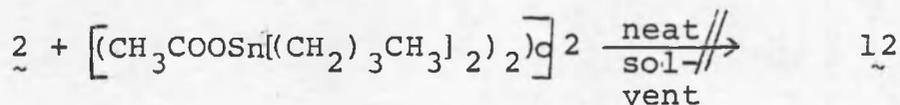
3 : X = I

Use of Tin Compounds. The affinity of tin for chloride was thought helpful to use in order to substitute the chloride by acetate. Tributyltin acetate and tetrabutyltin diacetate were used neat or with acetonitrile as solvent with nitrile 2 but in both cases no acetate was formed.



2

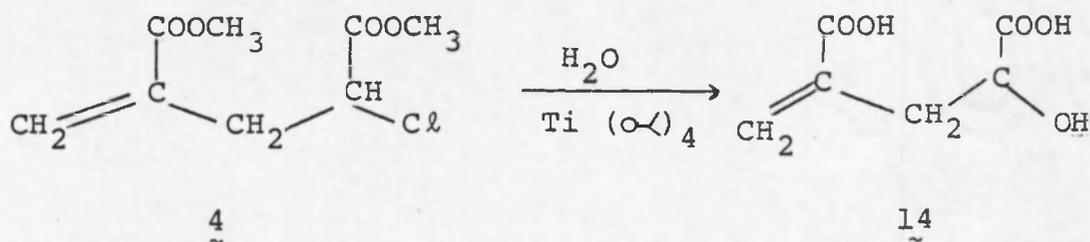
12



Attempted Synthesis of
4-Methylenepyran-2,6-dione 17

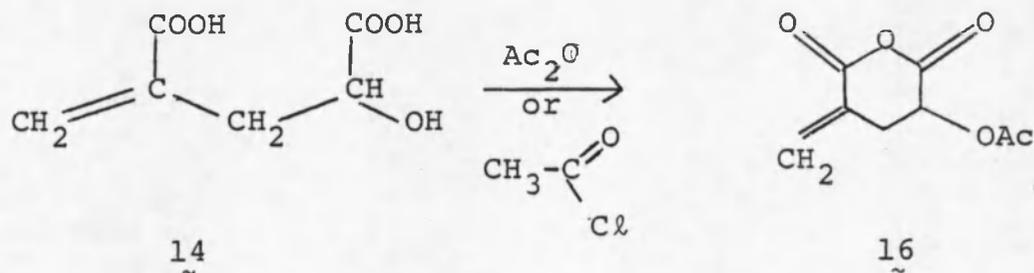
Synthesis of 4-Methylene-2-hydroxy-glutaric Acid 14

The best route by which 4-methylene-2-hydroxy-glutaric acid 14 was obtained was the hydrolysis of dimethyl 4-methylene-2-chloroglutarate 4 with water in the presence of tetraisopropyl titanate as catalyst.



Synthesis of 2-Acetoxy-4-methylene-glutaric Anhydride 16

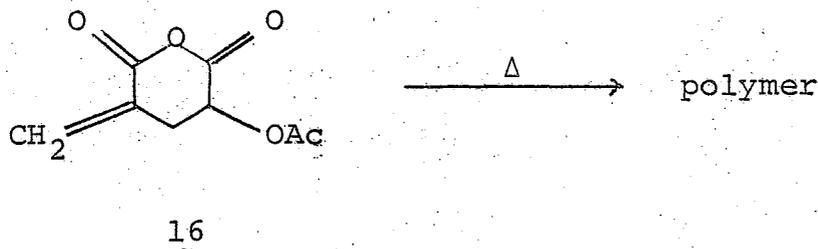
When the hydroxy diacid 14 was treated with either acetic anhydride or acetyl chloride the anhydride 16 was formed with yields of 56% and 73%, respectively.



Attempts to Crack 2-Acetoxy-4-methyleneglutaric Anhydride 16

These attempts were done first in a Pyrex tube packed with glass beads with flow of nitrogen and heated to 250°C. The anhydride 16 gave a polymer on contact with the heated beads. Only traces of acetic acid were collected in the liquid nitrogen-cooled flask. This probably means that the anhydride 16 polymerizes before cracking.

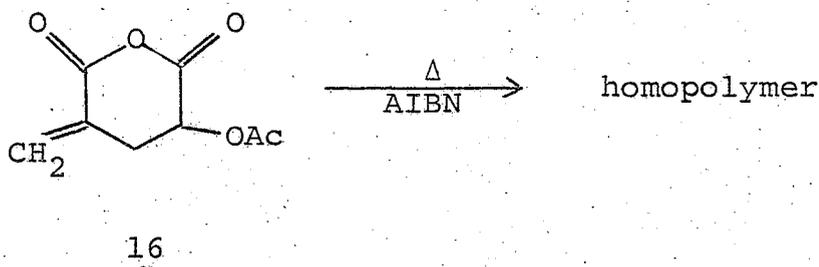
Attempts were made at lower temperatures but essentially no reaction was observed. Another attempt to crack this compound 16 in a quartz tube packed with quartz chips (13) under 25 mm Hg at 300°C failed, giving a polymer on contact with the heated chips.



Polymerization of 2-Acetoxy-4-methyleneglutaric Anhydride 16

The above results indicated that the anhydride 16 might polymerize before cracking. Analogous itaconic (methylenesuccinic) anhydride is known to polymerize.

A trace of AIBN was added to the anhydride 16 which was then heated at 70°C for 16 hours. A polymer was formed

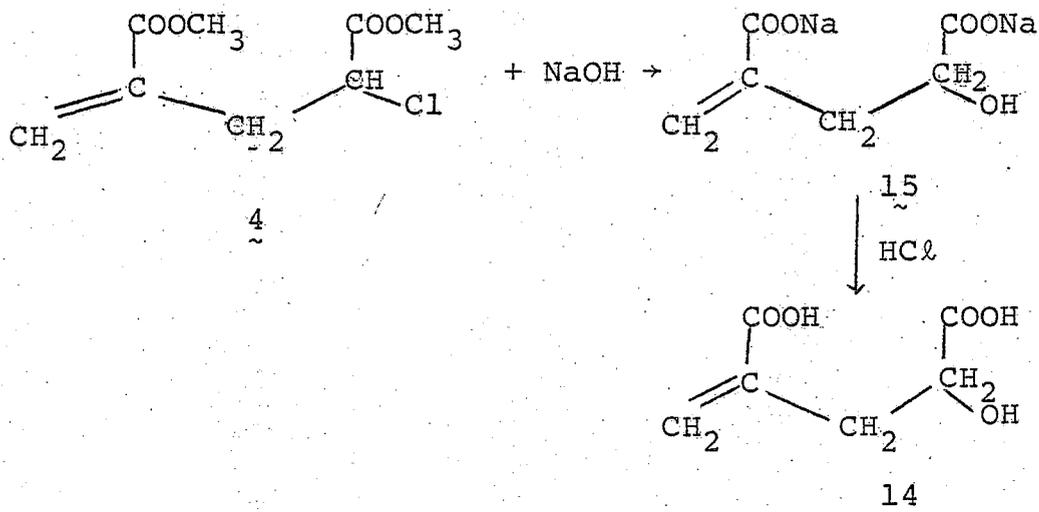


Unlike the starting material, it was insoluble in chloroform. Its nmr spectrum in acetone- d_6 showed monomer to be absent and showed broad peaks characteristic of a polymer.

Other Results

Attempted Synthesis of 1,3-butadiene-dicarboxylic Acid 24

The diester 4 was hydrolyzed with sodium hydroxide giving disodium 2-hydroxy-4-methyleneglutarate 15. Our best evidence of the preparation of the sodium salt was that when treated with hydrochloric acid the product was 2-hydroxy-4-methyleneglutaric acid 14.

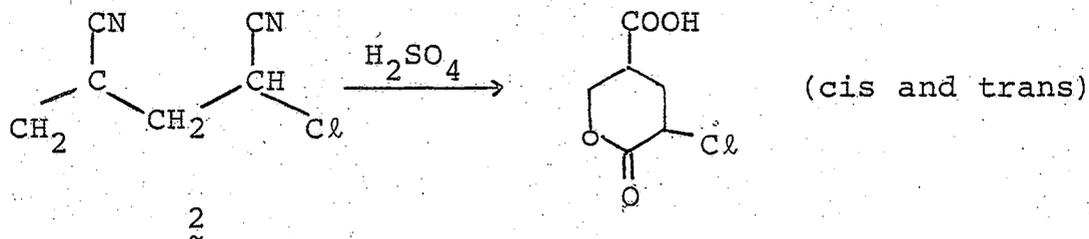


Preparation of Lactones

3-Chlorotetrahydropyran-2-on-5-carboxylic Acid 18.

It is known that olefinic carboxylic acids undergo lactonization under acidic conditions.

In our first attempt to synthesize 2-chloro-4-methyleneglutaric acid 25, we allowed the dinitrile 2 to react with concentrated sulfuric acid. Instead of the desired product we isolated two isomeric lactones:

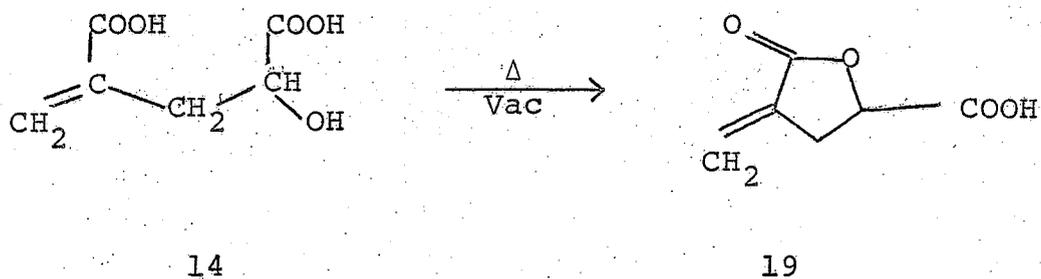


They have the same nmr, same analysis, but different melting points.

Under such acidic conditions 2-chloro-4-methyleneglutaric acid 25 was probably formed in a first step, then lactonized rapidly.

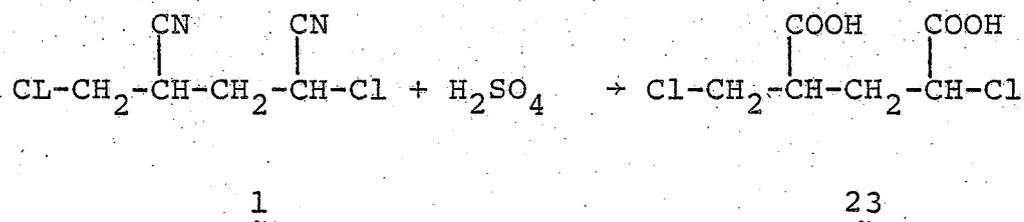
3-Methylenetetrahydrofuran-2-on-5-carboxylic acid

19. Another lactone was obtained by heating at 160° C under vacuum 2-hydroxy-4-methyleneglutaric acid 14. This lactone was formed by elimination of one molecule of water between the hydroxyl and carbonyl groups.

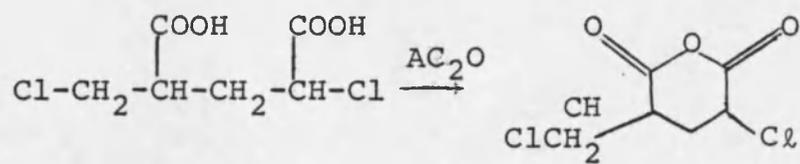


Preparation of 2-Chloro-4-(chloromethyl)glutaric acid 23.

The hydrolysis of 2-chloro-4-(chloromethyl)-glutaronitrile 1 in sulfuric acid yielded as expected 2-chloro-4-chloromethylglutamic acid 23:

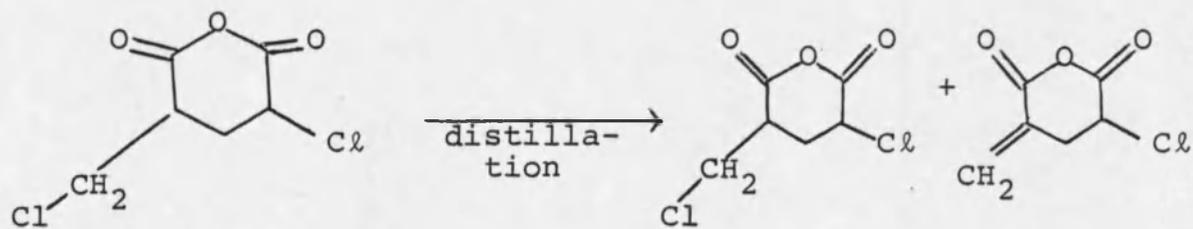


This diacid was treated with acetic anhydride to yield a mixture of 2-chloro-4-chloromethylglutaric anhydride 20 and 2-chloro-4-methyleneglutaric anhydride 21. The two compounds could not be separated by distillation because of the ready elimination of one molecule of hydrochloric acid from the former upon heating the distillation mixture.



23

20



20

21

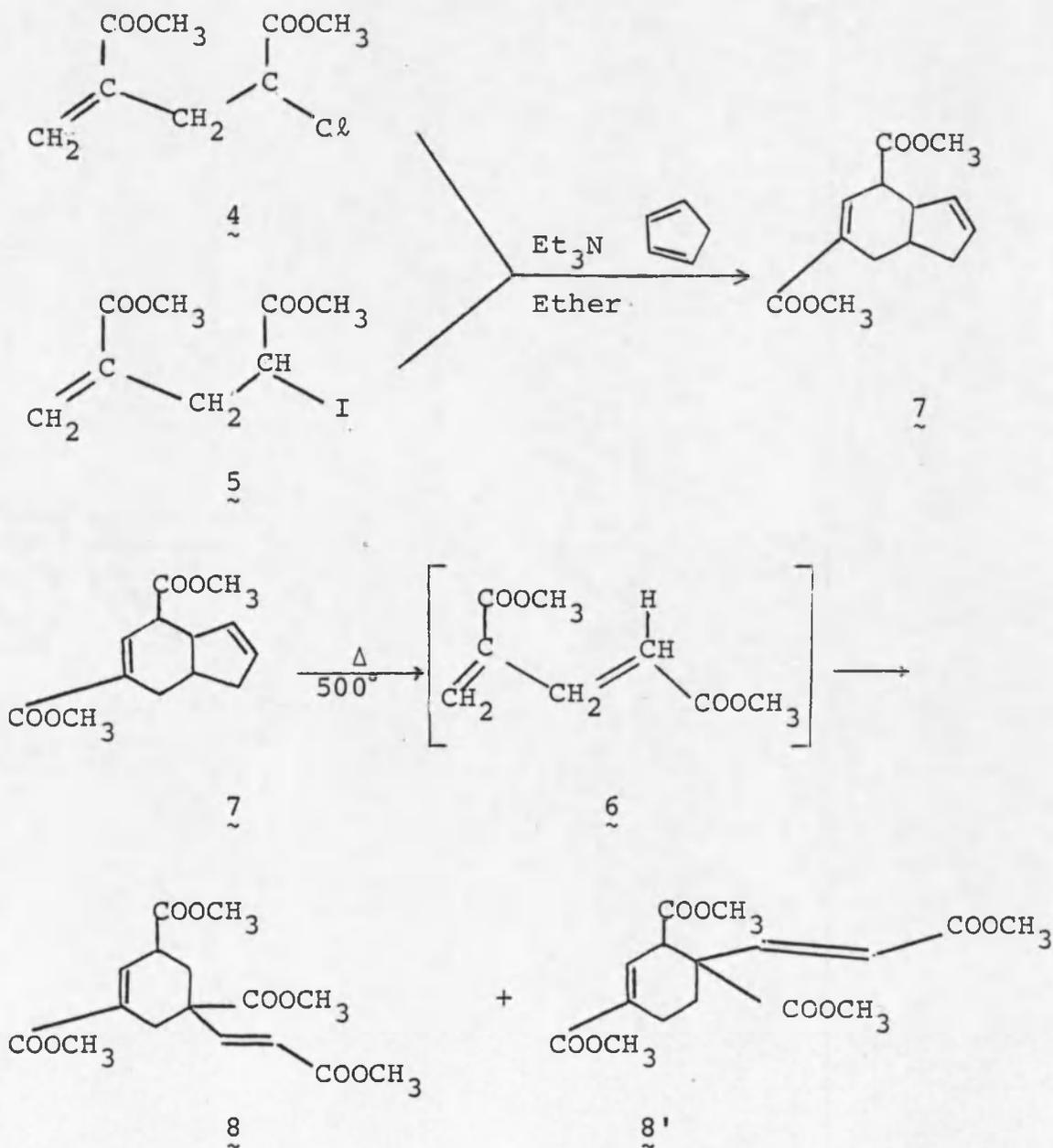
CHAPTER 3

DISCUSSION

Our literature search showed a total absence of 1,3-electronegatively disubstituted-1,3-butadienes. However, the 2-chloro-4-methyleneglutaronitrile looked like a very promising intermediate for attempts to synthesize 1,3-butadiene-1,3-dicarbonitrile 22.

The diesters are known to be more stabilizing groups than the nitrile groups but still in our opinion reactive enough.

The diesters 4 and 5 were prepared and treated with triethylamine in the presence of cyclopentadiene as trapping agent. The isolation of cyclopentadiene adduct was our most informative experiment that 1,3-butadiene-1,3-dimethyl ester 6 was formed from both the diesters 4 and 5. The cracking of the cyclopentadiene adduct 7 did not give the monomeric butadiene derivative 6 desired but its dimers 8.



This was strong evidence that the diolefin was very reactive even at low temperature.

An analogous reaction done using furan as trapping agent did not give the furan adduct. Attempts to synthesize the 1,3-butadiene-1,3-dimethylester 6 by simple

heating of the dimethyl 2-halo-4-methyleneglutarate 4 or 5 in the presence of quinoline failed, indicating that the elimination of hydrochloric or hydroiodic acid needed a stronger base.

This dehydrohalogenation was done with triethylamine in the presence of cyclopentadiene as trapping agent. Extensive work was done in order to dehydrohalogenate the diesters 4 and 5 with bases. Strong amine bases such as triethylamine, DABCO, and N,N-diethylcyclohexylamine were used. Strong and non-nucleophilic bases such as potassium or sodium hydride and triphenylmethyl sodium all gave negative results. Only oligomers were obtained along with the by products which were characterized, thus indicating that the diolefin 6 might have been formed but was just too reactive under basic conditions.

The switch to another kind of chemistry was no more encouraging than the other. The attempts to make the acetate or benzoate 9 10 derivatives in order to crack out acetic or benzoic acid have failed. Some oligomers have formed in all cases, indicating that the nucleophilicity of acetates or benzoates had had effect on the substitution of the halide. This is probably due to anionic oligomerization even of the dimethyl 2-chloro-4-methyleneglutarate 4.

The formation of the acetate derivative in the experiment using potassium acetate and crown ether occurred

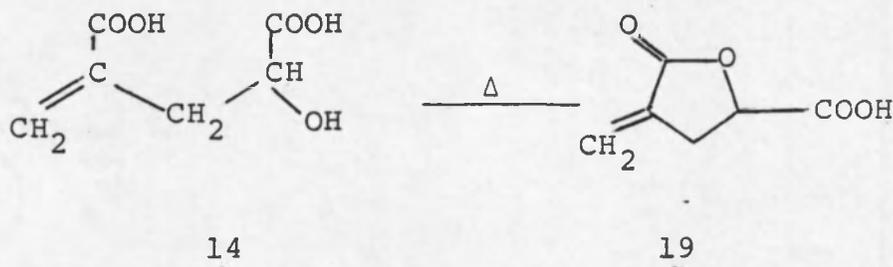
in very low yield and was not practical for large scale chemistry.

Similar attempts to synthesize 1,3-butadiene-1,4-dicarbonitrile 22 were made. Triethylamine and cyclopentadiene or furan as trapping agent did not give the desired adducts showing that even at very low temperature the 1,3-butadiene-1,3-dicarbonitrile 22 was extremely reactive even at low temperature and in the presence of cyclopentadiene or furan.

Dehydrohalogenation by heating was not conclusive and by the use of bases have completely failed.

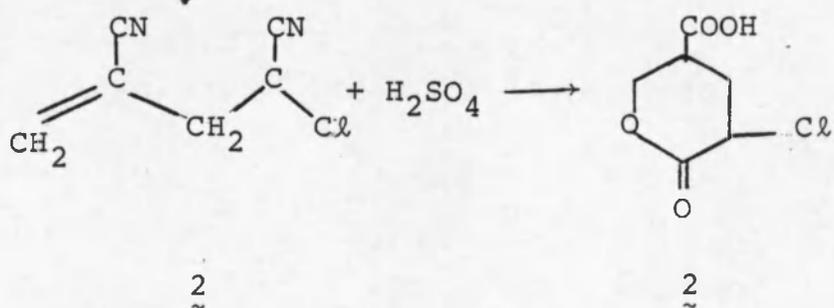
The attempts to make the acetate 12 or benzoate 13 have also failed because of the high sensitivity of the molecule to the nucleophilicity of the acetates and benzoates.

1,3-Butadiene-1,3-dicarboxylic acid 24 was another derivative we hoped to make. The 2-hydroxy-4-methylene-glutaric acid 14 did not present any problem in the making by the hydrolysis of 2-chloro-4-methyleneglutarate 4 in water with tetraisopropyl titanate as catalyst. The first attempt to synthesize the 1,3-butadiene-1,3-dicarboxylic acid 24 was dehydration of the hydroxydiacid 14 but this resulted in the formation of a lactone.



The making of 2-acetoxy-4-methyleneglutaric anhydride 16 was recommended with the hope to synthesize the 4-methylenepyran-2-6-dione 17 by simple cracking methods. These attempts failed, giving polymer on contact with heated beads. By the similarity of 2-acetoxy-4-methyleneglutaric anhydride 16 and methylenesuccinic anhydride (whose polymerization has been studied) we allowed the anhydride 16 to homopolymerize in the presence of AIBN. It indeed polymerized.

Other attempts were done in order to make 2-chloro-4-methyleneglutaric acid 25 under acidic conditions and resulted in lactonization.



2-Chloro-4-(chloromethyl)glutaric acid 23 was made even though its purification was a problem. When treated crude

as it is with acetic anhydride, 2-chloro-4-chloromethylglutaric anhydride 20 was made but never isolated. The ready dehydrochlorination gave always a mixture of 2-chloro-4-chloromethylglutaric anhydride 20 and 2-chloro-4-methylene-glutaric anhydride 21 just by distillation.

Conclusions

The conclusion from this investigation is that 1,3-di(electronegatively substituted)-1,3-butadienes dimerize too readily to be useful new monomers. A new polymerizable monomer 16 has been synthesized.

CHAPTER 4

EXPERIMENTAL

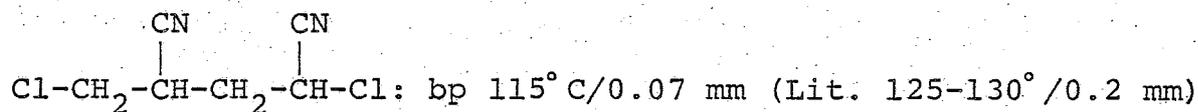
All boiling and melting points are uncorrected. Capillary melting points were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were obtained using a Perkin-Elmer 337 spectrophotometer with sodium chloride plates. A Varian T60 was used to obtain nmr spectra.

Elemental analyses were performed by Chemalytics Inc., Tempe, Arizona.

The gas chromatograms were obtained on a Varian Aerograph 1700 instrument using the following columns:

- a. 3% SE 30 on 80-100 mesh Chromosorb WAW/DMCS HP 5 ft x 0.25 in, and
- b. 50% Carbowax 20 M on 80-100 mesh Chromosorb W-AW/DMCS, 5 ft x 0.25 in.

The 2-chloro-4-chloromethylglutaronitrile and 2-chloro-4-methyleneglutaronitrile were prepared from photochlorination of acrylonitrile (11).



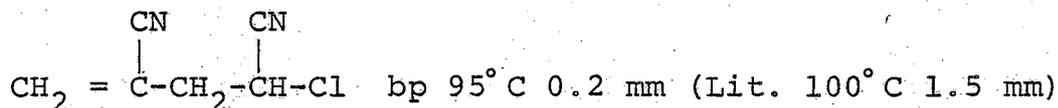
1

nmr: τ : 6.5-5.5 t (1H) 6.2 t(2H) 6.4-7 m (1H) 7.2-8 m 2H

ir: C \equiv N 2225 cm^{-1} (5)

Analysis calculated: C 40.63; H 3.17; Cl 40.01

found: C 40.71; H 3.17; Cl 40.01



2

ir: C \equiv N 2225 cm^{-1} , C = C 1620 cm^{-1}

nmr: τ : 3.6; s(1H); 4 s(1H); 5.2 t(1H); 6.75 d(2H)

Analysis calculated: C 50.97; H 3.74; Cl 25.50

found: C 51.27; H 3.74; Cl 25.50

Dimethyl-2-chloro-4-methyleneglutarate 4

In a three-neck flask equipped with a condenser, 40 g (0.28 mole) of 2-chloro-4-methyleneglutaronitrile 2 was dissolved in 300 ml of anhydrous methanol. Sulfuric acid (95%), 100 g, was added very slowly, and the reaction mixture heated to reflux for 10 days (14).

Sodium bicarbonate solution was dripped into the cool reaction flask. The salts were then filtered and the

methanol evaporated. The residue was poured into water and the organic materials extracted three times with ether. The combined ether layers were dried over magnesium sulfate. The ether was evaporated and the residue distilled at 90-93°C (0.1 mm) yielding 42 g (72.6%) of dimethyl 2-chloro-4-methyleneglutarate 4.

ir neat: C = C-H	3010 cm ⁻¹
C-H	2940
C ≡ N	2225 traces always present
C = O	1740
C = C	1620

nmr: τ : 3.62 s(1H); 4.22 s(1H); 5.41 9(1H); 6.21 s(6H);
7.15 d(2H)

Dimethyl 2-Iodo-4-methyleneglutarate 5

In an Erlenmeyer flask, 9 g (0.06 mole) of sodium iodide were dissolved in 100 ml of dry acetone under a nitrogen atmosphere in the dark. Dimethyl 2-chloro-4-methyleneglutarate 4, 5 g (0.02 mole) was then added and allowed to stand in the dark for 3 days (12).

The GC shows an 80% conversion. The acetone was evaporated and to the residue water was added. The organic materials were extracted with ether and dried over magnesium sulfate.

The ether was evaporated and the residue distilled yielding 1 g (20%) of starting material 4 and 4.3 g (60%) of dimethyl 2-iodo-4-methyleneglutarate 5; both fractions were reddish.

bp: 100-110° C (0.1 mm)

ir: $\text{C} = \overset{\text{H}}{\text{C}}$ 3010; C-H 2950; C≡N 2225 traces; C = O 1750; C = C 1625 cm^{-1} .

nmr: τ : 3.62 s(1H); 4.22 s(1H); 5.51 9(1H); 6.21 s(6H); 7.15 d(2H).

2-Iodo-4-methyleneglutaronitrile 5

In an Erlenmayer flask 2 g (0.06 mole) of sodium iodide were dissolved in 100 ml of dry acetone under nitrogen atmosphere in the dark. 2-Chloro-4-methyleneglutaronitrile 2, 2.81 g (0.02 mole), were added and the mixture allowed to stand for 3 days (12).

The GC shows a 40% conversion.

The acetone was evaporated and to the residue water was added. The organic materials were extracted with ether. The ether layers were dried over magnesium sulfate. The ether was evaporated and the residue distilled yielding 1.2 g of starting material 2 (42.7%), 0.93 g of the 2-iodo-4-methyleneglutaronitrile 3 (20%); bp 105° C (0.1 mm). Both fractions were reddish.

ir neat:	= C-H	3010 cm ⁻¹
	C-H	2950
	C≡N	2230
	C=C	1620

nmr: τ : 3.6 s(1H); 4 s(1H); 4.2 s(1H); 6.75 d(2H).

Cyclopentadiene Adduct of
1,3-Butadiene-1,3-Dimethylester 7

In a 50 ml round bottomed flask, 9 g (0.03 mole) of dimethyl 2-iodo-4-methyleneglutarate 5 was dissolved in ether and cooled to -78°C. Excess of cyclopentadiene (freshly distilled) was added at -78°C (15).

A mixture of 6 g of triethylamine (0.06 mole) in ether at -78°C was added to the reaction flask.

No reaction seemed to happen at -78°C. The reaction mixture was left in the dry ice/acetone bath to warm up slowly to room temperature overnight.

After 18 hours, a precipitate formed; water was added to the reaction mixture and the organic materials extracted with ether three times. The combined ether layers were dried over magnesium sulfate. The ether was then evaporated and the residue distilled at 120-140°C (0.5 mm) yielding 5.50 g (77%) of the cyclopentadiene adduct of dimethyl 1,3-butadiene-1,3-dicarboxylate 7.

ir: = C-H	3010 cm ⁻¹
C-H	2940
C=O	1750
C=C	1620

nmr: τ : 2.84 - 3 m(1H); 3.6 m(1H); 4.22 s(2H);
4.84-5.6 m(2H); 6.2 s(6H); 6.4-8.4 m(4H)

Analysis: Calculated 66.08% C; 6.83% H

found: 66.17% C; 6.38% H.

Dimethyl 1,3-Butadiene-1,3-dicarboxylate
Dimer 8

The cyclopentadiene adduct 7 used in this experiment was always a mixture of esters and nitrile because of the difficulties encountered in the making of dimethyl 2-chloro-4-methyleneglutarate 4.

The cyclopentadiene adduct 7, 7 g (0.03 mole), was added over 15 min at the top of a vertical quartz tube (20 in x 1 in) packed with quartz chips kept at 500°C. The crude product was collected under vacuum (20 mm) in a receiver cooled with liquid nitrogen (13, 16, 17).

The cyclopentadiene formed was pumped off under vacuum (.07 mm) and collected in a liquid nitrogen cooled trap (1.5 ml). The cyclopentadiene was identified by nmr:
 τ : 3.4 s(4H); 7.06 s(2H).

The residue was distilled in a short path distillation apparatus and the product collected between 123 °C and 130 °C (0.1 mm). Product weight: 3.5 g (68%).

	H	
ir neat:	= C	3010 cm^{-1}
	C-H	2950
	C=O	1750
	C=C	1620
nmr:	τ : 2.8-3.2 m ; 3.66 t ; 4.25 s ;	
	5.9 ; 6.25 s ; 6.25-7.4 m	

Dimethyl 2-Acetoxy-4-methylene-
glutarate 9

In a 100 ml three-neck flask 4 g (0.013 mole) of dimethyl 2-iodo-4-methyleneglutarate 5 was dissolved in 30 ml of CH_3CN in the presence of a small amount of inhibitor. Potassium acetate, 1.97 g (0.013 x 1.5 mole), was added along with a small amount of 18-crown-6 ether.

The reaction mixture was refluxed for 6 days. The CH_3CN was then evaporated and to the residue water was added and the organic materials extracted with ether three times. The ether layers were combined and dried over magnesium sulfate.

The ether was then evaporated and the residue distilled yielding 40.0 mg (2.3%) of the desired product 9; bp: 82.87 °C (0.1 mm).

nmr: τ : 3.7 s (1H); 4.3 s (1H); 4.6-4.9 9 (1H);
6.2 s (6H); 7-7.25 m (2H); 7.9 s (3H).

2-Hydroxy-4-methyleneglutaric Acid 14

In a one l round bottomed flask equipped with a condenser, 30 g (0.145 mole) dimethyl 2-chloro-4-methylene-glutarate 4 was added to 400 ml of distilled water. A small amount, 0.5 g, of tetraisopropyl titanate was added to the mixture. The mixture was refluxed for 72 hours. Tetraisopropyl titanate was filtered off and the desired diacid 14 extracted continuously with ether. The ether was dried over magnesium sulfate, evaporated, leaving a viscous liquid which was dissolved in hot chloroform and left to crystallize in the refrigerator.

The 2-hydroxy-4-methyleneglutaric acid 14 is a white solid mp 112°C; weight 7 g (27.4%).

nmr in DMSO: τ : 3.6 s (1H), 4.05 s (1H); 5.45-5.67 9 (1H);
7.1-7.4 m (2H); 0.3 broad (3H).

Analysis: Calculated 45.00% C; 5.04% H

found: 44.79% C; 4.87% H.

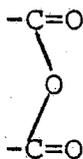
2-Acetoxy-4-methyleneglutaric
Anhydride 16

In a round bottomed flask equipped with a condenser, 5 g (31.3 mmole) of 2-hydroxy-4-methyleneglutaric acid 14 was mixed with 50 ml of acetyl chloride and heated to

reflux for 4 hours. The reaction mixture became homogeneous.

The acetyl chloride was evaporated and the residue distilled at 120-127° C (0.1 mm) yielding 4.2 g of the desired anhydride (73%).

ir: no O-H



1740-1850 cm^{-1}

C=C

1620

nmr: τ : 3.45 s(1H); 4 s(1H); 4.37-4.62 m(1H);
6.8-7.15 m(2H); 7.7 s(3H).

Although the nmr and ir suggest the anhydride structure the product seems to hydrolyze when analyzed. The analysis suggests the 2-acetoxy-4-methyleneglutaric acid. For the diacid: calculated C 47.52, H 4.72; found C 47.47, H 4.38.

Pyrolysis of 2-Acetoxy-4-methylene-
glutaric Anhydride 16

The 2-acetoxy-4-methyleneglutaric anhydride 16, 5 g (0.027 mole), was added over 15 min to top of a vertical quartz tube (20 in x 1 in) packed with quartz chips kept at 300° C. The anhydride polymerizes on contact with the heated chips giving a polymer.

A negligible amount of acetic acid was collected in the liquid nitrogen cooled receiver. This probably means that the anhydride itself polymerizes.

Disodium 2-Hydroxy-4-methylene-
glutarate 15

In a 500 ml three-neck flask equipped with a condenser, a mechanical stirrer, and a dropping funnel containing 50 ml of a 3 M sodium hydroxide solution, 10 g (0.07 mole) of dimethyl 2-chloro-4-methyleneglutarate 4 and 100 ml of water were added.

The sodium hydroxide was added dropwise with energetic stirring. The addition took over 30 min. The mixture was refluxed for 6 hours.

Water and ammonium hydroxide were evaporated and residual salt was dried under vacuum at 50°C. The dry salt was heated to 180°C (0.1 mm) but no dehydration was observed.

In a 100 ml flask, 10 g of the salt 15 was treated with hydrochloric acid. The organic materials were extracted continuously with ether. The ether solution was dried over magnesium sulfate then evaporated. The residue was crystallized from chloroform yielding 6 g (60%) of 2-hydroxy-4-methyleneglutaric acid 14. The ir and nmr are identical to those reported earlier. Analysis: calculated 45.00 C, 5.04 H; found 45.34 C, 5.10 H.

3-Chloro-tetrahydropyran-2-on-5-
carboxylic Acid 18

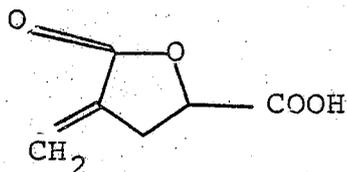
Dimethyl 2-chloro-4-methyleneglutarate 4, 10 g (0.048 mole) was added to a mixture of 100 ml of water and 35 g of sulfuric acid (95%). The mixture was refluxed for 40 hours. Then cooled down. The organic materials were extracted 10 times with ether. The ether layers were mixed together and dried over magnesium sulfate. Total weight of the crude residue was 7.1 g (82%). The crystallization in chloroform led to 2 isomeric lactones of different melting points: 93-95°C and 121-123°C; but having the same nmr in D₂O: τ = 4.63-5.19; 5.6-7.8 broad; 5.25 HOD. Analysis:

	C	H	Cl
1/ Calculated	40.34	3.92	19.59
Found	40.44	3.89	19.81
2/ Calculated	40.34	3.92	19.89
Found	40.71	3.95	19.45

3-Methylenetetrahydrofuran-2-on-5-
carboxylic Acid 19

In a small distillation apparatus, 3 g (0.019 mole) of 2-hydroxy-4-methyleneglutaric acid was heated at 160°C (1 mm). The liquid distillate solidified immediately. The nmr of the product was identical to that of the starting

material but the integration shows a loss of 2 protons. The product is thought to be the lactone:



The product weighed 2.5 g (93%), mp 110° C.

2-Chloro-4-(chloromethyl)glutaric Acid 25

Dinitrile 1, 21 g (0.12 mole), was mixed with 200 ml of concentrated hydrochloric acid with energetic stirring and heated to reflux for 2 hours.

The solution was then cooled down and extracted continuously with ether for 24 hours. The ether layer was then dried over magnesium sulfate, then evaporated. The crude organic residue (22 g 86%) was dissolved in chloroform and allowed to crystallize. The pure compound weighed 16 g (62.5%).

ir: C=O 1725-1775 cm^{-1}

nmr in CDCl_3 : τ : 3.35 s(2H); 4.8-8 br(4H);
8.75 t(2H)

in D_2O : τ : 5.9(1H); 5.4 s(HD); 6.2 d(2H);
6.4-7 m(1H); 7.2-7.6 m(2H).

Although the ir and nmr indicate that the compound is the dichloro the analysis fits the compound that lost a hydrochloric acid in an unknown way.

Analysis: for $C_6H_7O_4Cl$:

	C	H	Cl
Calculated:	40.34	3.82	18.87
Found	39.60	4.02	17.88

2-Chloro-4-(chloromethyl)glutaric Anhydride 20

The dichloro diacid 23 20 g (0.092 m), was dissolved in 100 ml of acetic anhydride and refluxed for 5 hours. The excess of acetic anhydride and acetic acid were evaporated. The residue was distilled twice using a flame to heat it at 160-170°C (1 mm).

The distillate weighed 8 g. The yield is not known because the product was a mixture of 2-chloro-4-(chloromethyl)glutaric anhydride 20 and 2-chloro-4-methyleneglutaric anhydride 21.

The nmr confirmed the existence of the mixture; the ir shows anhydride at 1740-1850 cm^{-1} ; C=C at 1610.

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