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Studies on the Cyclization of Cis-1,4-dichloro-2-butene with Sodium Dialkylmalonates

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STUDIES ON THE CYCLIZATION OF *CIS*-1,4-DICHLORO-2-BUTENE WITH SODIUM DIALKYLMALONATES

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First and foremost, I would like to thank God for everything. Secondly, my uncle, Mr Dickson Imasogie who has been very instrumental in every stage of my life.

I am particularly grateful to Dr. David S. Crumrine for not only directing this research project but for the wisdom and encouragement that he offered along the way. My thanks also to Dr Al Herlinger for his support, morally and otherwise. My sincere thanks to the people behind the scene (the entire office staff: Robbie, Hazel, Sonya, and Carol) who are involved with the day to day running of the Department. I want to also express my appreciation to Allison for the helpful suggestions with the drawing of the structures. I would like to thank the entire group in our lab. I also like to thank all my friends for their support and encouragement.

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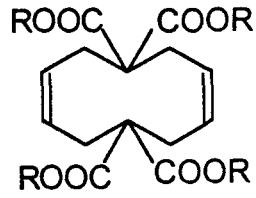
To my uncle, Mr Dickson Imasogie.

CHAPTER I

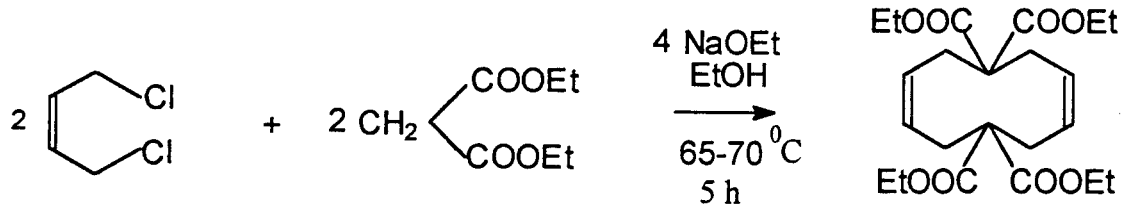
STATEMENT OF THE PROBLEM

The goal of this research is the synthesis of tetraalkyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate[1] (**1**).



1

The synthesis of the compound had earlier been reported from the reaction of *cis*-1,4-dichloro-2-butene (**2**) and diethyl malonate(R = ethyl) (**3**) with a yield of 2.6%.[2]



2 **3** **1**

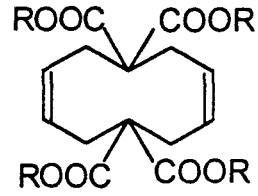
An attempt will be made to overcome this limitation by varying the reaction conditions, some of which will be a change of starting material, reaction times, and chromatographic techniques. The tetraester will be synthesized from *cis*-1,4-dichloro-2-butene and dialkyl malonates, where the R group may vary from methyl through pentyl. Propyl, butyl, and pentyl malonates needed for these reactions are not available commercially, but will be synthesized by a transesterification process. The product esters will be characterized by ^{1}H-NMR, ^{13}C-NMR, and Infrared spectroscopy.

The two major products, dialkyl cyclopent-3-ene-1,1-dicarboxylate (**5**) and 2-vinylcyclopropane-1,1-dicarboxylate (**6**) will be quantitatively analyzed with a highly sensitive GC-MS. It is expected that numbers reliable enough to quantitate the relative proportion of each of the products will be generated.

CHAPTER II

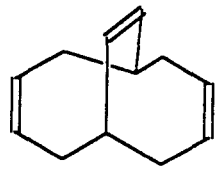
INTRODUCTION

The objective of this project is to synthesize, and identify tetraalkyl *cis,cis*-cyclodeca-3,8-diene-1,1,6,6-tetracarboxylates.[3] The unique geometry of this compound makes it an interesting target for research.



1

Compound 1 is reportedly a precursor to the syntheses of other molecules of interest to organic chemists, one of which is bicyclo[4.4.2]dodeca-3,8,11-triene **(4)**.

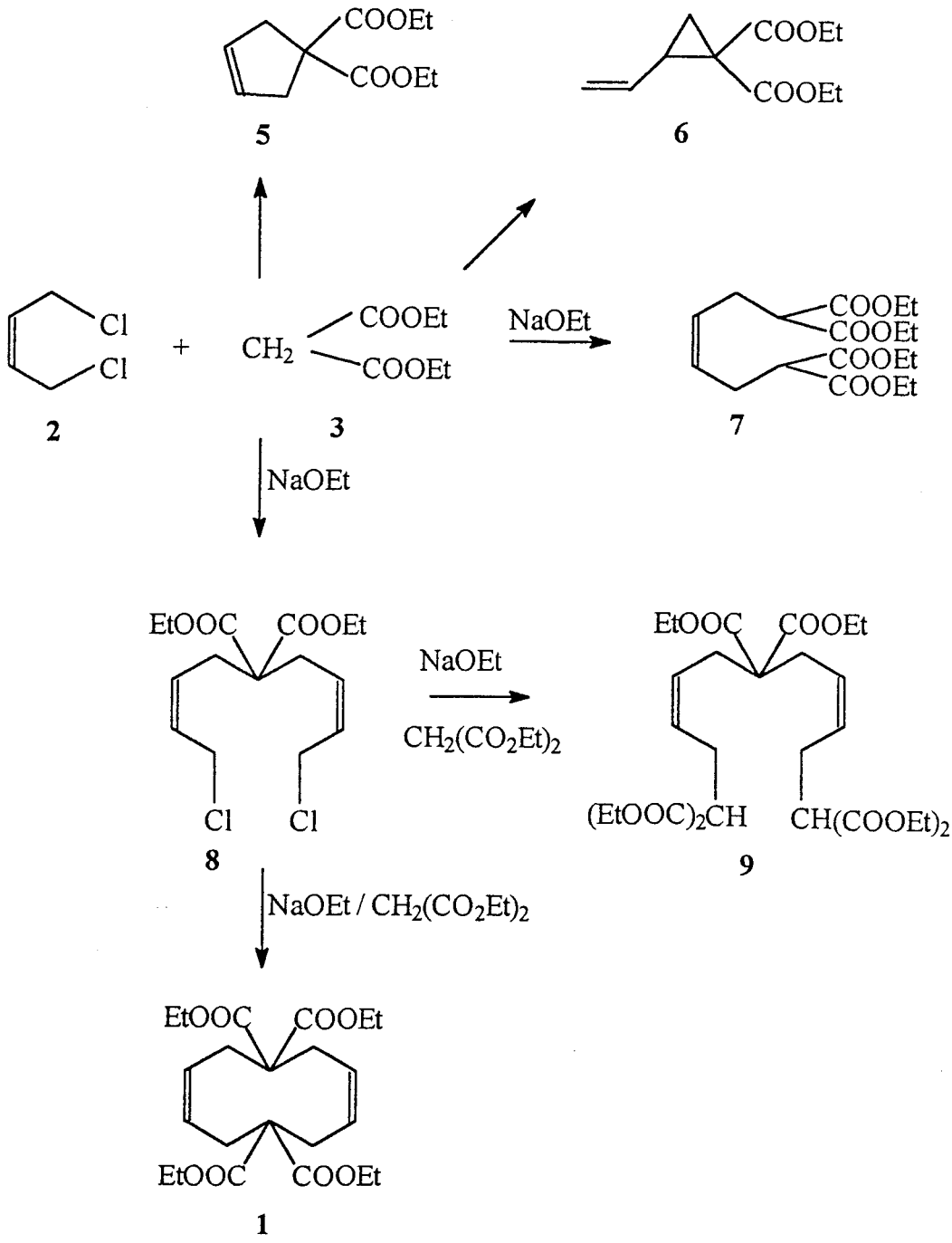


4

However, a major drawback associated with the synthesis of the tetraester

was the low yield of about 2.6%. The synthesis of the tetraester 1 is accompanied by a number of products (Scheme I), some of which are formed in much higher yield than 1. Some of these products were identified (for R = ethyl) as diethylcyclopent-3-ene-1,1-dicarboxylate (**5**) and diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**6**). There are two competing reaction products, diethyl 2,7-dicarboethoxy-octa-4-enedioate (**7**) and diethyl 1,9-dichloro-2,7-nonadiene-5,5-dicarboxylate (**8**). A major intermediate leading to the formation of the tetraester is the dichloro compound 8. This dichloro compound further reacts with the diethyl malonate anion to give the desired tetraester and hexaester 9. (Scheme I)

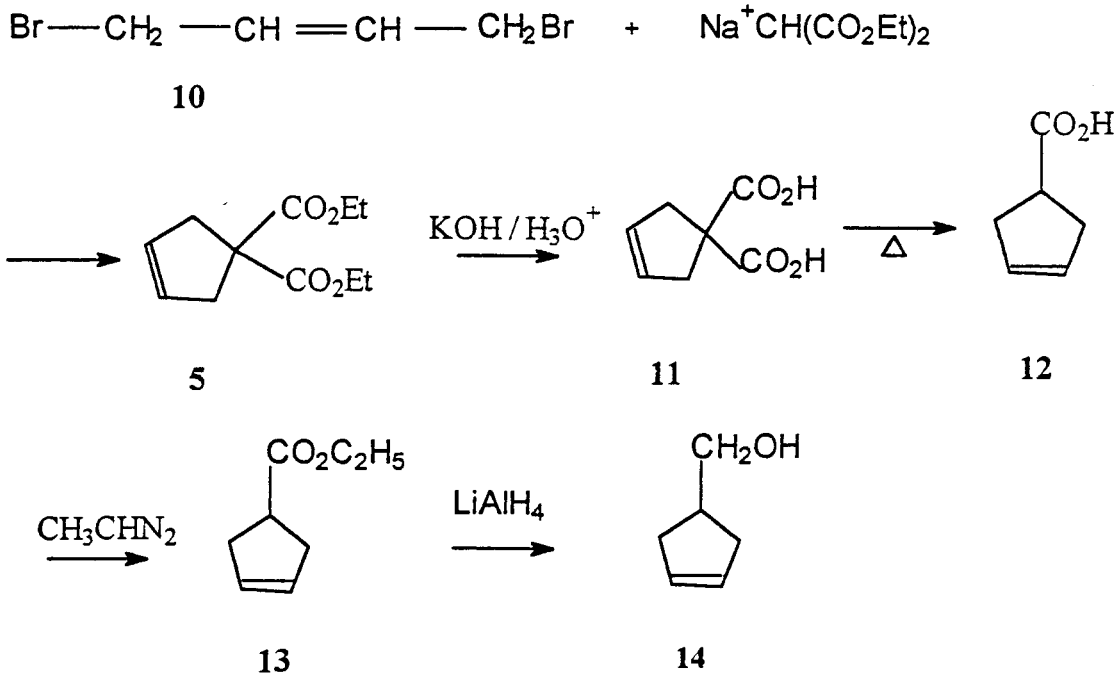
SCHEME I


COOEt
COOEt
5
COOEt
COOEt
6
Cl
Cl
2
+
CH2
COOEt
COOEt
3
NaOEt
COOEt
COOEt
COOEt
COOEt
7
NaOEt
EtOOC
COOEt
Cl
Cl
8
NaOEt
CH2(CO2Et)2
EtOOC
COOEt
(EtOOC)2CH
CH(COOEt)2
9
NaOEt / CH2(CO2Et)2
EtOOC
COOEt
EtOOC
COOEt
1

Diethyl cyclopent-3-ene-1,1-dicarboxylate (**5**) is reportedly a likely precursor for the synthesis of 3-cyclopenten-1-ylamine, which is also synthetically useful for deoxyribonucleosides, anticancer agents.[4,5]

Meinwald, Gassman, and Crandall obtained 54% of the cyclopentene ester from the condensation of the *cis*-1,4-dibromo-2-butene (**10**) with malonic ester.[6,7,8] (Scheme II)

SCHEME II

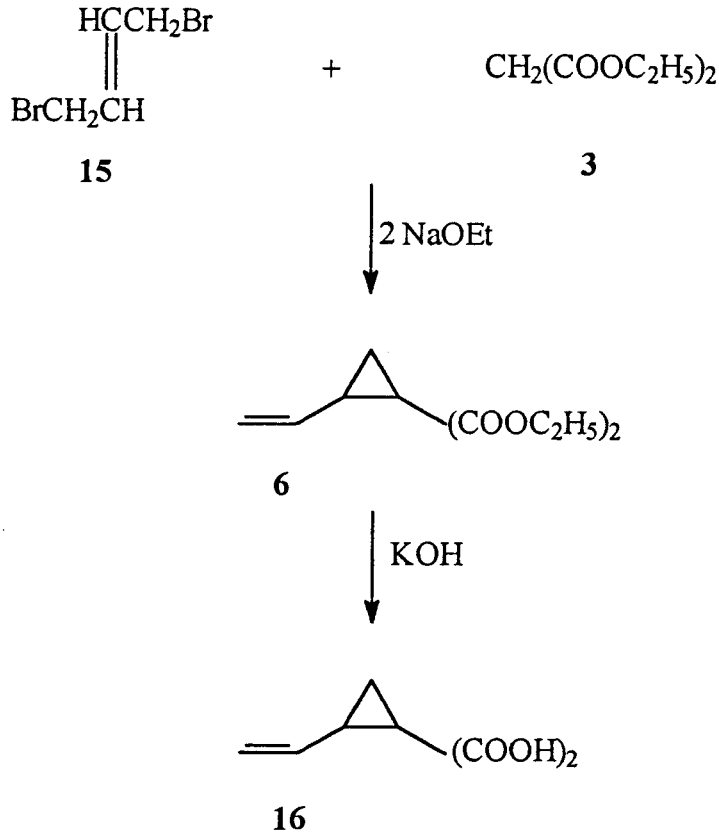


Alkaline hydrolysis of ester 5 gave a crystalline diacid 11 which was decarboxylated by heating to 170°C to give 3-cyclopentene-1-carboxylic acid (**12**) in 30% yield. They treated the monoacid with diazoethane to give its ethyl ester

(**13**), which was converted to the corresponding primary alcohol **14** by reduction with lithium aluminum hydride.

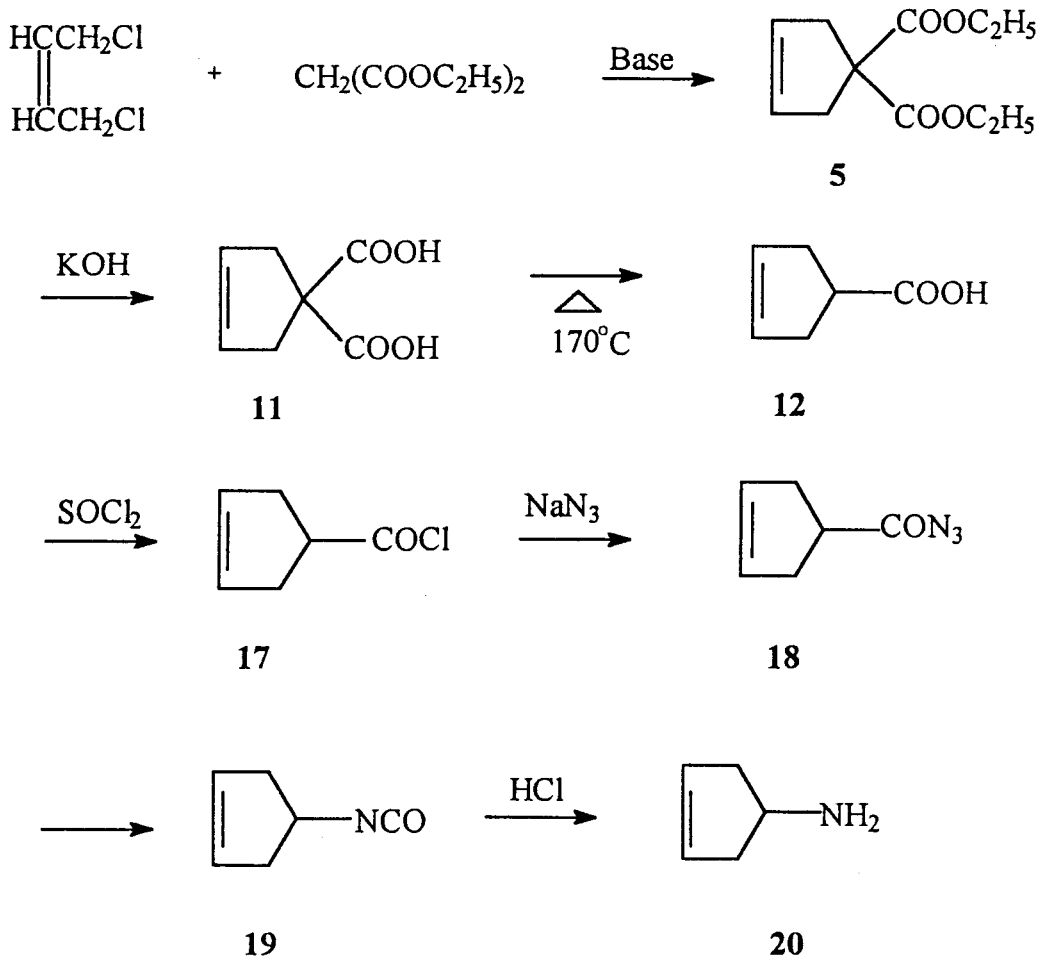
In studying the condensation of *trans*-1,4-dibromo-2-butene (**15**) with malonic ester **3**, Kierstead, et al., reported that the major product of the reaction was diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**6**) obtained via internal S_N2 displacement,[9] which was then hydrolyzed to diacid **16** (Scheme III). No mention was made of the formation of cyclopentene diester **5**.

SCHEME III

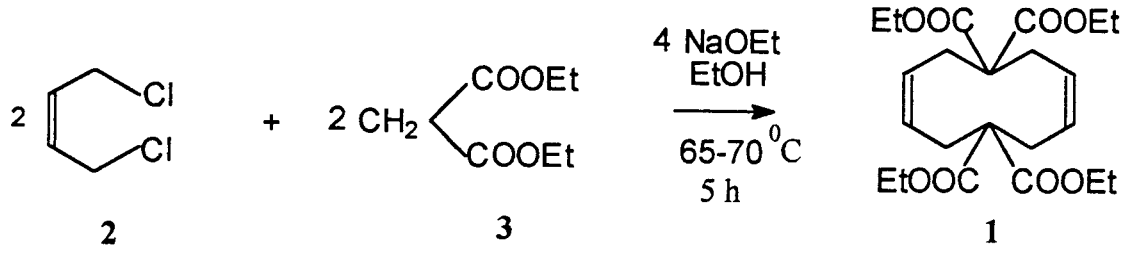


The synthetic route leading to the formation of cyclopentene derivatives involved condensation of malonic ester 3 with *cis*-1,4-dichloro-2-butene (2)[10,11,12] to give the desired cyclopentene diester 5, which was reportedly formed along with a roughly equal proportion of the cyclopropane isomer 6, including a 2.6% yield of a third product which was under investigation at the time. The mixture of diesters was saponified to give a mixture of crystalline diacids (11 & 16). The higher melting diacid was isolated in 31% yield, and identified as the cyclopentene diacid 11, which was decarboxylated to give the monoacid 12. This was further converted to the corresponding acid chloride 17, and treated in a cold aqueous medium with activated sodium azide[13] in dry benzene to afford an acyl azide 18. The azide was then converted to its isocyanate 19, which was subsequently treated with concentrated hydrochloric acid to give the corresponding amine 20. These two papers clearly demonstrated the structures of the major products and the importance of the dihalobutene stereochemistry in the cyclization reactions (Scheme IV).

SCHEME IV

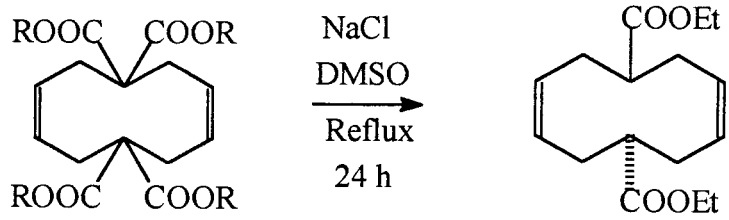


In an attempt to also improve upon the yield, Choubal studied the cyclization by varying the reaction conditions such as temperature, time, media, etc.



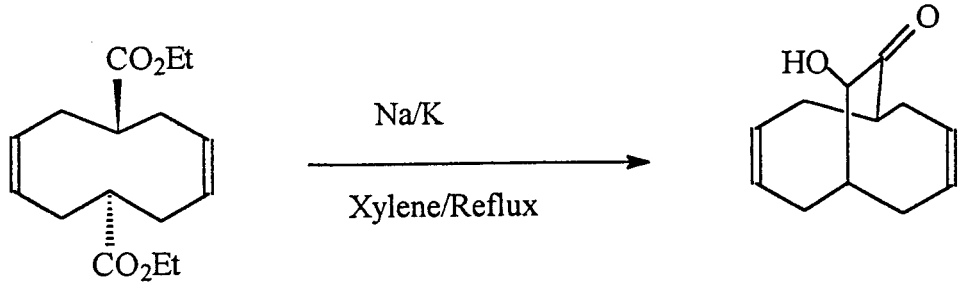
A maximum yield of 2.6% of the tetraester 1 was observed from the treatment of *cis*-1,4-dichloro-2-butene with the sodium salt of diethyl malonate regardless of conditions.[14]

The tetraester 1 was then subjected to decarboalkoxylation[15] by refluxing with NaCl/DMSO (Krapcho reaction) to give the diester 21 in 78% yield. The structure was confirmed by X-ray crystallography.[16]



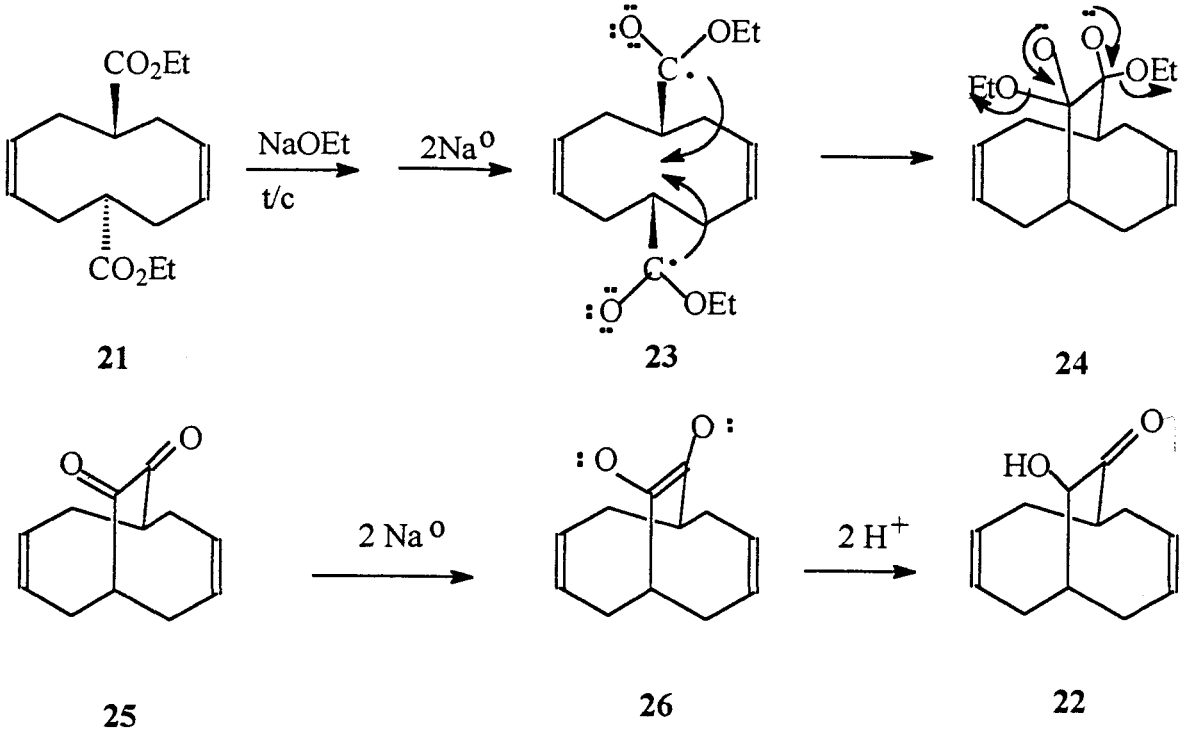
1 21

The resulting diester was converted in low yield (4%) to hydroxyketone 22 by reacting with Na/K in refluxing xylene.[17]

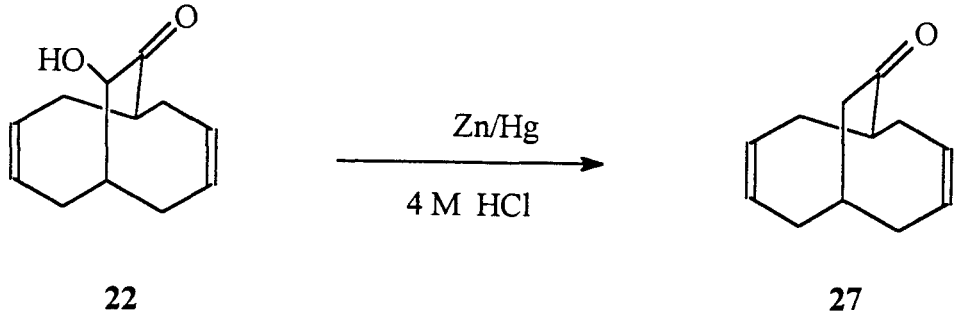


21 22

MECHANISM OF THE LATTER REACTION IS DEPICTED AS FOLLOWS:

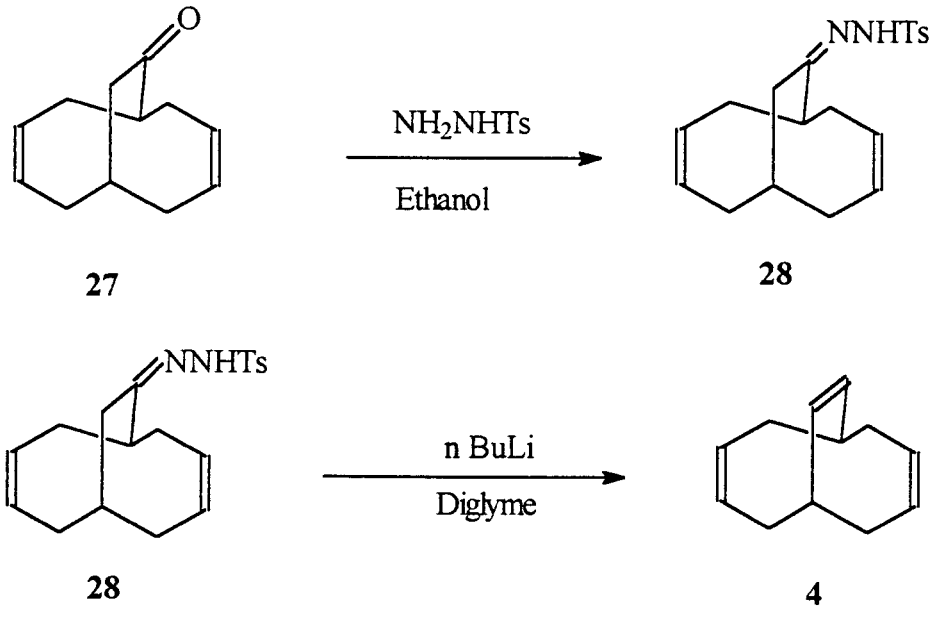


The hydroxyketone so formed was selectively reduced to the ketone 27 in the presence of Zn/Hg in 4M-HCl.

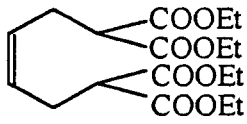


The final step of the reaction was the conversion of the ketone 27 to the desired triene 4 through the Shapiro reaction[18]. This involved a two-step process: first, the initial conversion of the ketone to the corresponding tosylhydrazone 28

by refluxing with tosylhydrazide in ethanol. The tosylhydrazone 28 was treated with BuLi in diglyme for 4 h at 60°C to give the desired triene 4.



The major products obtained in the alkylation of *cis*-1,4-dichloro-2-butene, diethyl cyclopent-3-ene-1,1-dicarboxylate (**5**) and diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**6**) were reportedly isolated by vacuum distillation in 67% yield. In investigating the uncharacterized product, the residue from the vacuum distillation was washed with heptane to obtain the crude tetraester. Column chromatography of the residue washing resulted in the isolation of two pure compounds, diethyl 2,7-dicarboethoxy-octa 4-enedioate (**7**) and diethyl 2,7,7,12-tetracarboethoxy trideca-4,9-dienedioate (**9**). Characterization of these products reportedly suggested the presence of diethyl 1,9-dichloronona-2,8-diene-5,5-dicarboxylate (**8**), as the reaction intermediate.



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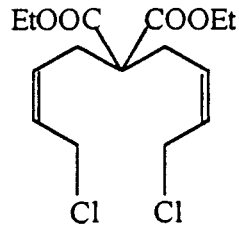

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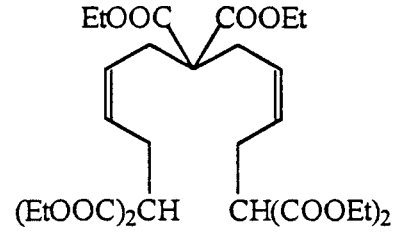


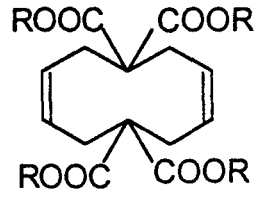
9

The intermediate leads to the formation of the tetraester when it reacts with one equivalent of diethyl malonate dianion, while reaction with two equivalents affords the undesired hexaester (**9**).

CHAPTER III

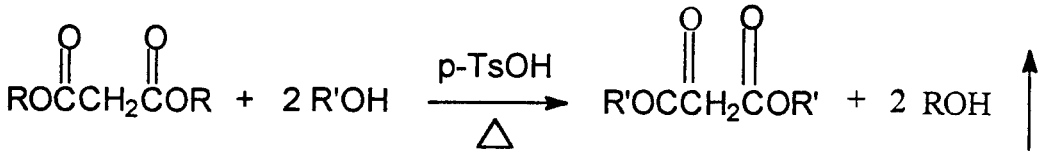
RESULTS AND DISCUSSION

Using the literature procedure[1,2] for the synthesis of tetraethyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate (1), the syntheses of similar molecules with other R groups was achieved.



1

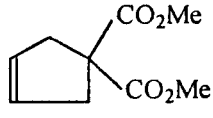
Since the major challenge of this project was the improvement of the yield relative to cited references, other routes were developed to achieve this goal; other R groups (methyl, propyl, butyl, and pentyl) were substituted for the ethyl group (literature procedure), and the reaction in each case was investigated. Since the dipropyl malonate is not commercially available, it is generated by transesterification[19] in the following manner:



To prepare the analogous compound possessing a methyl ester groups, dimethyl malonate was used in place of diethyl malonate, whereas sodium methoxide was generated by slowly reacting hexane-washed sodium spheres with methanol. When the malonic ester was being added to the sodium methoxide, theresulting mixture began to separate into two phases (solid and liquid), making it difficult to add directly to the reaction flask. A heating tape was wrapped around the addition funnel to keep the solution more homogeneous. A small portion of methanol was added to dissolve the precipitate but this proved to be unsuccessful. It was then scooped out and placed directly into the main reaction flask containing *cis*-1,4-dichloro-2-butene, and the slow addition of the remaining portion was continued.

To investigate if longer reaction time would improve the yield, three runs were attempted with refluxing times of 4.5 h, 15 h and 21 h respectively, but no significant change in yield was observed.

The more volatile major products of the reaction [dimethyl cyclopent-3-ene-1,1-dicarboxylate (**29**), and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**30**)] were removed by vacuum distillation to give 44.2 g (0.240 mol, 59% yield) of the mixture.



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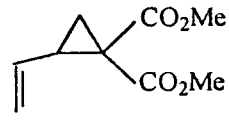

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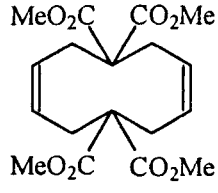
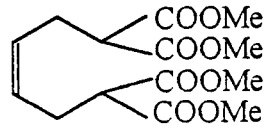


31

Four other products were obtained: the tetraester **31**, dimethyl 2,7-dicarboethoxy-oct-4-enedioate (**32**), dimethyl 2,7,7,12-tetracarboethoxytrideca-4,9-dienedioate (**33**), and dimethyl 1,9-dichloronona-2,8-diene-5,5-dicarboxylate (**34**). Of these, the desired tetraester **31** was isolated by column chromatography in 1.2% yield. Product **34** is reportedly a reaction intermediate that leads to the formation of the tetraester **31** by reacting with dimethyl malonate dianion. However, reaction of **34** with two equivalents of the anion derived from dimethyl malonate would more likely result in formation of product **33**.

The tetraester yield of 1.2% (when R = methyl) indicates a 54% decrease in yield relative to the reported 2.6% (when R = ethyl). We then investigated the reaction further to see if increasing the size of the R group to n-propyl, and then using 1-propanol, a higher boiling point solvent than both methanol and ethanol, would induce more cyclization to the desired tetraester. In studying this reaction, dipropyl malonate (**35**) was first synthesized and characterized. The sodium spheres took a much longer time to react with 1-propanol, which indicates a decrease in reactivity of alkaline metals with longer chain alcohols.



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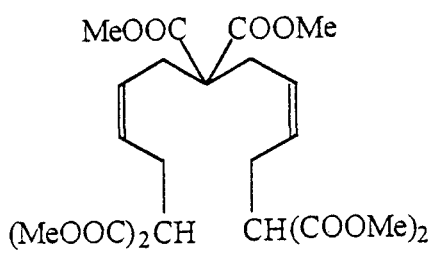

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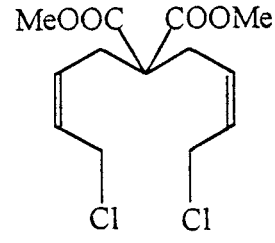
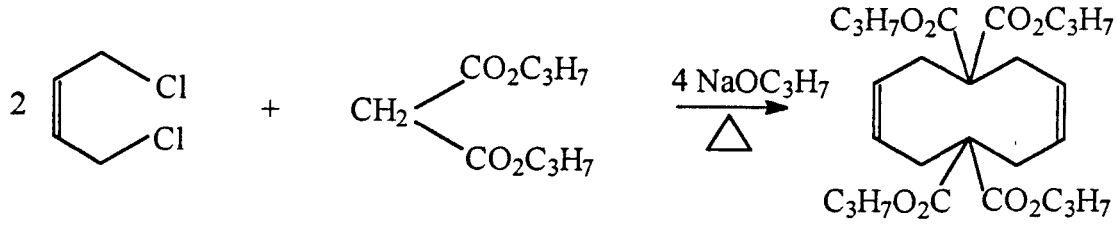


34

The yield of 6.9% realized from this reaction confirmed the presumption that larger size R groups and increased temperature may infuence cyclization. Once again, a mixture of diesters [dipropyl cyclopent-3-ene-1,1-dicarboxylate (**37**), and dipropyl 2-vinylcyclopropane-1,1-dicarboxylate (**38**)] were separated from the reaction mixture by vacuum distillation to give 34.20 g (0.143 mol) of the low boiling products.



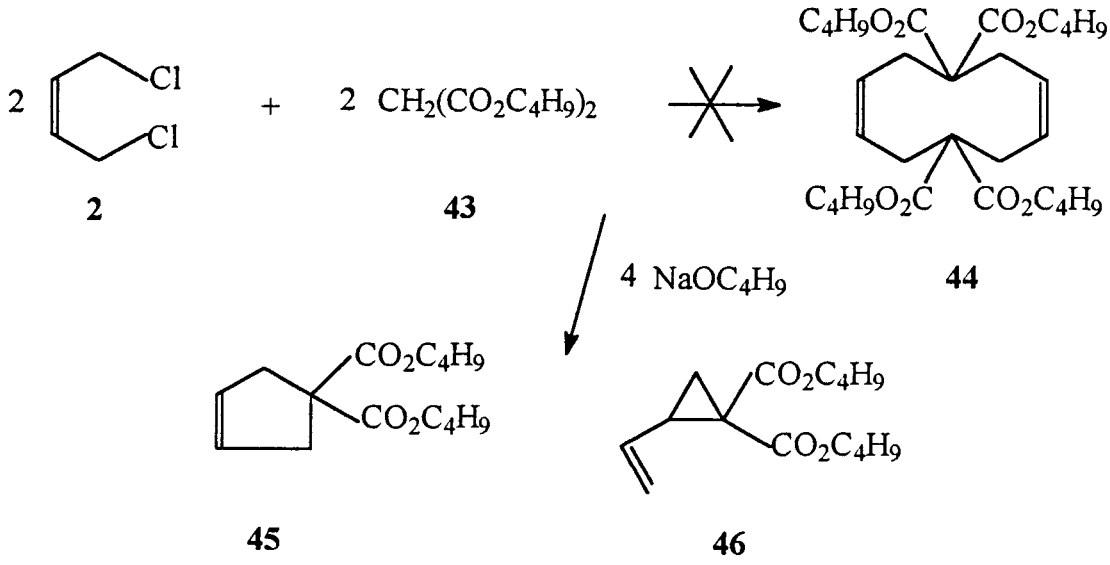
2 **35** **36**

37 **38**

The reaction was next attempted with butyl as the ester group on a smaller scale. Again, formation of sodium n-butoxide, the base in this case, from sodium spheres and n-butanol took much longer to form. Also, since this was a small scale reaction, the reactants were easily stirred by a magnetic stirrer instead of mechanical stirrer to avoid any interruption in stirring as had earlier been experienced. The removal of the major products by vacuum distillation was achieved without any difficulty. But an attempt to chromatograph the crude

portion of the distillation residue on a 100 - 200 mesh Florisil-packed column did not give the desired tetraester. The distilled product was subjected to thermal conductivity detector/GC on a silicone-packed column at column temperature of 212°C and detector temperature 255°C. However, none of the desired tetraester **44** was detected.

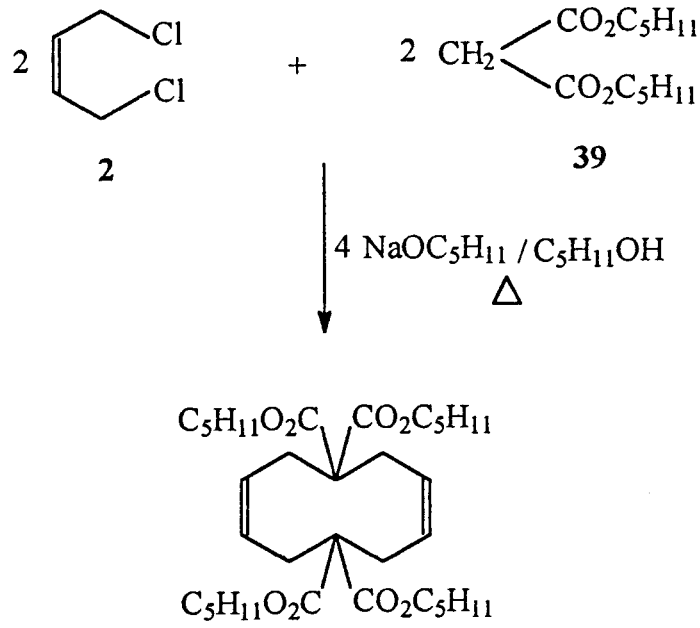
Other attempts to synthesize a tetraester from dibutyl malonate (**43**) and *cis*-1,4-dichloro-2-butene did not show cyclization to the desired tetraester - a problem, related perhaps to the size of the butyl groups or perhaps decomposition of one of the intermediate (at the higher reaction temperature).



2 **43** **44** **45** **46**

Another attempt at synthesizing a tetraester involved the use of dipentyl malonate (**39**) and *cis*-1,4-dichloro-2-butene (**2**) in the presence of sodium pentoxide, again, on a smaller scale. After a 36 h reflux, a slight modification of the procedure was made in removing the products. Since the 1-pentanol could not be completely removed on the rotary evaporator, initial distillation was performed

using an aspirator to reduce the pressure, and to be sure every trace of 1-pentanol was removed. The vacuum distillation was next carried out using a sandbath as a heating source instead of a heating mantle. A 1.17 g sample of distillate, bp 80 - 84°C was eventually collected which was identified by NMR as 1-pentanol.



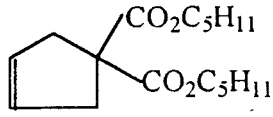
2 **39**

40

Since the expected diesters [dipentyl cyclopent-3-ene-1,1-dicarboxylate (**41**), and dipentyl 2-vinylcyclopropane-1,1-dicarboxylate (**42**)] were not recovered by this vacuum distillation, we went ahead and chromatographed the crude reaction mixture, this time changing the ratio of ether-hexane solvent used for elution to achieve a steady increase in polarity.

The fractions collected were studied by thin layer chromatography using

ethyl acetate, acetonitrile, and methanol as media to find how the components separate relative to the reaction solvent, 1-pentanol. Some of the fractions were combined based on the TLC result, but further analysis showed that neither the diesters **41** & **42** nor the tetraester **40** could be identified.



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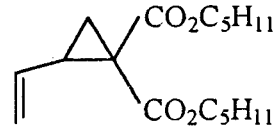
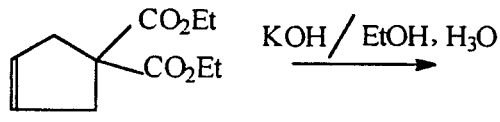


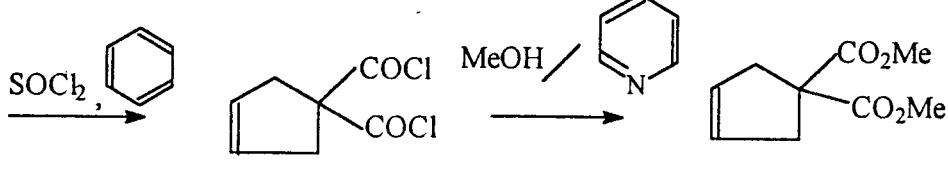
42

Finally ethyl acetate, acetonitrile, and methanol were run through the column to elute any and all components that might be left in the column. Analysis of these fractions, again, did not show the formation of the desired compounds.

An effort was made to determine quantitative yields of the major products in these experiments, i.e., yields of dialkyl cyclopent-3-ene-1,1-dicarboxylate and dialkyl 2-vinylcyclopropane-1,1-dicarboxylate. To achieve this goal, diethyl cyclopent-3-ene-1,1-dicarboxylate (**5**) was hydrolyzed and subsequently esterified with methanol to yield the known ester. Diethyl cyclopent-3-ene-1,1-dicarboxylate (**5**) was first converted to the corresponding diacid[7] by treating with potassium hydroxide in the presence of ethanol and water.



5 **11**



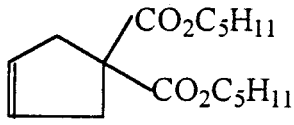
47 **29**

The product was further treated with thionyl chloride to give the acid chloride[20], which was subsequently treated with methanol in pyridine to afford the desired diester **29**.

Also, small scale reactions involving each of the dialkyl malonates were set up to obtain a crude reaction mixture for GC/MS and ^{1}H NMR analysis of the products obtained in each case. We were able to determine the ^{1}H NMR and GC/MS ratios of dialkyl 2-vinyl cyclpropane-1,1-dicarboxylate to dialkyl cyclopent-3-ene-1,1-dicarboxylate as shown on Table I. It was interesting to note that the cyclopentenyl diester to vinylcyclopropane diester ratio increased as the size of R increased. This trend was also observed in the total reaction yields shown on Table II.

As R increased from methyl to n-butyl, the yield of the cyclopentenyl diester product increased. The biggest increase was observed with a butyl group for which 88% of the product was cyclopentenyl diester, while only 10% of the product was cyclopropane diester. This may very well be the preferred synthetic route to dibutyl cyclopent-3-ene-1,1-dicarboxylate. As the size of the R group increased, the temperature of the reaction increased because the alcohol solvent boiled at a higher temperature. Perhaps, the preference for the cyclopentene product comes from a vinyl cyclopropane to cyclopentene[21] rearrangement instead of a preference for alkylation sites, but the temperature (118°C) is less than that reported[22] for the diester, diethyl cyclopent-3-ene-1,1-dicarboxylate.

We also note that the NMR numbers and the GC/MS numbers agree, so little rearrangement occurred in the GC injection port (245°C).



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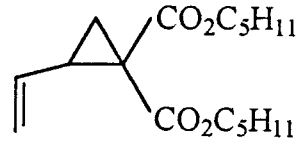


42

The reaction was also performed using dipentyl malonate, but no reaction products were isolated and it was not repeated.

TABLE I CYCLOPROPYL AND CYCLOPENTENYL DIESTER RATIOS

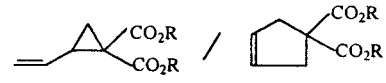
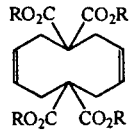
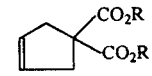
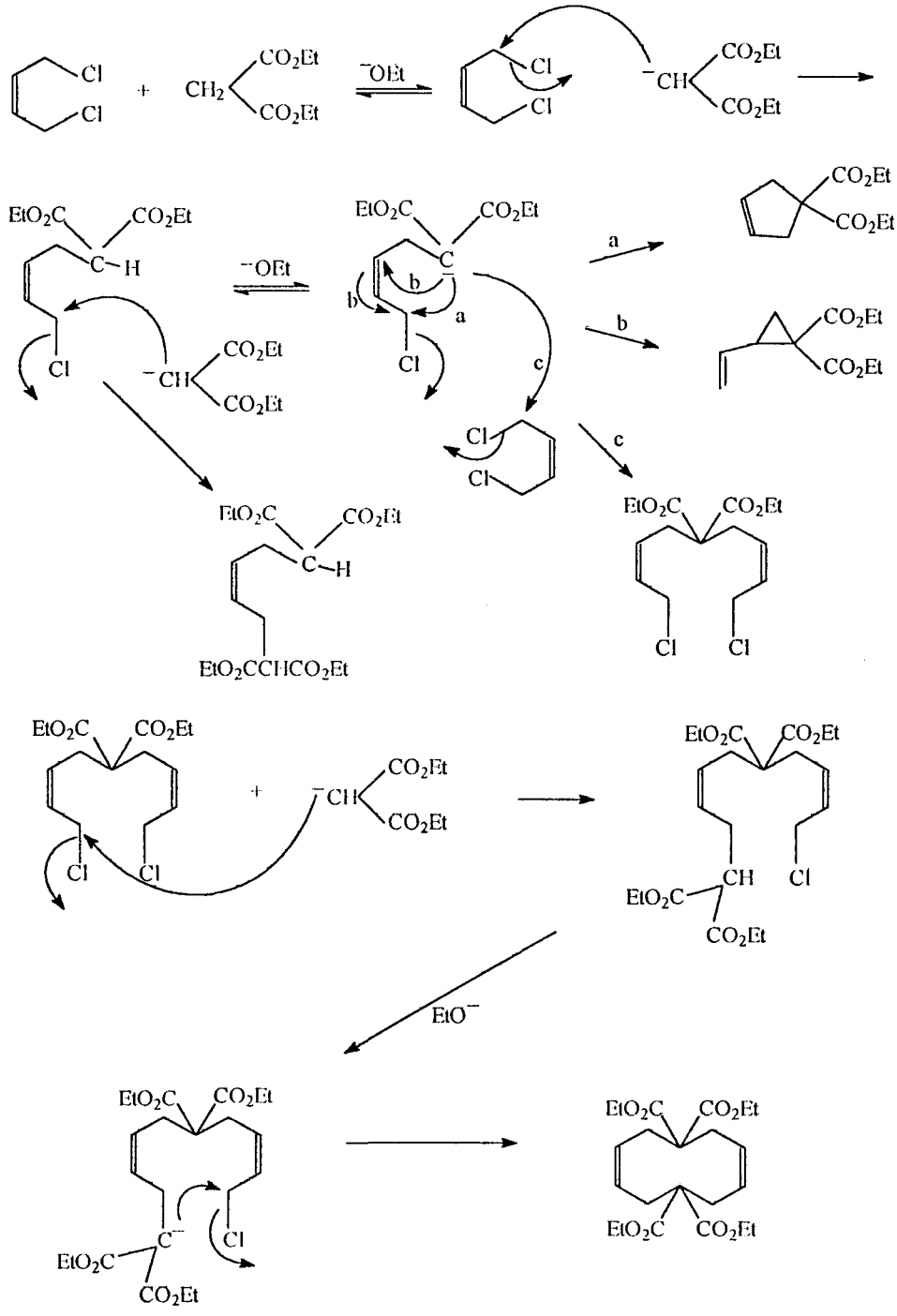
R		
	NMR	GC/MS
Me	1/0.85	1/0.87
Et	1/1.3	1/1.3
n-Pr	1/4	1/3.4
n-Bu	1/8	1/10

TABLE II TOTAL REACTION YIELDS(%)

R			
Me	1.2	32	27
Et	2.6	39	52
n-Pr	6.9	18	71
n-Bu	--	10	88

SCHEME V OVERALL REACTION MECHANISM



CHAPTER IV

CONCLUSIONS

The synthesis of tetraalkyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylates (1) was achieved using the literature method when the alkyl groups were methyl, ethyl, and propyl. The yields were 1.2, 2.6, and 6.9% respectively. It was interesting that no tetraester was observed in the butyl case. As expected, the major products in all cases were identified to be dialkyl cyclopent-3-ene-1,1-dicarboxylate or dialkyl 2-vinylcylopropane-1,1-dicarboxylate.

Repeated attempts were made to synthesize the tetraester with butyl and pentyl R groups but were not successful. In the pentyl case, the reactions were very very slow. The condensation of dialkyl malonates and cis-1,4-dichloro-2-butene to give the desired tetraester is limited to methyl, ethyl and propyl as R groups. While the highest yield for the tetraester was obtained with propyl ester, it was observed that the butyl ester reaction greatly favored the formation of cyclopentenyl diester and no tetraester was isolated.

The yield of the major product, dialkyl cyclopent-3-ene-1,1-dicarboxylate increased with increasing R group, suggesting that the size of the R group and temperature favor cyclization to the cyclopentenyl diesters. However, this may also be the result of the dialkyl vinyl cyclopropane product rearranging to the

cyclopentene product under the reaction conditions.[21] It was, however, reported that the rearrangement with R = ethyl required higher temperatures,[22] and our analytical GC results (injector temp 245°C) agreed with the NMR results.

CHAPTER V

EXPERIMENTAL

Dimethyl malonate, diethyl malonate, and *cis*-1,4-dichloro-2-butene were purchased from Aldrich. However, dipropyl malonate, dibutyl malonate, and dipentyl malonate had to be synthesized. Melting points were taken on a Fischer-Johns melting point apparatus. The infrared spectra were taken on a Perkin-Elmer 1310 Infrared Spectrophotometer or a Matson-Genesis FTIR, while the NMR spectra were taken on a Varian VXR-300 Instrument. Both ^{1}H-NMR and ^{13}C-NMR were run in deuterated chloroform, with TMS internal standard.

Dipropyl malonate: Into a 250 mL two-necked round bottom flask was placed 74.2 g (1.24 mol) 1-propanol, 86.1 g (0.538 mol) of diethyl malonate, and 1 g of p-toluenesulfonic acid as catalyst. The flask was then attached to an all-glass fractionating column (Vigreux type) fitted with a condenser and a receiving flask at the other end. The solution was heated using a heating mantle, and refluxed under nitrogen for 13 h. At that point, a total of 39.39 g (0.856 mol) of ethanol had been collected.

To isolate the dipropyl malonate, another apparatus was set up involving a 250 ml round bottomed flask fitted with a thermometer adapter, a water

condenser, and a receiving flask under vacuum. By the end of the distillation, 91.40 g (0.486 mole, 90%, bp 93 - 97°C, 1.0 mm Hg) of dipropyl malonate[23] had been collected. ^{1}H-NMR($CDCl_3$): δ 4.1(4H, t, -OCH_2), 3.4(2H, s, CH_2), 1.65(4H, m, CH_2), 0.9(6H, t, CH_3); ^{13}C-NMR: δ 166.5, 66.8, 41.5, 21.7, 10.1.

Dibutyl Malonate: A 250 mL two-necked round bottom flask was charged with 77.89 g (1.05 mol) 1-butanol, 80.10 g (0.500 mol) diethyl malonate, and 1.02 g of p-toluenesulfonic acid. The reaction flask, fitted with an all-glass (Vigreux type) fractionating column was set up with a condenser and the mixture was refluxed under nitrogen gas for 15 h during which 22.30 g of ethanol was distilled off.

Vacuum distillation apparatus was then set up to distill the desired ester. The first fraction collected [24.01 g , bp range 75 - 98°C] was discarded as an ethanol-propanol mixture, and a second fraction, 83.05 g, bp 160 - 168°C, was shown to contain some unresolved impurities as determined by ^{1}H-NMR characterization. This second portion was redistilled to give 65.72 g (61%) of distillate which still showed ethyl groups by ^{1}H NMR analysis.

Since we concluded that the very first reaction may not have gone to completion, another attempt was made that involved addition of 13.20 g of 1-butanol (20% of the distillate) to the distillate to further drive the reaction to the direction that produces more ethanol. The reaction mixture was refluxed for 12 h to give 5.47 g of distillate, temperature range 65 - 75°C. The resulting mixture was again subjected to vacuum distillation to give 62.54 g, 58% yield of dibutyl malonate,[23] bp 142 - 145°C. The structure was confirmed by ^{1}H and ^{13}C NMR.

^{1}H-NMR($CDCl_3$): δ 4.2(4H, t, -OCH_2), 3.4(2H, s, CH_2), 1.65(4H, m, CH_2), 1.4(4H, m, CH_2), 0.95(6H, t, CH_3).

Dipentyl malonate: Into a 250 mL two-necked round bottom flask was placed 97.08 g (1.10 mol) 1-pentanol, 81.08 g (0.506 mol) diethyl malonate, and 1.034 g p-toluenesulfonic acid as catalyst. The flask, fitted with an all-glass Vigreux-type fractionating column to which a condenser was attached. The mixture was put under a nitrogen atmosphere and subsequently heated with a heating mantle for 12 h. At the completion of the reaction, 39.47 g of ethanol had been collected. The reaction mixture was vacuum-distilled to give 110.85 g (89%, bp 134 - 138^{0}C, 1.0 mm Hg) of dipentyl malonate. ^{1}H-NMR($CDCl_3$): δ 4.15(4H, t, -OCH_2), 3.36(2H, m, CH_2), 1.65(8H, m, CH_2), 1.35(4H, m, CH_2), 0.9(6H, t, CH_3). ^{13}C-NMR: δ 165.9, 64.8, 41.0, 27.6, 21.7, 13.3.

Tetramethyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate: Into a 1 L three-neck round bottom flask fitted with a reflux condenser, a mechanical stirrer, and two addition funnels (one placed vertically on top of the other), was placed 33.3 g (0.266 mol) of *cis*-1,4-dichloro-2-butene. Then 200 ml of methanol was placed in the lower funnel followed by slow addition of 12.6 g (0.548 mol) of hexane-washed sodium spheres. At the completion of this exothermic reaction, 42.6 g (0.322 mol) of dimethyl malonate was added to the sodium methoxide so formed over 5 min. The resulting reaction mixture (which was kept hot by heating tape to prevent precipitation) was then slowly added to the 1,4-dichloro-2-butene in

the flask over a 1 h period while heating the 1 L flask. The reaction mixture was allowed to reflux under nitrogen, with mechanical stirring for 18 h. The mixture was vacuum filtered to remove sodium chloride, and the solvent was removed from the filtrate with a rotary evaporator, leaving a crude yellow oil in the flask.

The crude mixture was then vacuum-distilled leading to the collection of a clear distillate, (44.2 g) which contained the more volatile major products identified as dimethyl cyclopent-3-ene-1,1-dicarboxylate, and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate. After distilling, the residue was further subjected to a (1x30cm) Florisil (100-200 mesh) column packed in hexane and eluted with increasing amounts of ether/hexane. The fraction eluted with 2/3 ether/hexane gave 60 mg (1.2%) of crystals mp 180 - 183°C, which was identified as the desired tetramethyl cyclodecadienetetracarboxylate.

CHARACTERIZATION: IR: 1710(C=O), 1660(C=C)cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.2(4H, m, -CH=CH-), 3.7(12H, s, $-OCH_3$), 2.7(8H, m, CH_2); ^{13}C-NMR: δ 171.0, 127.5, 56.7, 52.7, 30.1.

Tetrapropyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate: A 1 L three-neck round bottom flask fitted with a reflux condenser, and two addition funnels vertically connected together, was set up with a mechanical stirrer in place. Into this flask, was placed 33.3 g (0.266 mol) of *cis*-1,4-dichloro-2-butene. Sodium propoxide was generated in the lower addition funnel by the addition of 12.6 g (0.548 mol) of hexane-washed sodium spheres to 200 ml of 1-propanol to which

42.6 g (0.226 mol) of dipropyl malonate was added over a period of 5 min. The resulting solution, kept hot by a heating tape, was slowly added to *cis*-1,4-dichloro-2-butene in the flask over a 1 h period. The mixture was left to reflux overnight while maintaining the temperature at 95 to 100°C. After cooling the reaction mixture to room temperature, it was vacuum-filtered, and concentrated to a light yellow viscous oil. The oil was vacuum-distilled to a brownish residue, from which 34.20 g of clear distillate was collected. This distillate was again identified as a mixture of the relatively more volatile major products; dipropyl cyclopent-3-ene-1,1-dicarboxylate, and dipropyl 2-vinylcyclopropane-1,1-dicarboxylate The residue was chromatographed on a Florisil (100-200 mesh) column packed in hexane and eluted with ether-hexane in increasing order of polarity to give 2.19 g(4.56 mmol, 6.85%) of the tetraester crystals, which was recrystallized using hexane; melting point recorded at 68 - 72°C.

CHARACTERIZATION: IR: 1738(C=O); H-NMR($CDCl_3$): δ 5.25(4H, m, -CH=CH-), 2.4(8H, m, CH_2), 1.6(8H, CH_2), 0.9(12H, t, CH_3); ^{13}C-NMR:δ 171.0, 127.7, 56.8, 52.8, 30.2.

Attempted Synthesis of Tetrabutyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate: Into a 250 mL three neck round bottom flask fitted with a reflux condenser, and two addition funnel vertically connected together was placed 5.72 g (0.0462 mol) of *cis*-1,4-dichloro-2-butene. Sodium butoxide was generated in the lower addition funnel by slowing dissolving 2.18 g (0.0948 mol) of sodium spheres (pre-washed in hexane) in 60 mL of 1-butanol. To this solution was added 10.02 g (0.0463

mol) of dibutyl malonate over a 5 min period. The resulting malonate salt was slowly added to *cis*-1,4-dichloro-2-butene in the flask over a period of 1 h. The mixture was allowed to reflux for 28 h under mechanical stirring while maintaining a temperature of 115 to 120°C. Filtration and solvent removal netted 13.13 g of crude oil from which 1.74 g was kept aside for GC/MS analysis.

Vacuum distillation of the remaining crude sample afforded 8.40 g of the mixture of the major products. The residue left after vacuum distillation was again chromatographed on a (100 - 200 mesh) hexane-packed Florisil column and eluted in increasing proportions of ether/hexane. Attempts to crystallize the fractions did not produce the desired cystals, and the ^{1}H NMR did not show signs of the desired tetraester.

Attempted Synthesis of Tetrapentyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate: Into a 1 L three-neck round bottom flask fitted with a reflux condenser, and two addition funnels was placed 33.30 g (0.266 mol) of *cis*-1,4-dichloro-2-butene. Sodium pentoxide was made in the lower addition funnel by slowing dissolving 12.6 g (0.548 mol) of hexane-washed sodium spheres in 250 mL of n-amyl alcohol (1-pentanol). Reactivity of sodium metal with the primary alcohols used so far was observed to decrease with increasing chain length (from methyl to n-pentyl alcohol). 42.6 g (0.174 mol) of dipentyl malonate was slowly added to the sodium pentoxide over 5 min, and the resulting solution was added to the reaction flask containing *cis*-1,4-dichloro-2-butene over a 1 h period. The solution in the addition funnel was kept hot by a heating tape to prevent

precipitation. The mixture was left to reflux for 36 h with mechanical stirring.

The reaction mixture was vacuum-filtered and concentrated on a rotary evaporator. Vacuum distillation of the resulting crude filtrate, using a sand bath yielded 7.32 g (85 - 90°C @ 1 mm Hg) of distillate which was identified by ^{1}H-NMR characterization as 1-pentanol. After several distillation attempts, none of the expected major products were obtained. The entire residue was chromatographed on a 100 - 200 mesh Florosil column followed by TLC of the fractions in ethyl acetate, acetonitrile, and in methanol, but no crystals were recovered, and the ^{1}H NMR showed no signs of the desired tetraester.

TABLE III **TETRAESTER YIELDS**

R	RXN TEMP(°C)	TETRAESTER YIELDS(%)
Me	**65**	**1.2**
Et	**79**	**2.6**
n-Pr	**96**	**6.9**
n-Bu	**118**	**---**
n-Pent	**136**	**---**

From the Table above, it is obvious that as you increase the size of the

R group of the malonate ester from methyl to ethyl, and to propyl, with increasing boiling point, the yield increased from 1.2 to 2.6, and then to 6.9%. But as we switch from propyl to pentyl, for example, in making the sodium alkoxide, the reaction was observed to be slower. The sodium was much less reactive in 1-pentanol thus, confirming the fact that primary alcohols tends to be less reactive as the chain gets longer. It is appropriate to conclude as this point that the systems that favor cyclization to the desired tetraester are limited to methyl, ethyl, and propyl esters.

In another attempt to obtain some quantitative numbers on the two major products [cyclopentyl and vinylcyclopropyl esters], small scale reactions to quantify 1:1 adducts were performed as follows:

Reaction of Dimethyl malonate with *cis*-1,4-dichloro-2-butene: A 100 mL three-neck round bottom flask charged with 4.807 g (0.0384 mol) of *cis*-1,4-dichloro-2-butene was fitted with a reflux condenser and two vertically connected 60 ml addition funnels. 1.811 g (0.0787 mol) of sodium spheres was slowly dissolved in 30 mL of methanol to form sodium methoxide which was then added to 5.085 g (0.0385 mol) of dimethyl malonate in the lower addition funnel over 5 min. The resulting solution was added to the reaction flask containing *cis*-1,4-dichloro-2-butene over a 1 h period. After refluxing for 21 h under nitrogen and magnetic stirring, the reaction mixture was vacuum-filtered. Solvent removal on a rotary evaporator afforded 7.007 g of light-yellow residue.

In analyzing the residue on the HP GC-MS, 2 μL of the crude mixture

in 2 mL of hexane was injected at a GC setting of 65°C (initial column temperature), with 5°C/min increase to 250°C, (final column temperature), to afford a 1/0.87 ratio of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**30**) to dimethyl cyclopent-3-ene-1,1-dicarboxylate (**29**), as compared to a 1/0.85 ratio determined via ^{1}H NMR analysis]. ^{1}H NMR analysis of the crude reaction product indicated the presence 0.84 g (6.4 mMol) of the starting material, dimethyl malonate; 1.86 g (10.11 mMol, 31.5%) of the product **30**; and 1.58 g (8.6 mMol, 26.8%) of **29**.

Reaction of Diethyl malonate with *cis*-1,4-dichloro-2-butene: A 100 mL three-neck round bottom flask charged with 3.92 g (0.0314 mol) *cis*-1,4-dichloro-2-butene was fitted with a water condenser, magnetic stirring bar, and put under nitrogen. One of the side arms was also fitted with two addition funnels linked vertically. Sodium ethoxide was prepared in the lower addition funnel by reacting 1.5 g (0.0652 mol) of hexane-washed sodium spheres with 35 mL ethanol, and 5.12 g (0.0320 mol) of diethyl malonate was added from the upper addition funnel over 5 min. The resulting mixture was added to the reaction flask over 1 h while stirring. Refluxing was stopped after 28 h, and the mixture subjected to vacuum-filtration and concentrated on a rotary evaporator to give 6.66 g of the yellow oily residue which was analyzed on the GC-MS to afford a 1/1.3 ratio of diethyl 2-vinyl cyclopropane-1,1-dicarboxylate (**6**) to diethyl cyclopent-3-ene-1,1-dicarboxylate (**5**). ^{1}H NMR showed the same ratio, and ^{1}H NMR analysis of the crude reaction product indicated the presence of 39% of diethyl 2-vinyl

cyclopropane-1,1-dicarboxylate (**6**), and 52% of diethyl cyclopent-3-ene-1,1-dicarboxylate (**5**).

Reaction of Dipropyl malonate with *cis*-1,4-dichloro-2-butene: Into a 100 mL three -neck round bottom flask was placed 3.35 g (0.0268 mol) of *cis*-1,4-dichloro-2-butene. The flask was fitted with a reflux condenser, and two 60 mL addition funnels vertically connected. Sodium propoxide was generated in the lower addition funnel by slowly reacting 1.30 g (0.0565 mol) of hexane-washed sodium spheres with 25.12 mL of 1-propanol, and to which 5.08 g (0.027 mol) dipropyl malonate was added from the top addtion funnel over 5 min. The reaction mixture was then added to the flask containing the dichloro compound over 1 h while stirring over a magnetic stirring bar. After a 36 h reflux under nitrogen, reaction mixture was vacuum-filtered and concentrated on a rotary evaporator to give 5.45 g of light yellow crude mixture which was subjected to GC-MS analysis under the same conditions as above. This afforded a 1/3.4 ratio of dipropyl 2-vinyl cyclopropane-1,1-dicarboxylate (**38**) to dipropyl cyclopent-3-ene-1,1-dicarboxylate (**37**) (versus a 1/4 ratio determination by ^{1}H NMR analysis). The ^{1}H NMR analysis indicated the presence of 2.015 g (10.72 mMol) of dipropyl malonate (**35**), 0.68 g (2.83 mMol, 17.6%) of 38, and 2.76 g (11.5 mMol, 71.5%) of the product 37.

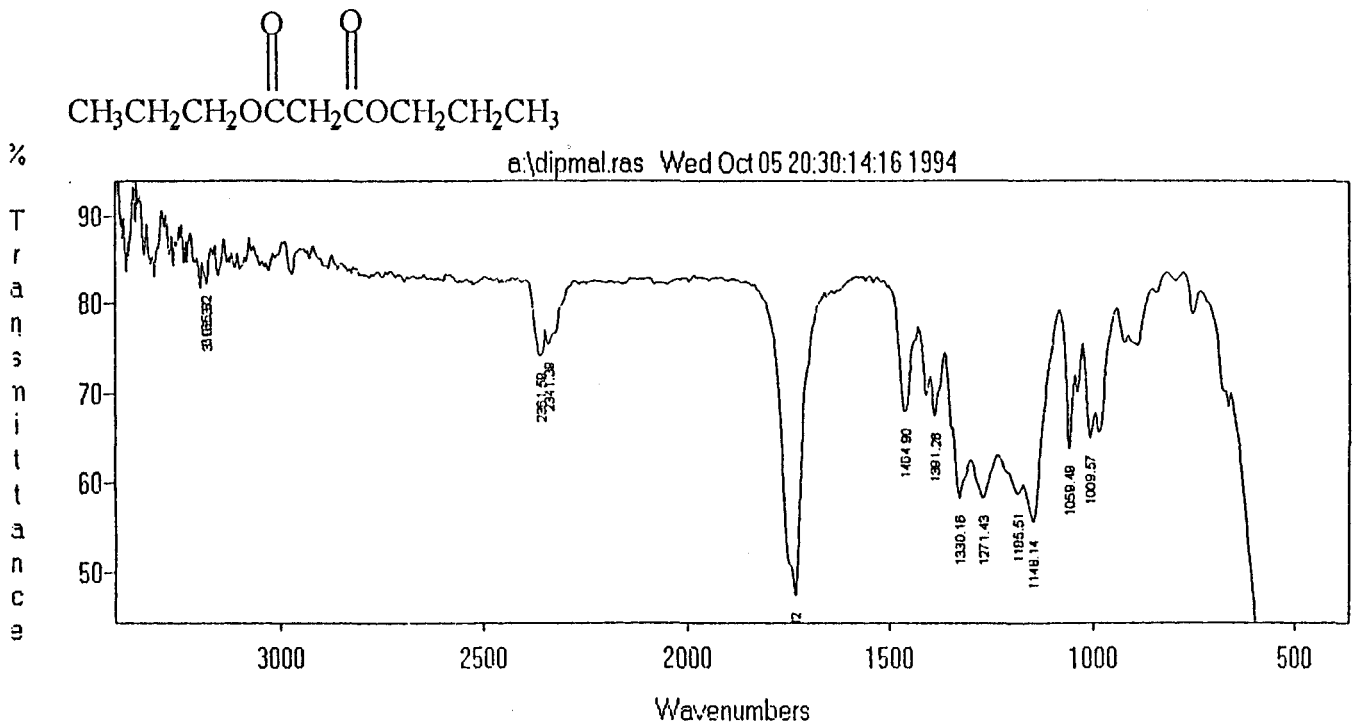
Cyclopent-3-ene-1,1-diacid: Into a 25 mL round bottom flask, was placed 5.030 g (0.0237 mol) of diethyl cyclopent-3-ene-1,1-dicarboxylate, 5.094 g (0.091 mol)

of potassium hydroxide, 1.85 mL of ethanol and 4.7 mL of water. The mixture was allowed to reflux for 4.5 h after which it was cooled and extracted three times with 10 mL portions of ether. The aqueous solution was saturated with sodium chloride and acidified with 6 M hydrochloric acid. The product was subsequently extracted with 3 more 10 mL-portions of ether. The combined extracts were dried over anhydrous magnesium sulfate, and solvent removed on a rotary evaporator to give 1.82 g (0.012 mol, 49% yield, mp 165 - 168°C) of the diacid. IR: 1704(C=O)cm^{-1}.

Cyclopent-3-ene-1,1-diacid chloride: A 25 mL round bottom flask was charged with 96.1 mg (0.616 mMol) of the diacid synthesized above and 883 mg (7.42 mMol) of the thionyl chloride. The mixture was stirred at room temperature for 12 h after which an IR indicated that the reaction was not complete. About 1 mL of benzene was then added to the reaction mixture and warmed up slightly while it refluxed for 7 h. The product was concentrated on a rotary evaporator to give 63 mg (0.326 mMol, 53%) of the acid chloride 17. IR: 1834(C=O)cm^{-1}.

Dimethyl cyclopent-3-ene-1,1-dicarboxylate: Into a 25 mL round bottom flask was placed (60 mg, 0.311 mMol) of the acid chloride 17, 15 μL of pyridine and 1 mL of methanol. The reaction mixture was stirred at room temperature for 12 h. The resulting crude diester was identified with IR. IR: 1729(C=O)cm^{-1}.

SPECTRA



Peak Report
File: a:\dipmal.ras
Title: a:\dipmal.ras Wed Oct 05 20:30:14:16 1994

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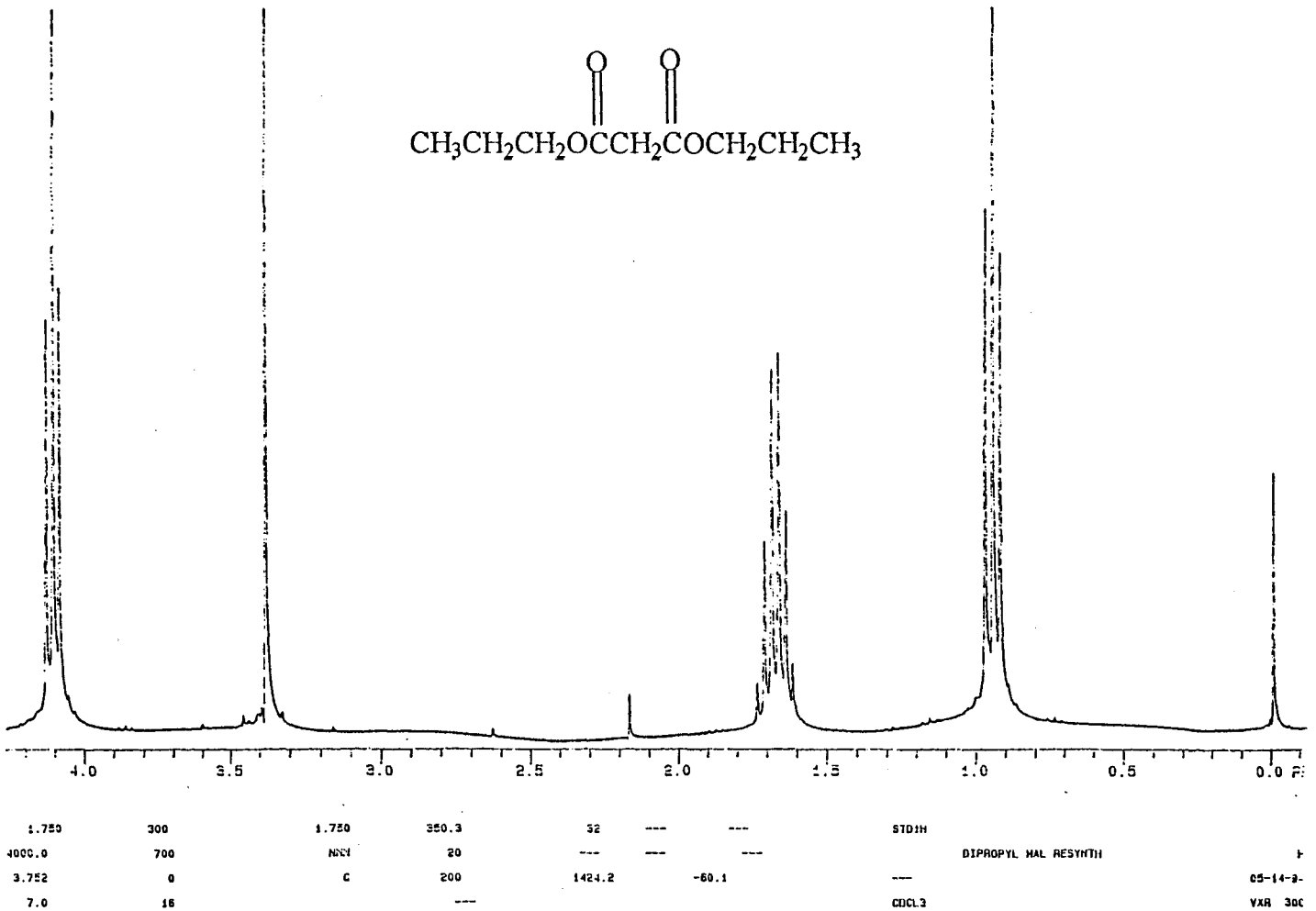
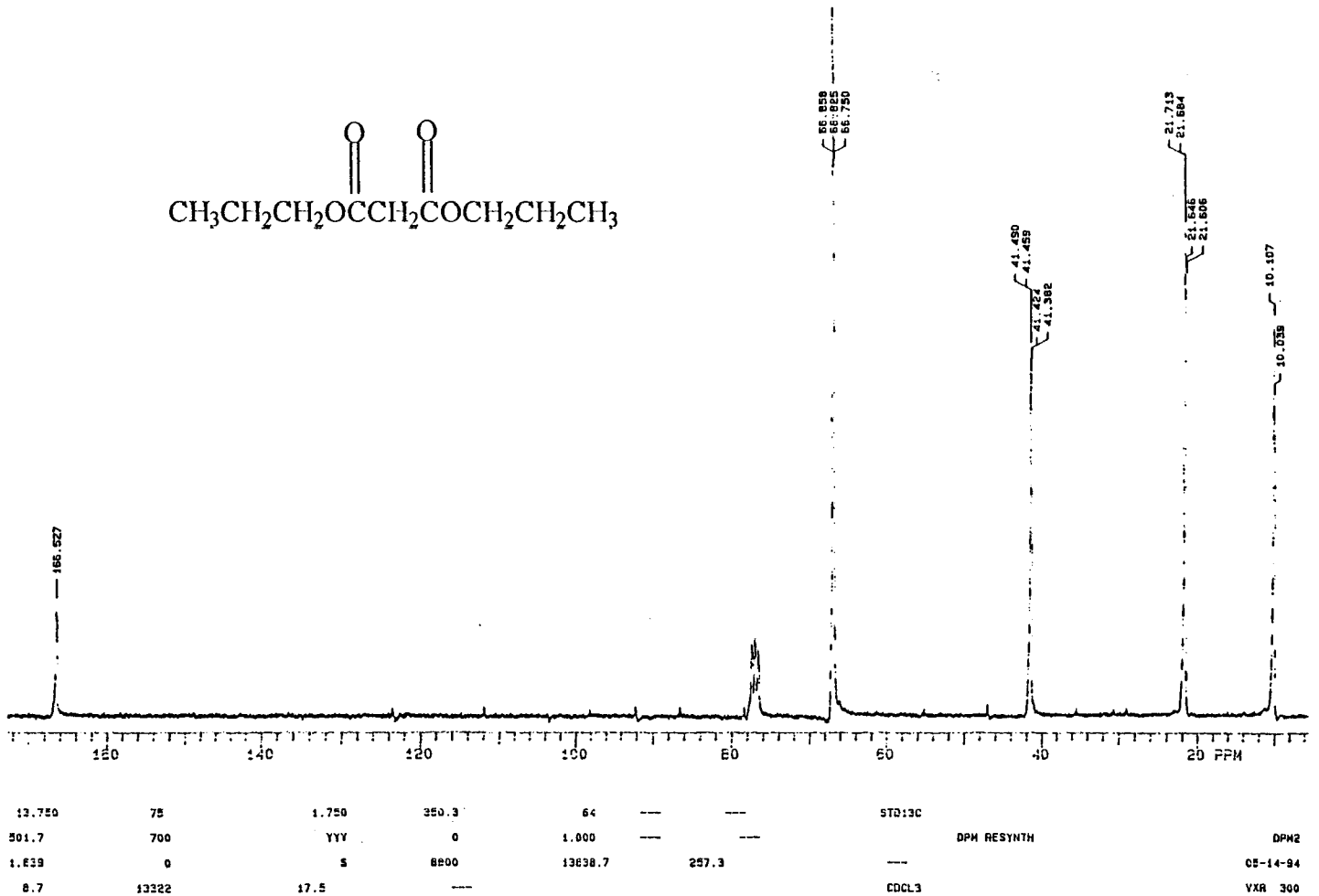
1271.43	58.33	1330.16	58.37	1391.26	67.54	1464.90	68.07
1734.82	47.36	2341.39	75.48	2361.59	74.25	3183.37	82.32
3185.82	82.85						

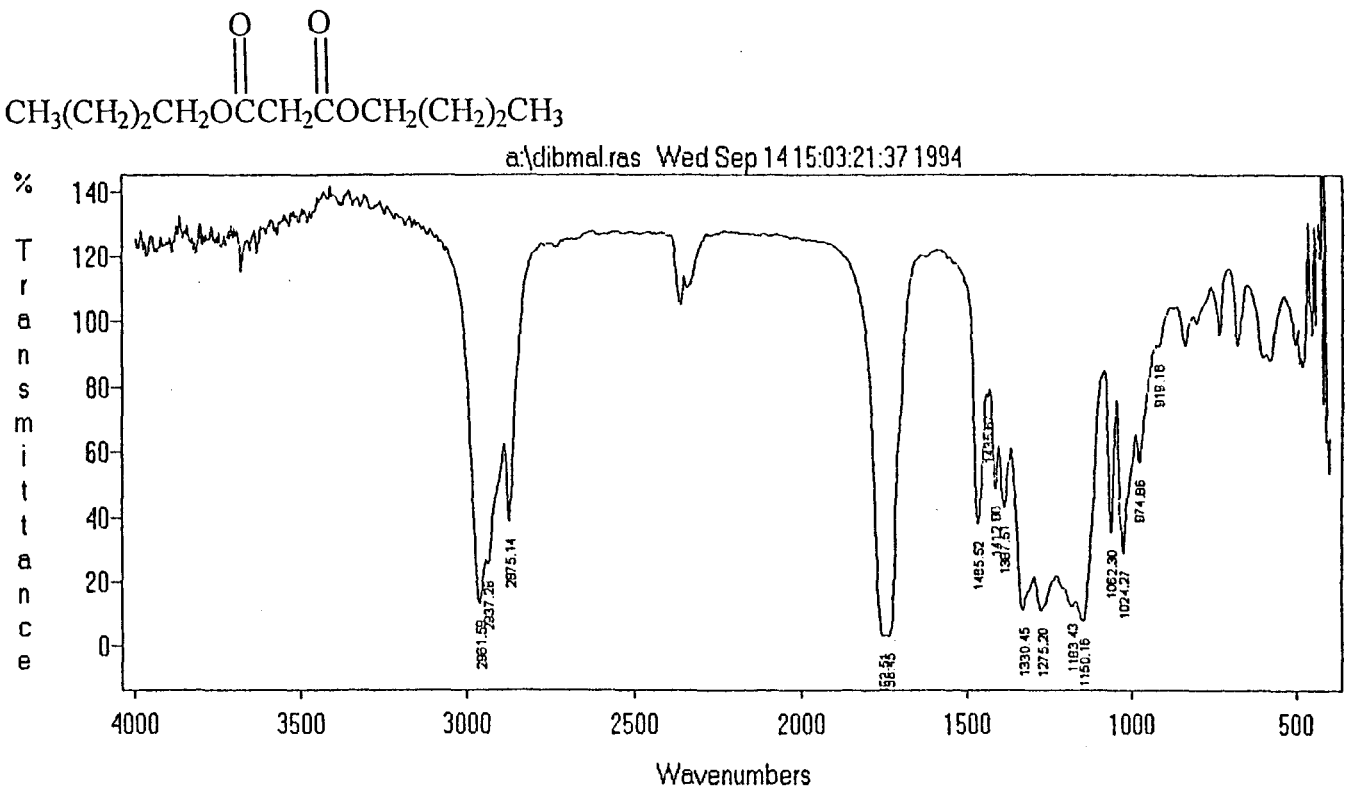
FTIR of Dipropylmalonate (35)



^{1}H NMR of Dipropylmalonate (35)



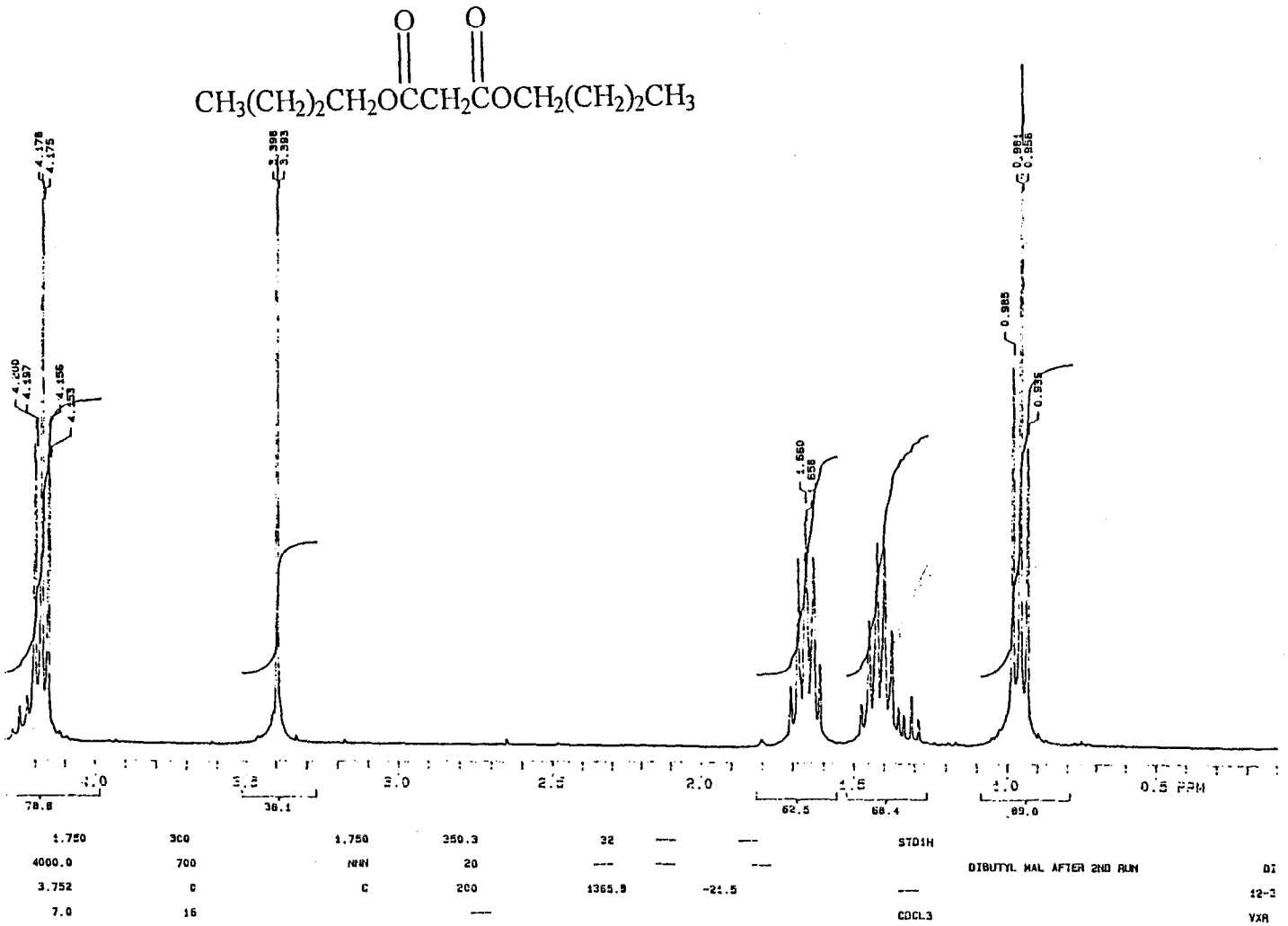
^{13}C NMR of Dipropylmalonate (35)



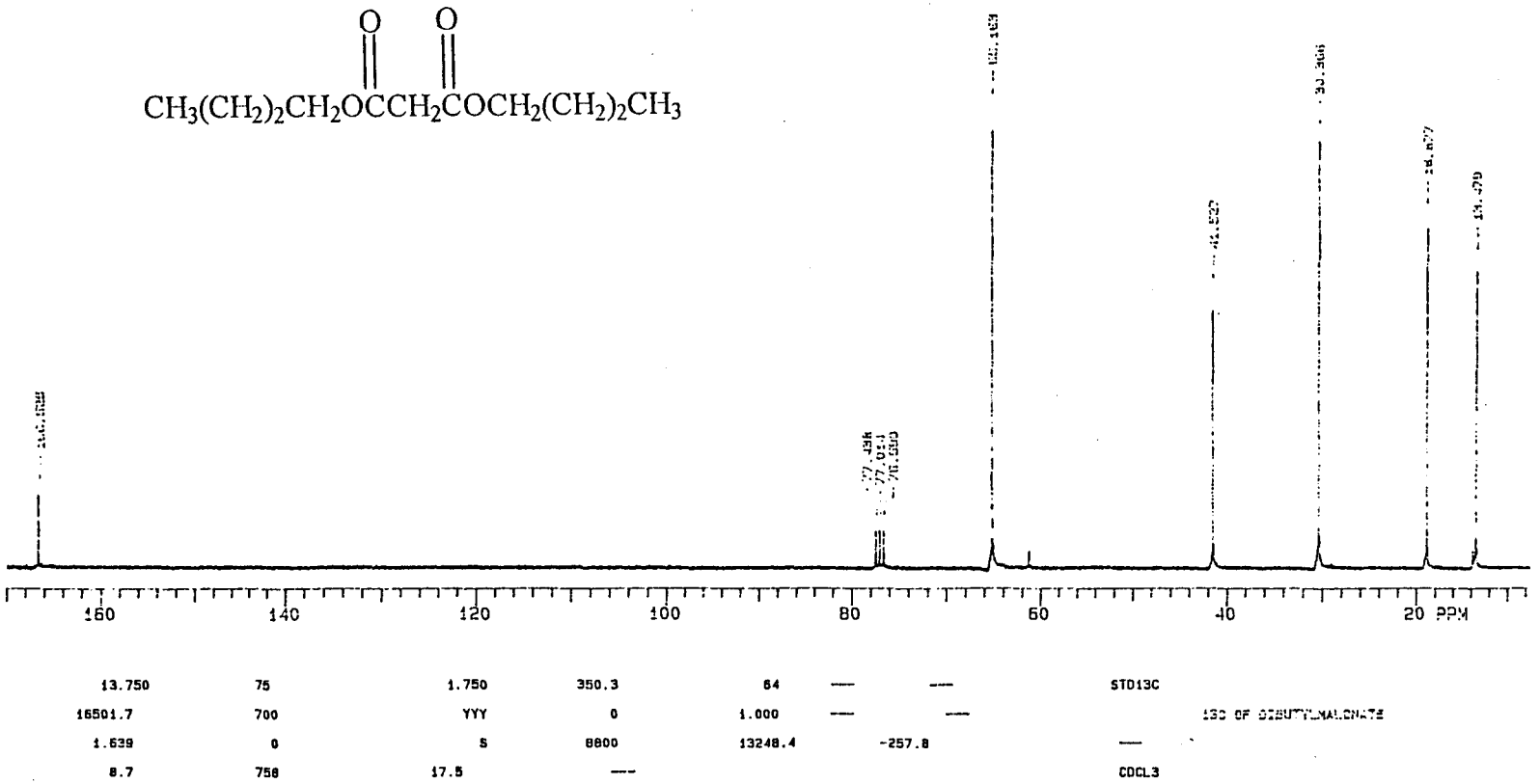
Peak Report
File: A:\DIBMAL.RAS
Title: a:\dibmal.ras Wed Sep 14 15:03:21:37 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
919.16	92.35	974.86	56.96	1024.27	29.16	1062.30	35.44
1150.16	8.08	1183.43	12.53	1275.20	11.25	1330.45	11.12
1387.51	43.23	1412.86	48.80	1435.67	77.13	1465.52	38.31
1738.45	3.29	1753.51	3.44	2875.14	38.86	2937.28	25.64
2961.59	13.39						

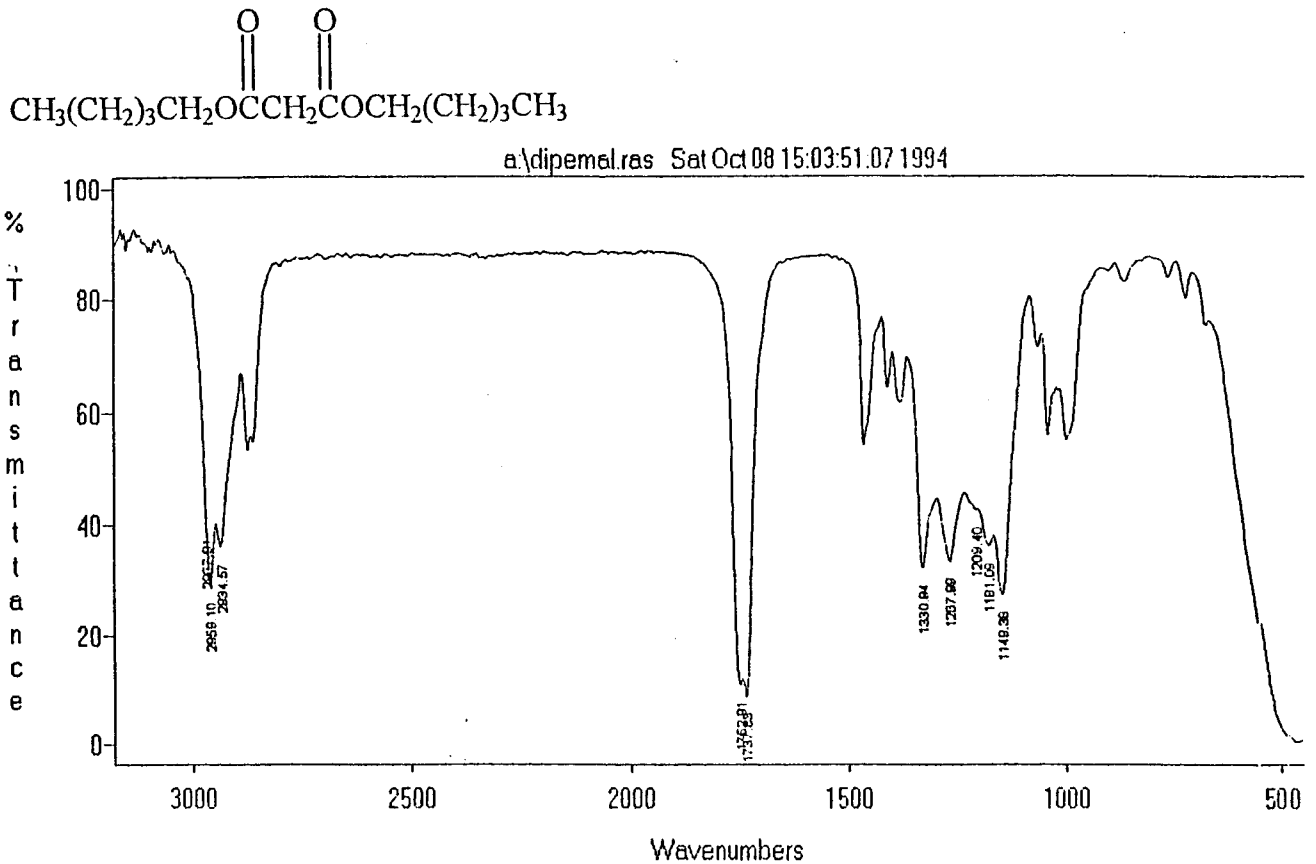
FTIR of Dibutylmalonate (43)



^{1}H NMR of Dibutylmalonate (43)



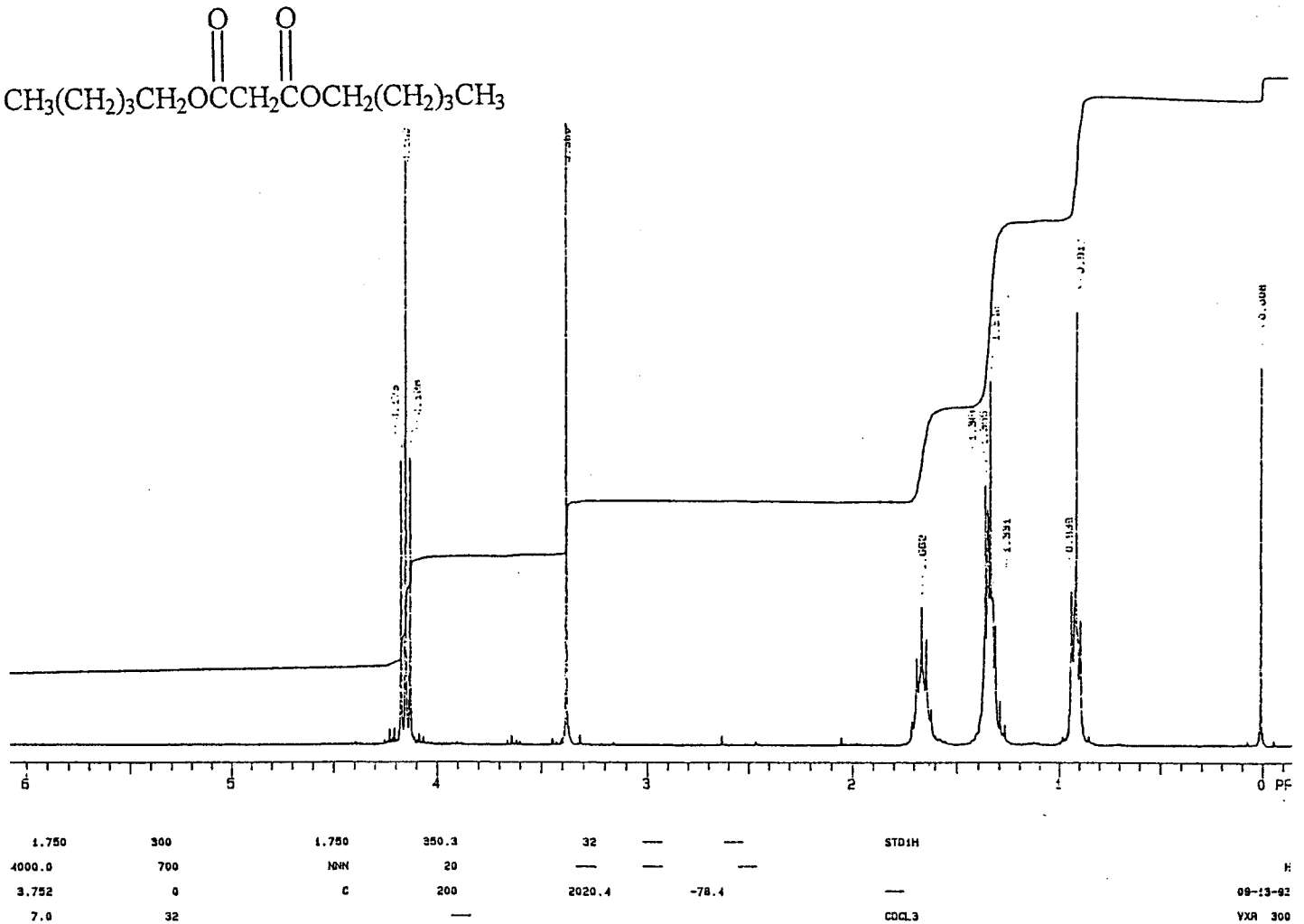
^{13}C NMR of Dibutylmalonate (43)



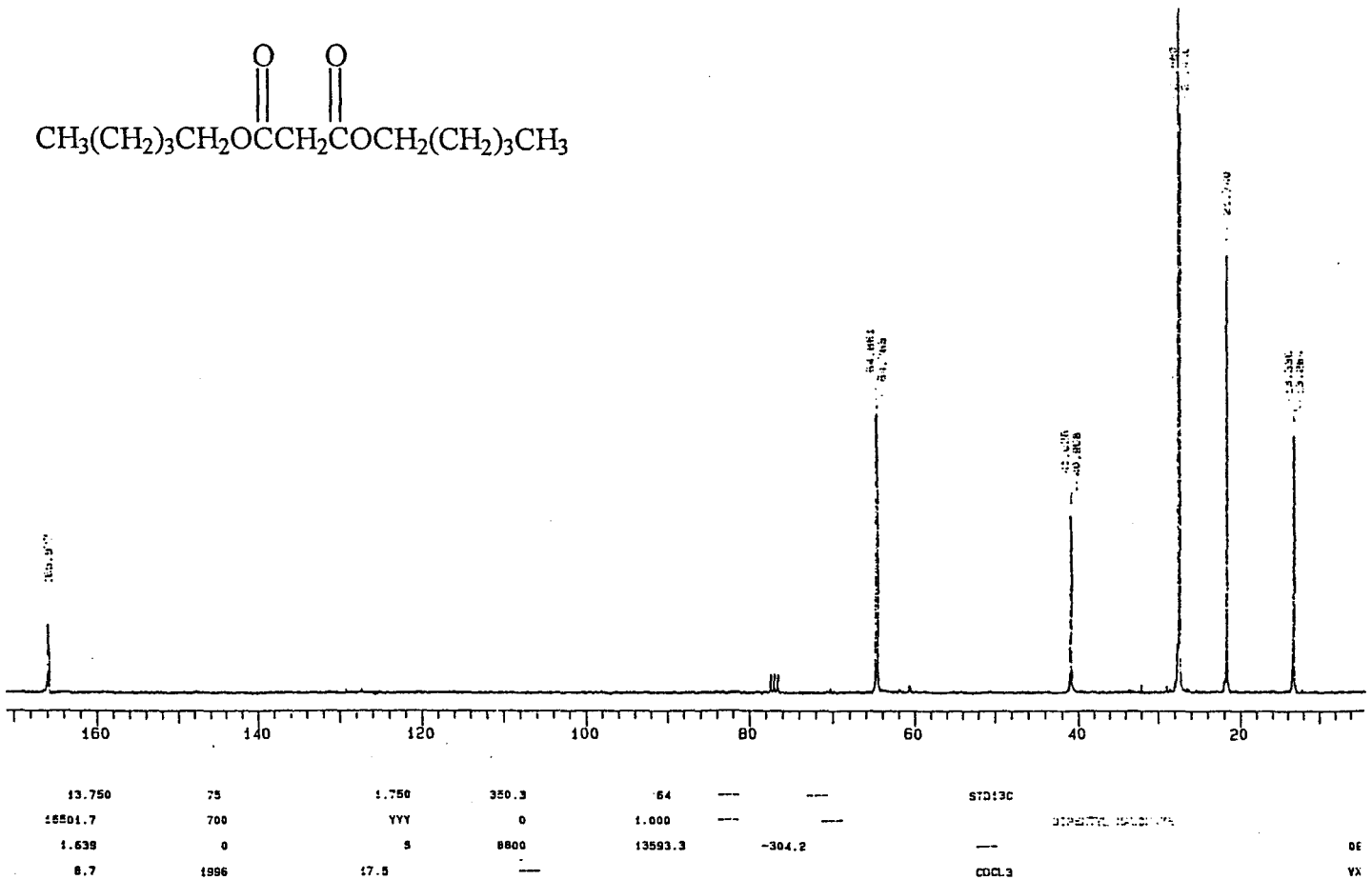
Peak Report
File: a:\dipemal.ras
Title: a:\dipemal.ras Sat Oct 08 15:03:51:07 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
1149.38	27.23	1181.09	36.10	1209.40	42.48	1267.99	33.32
1330.94	32.16	1737.83	8.85	1752.91	10.95	2934.57	36.33
2959.10	29.23	2967.91	40.58				

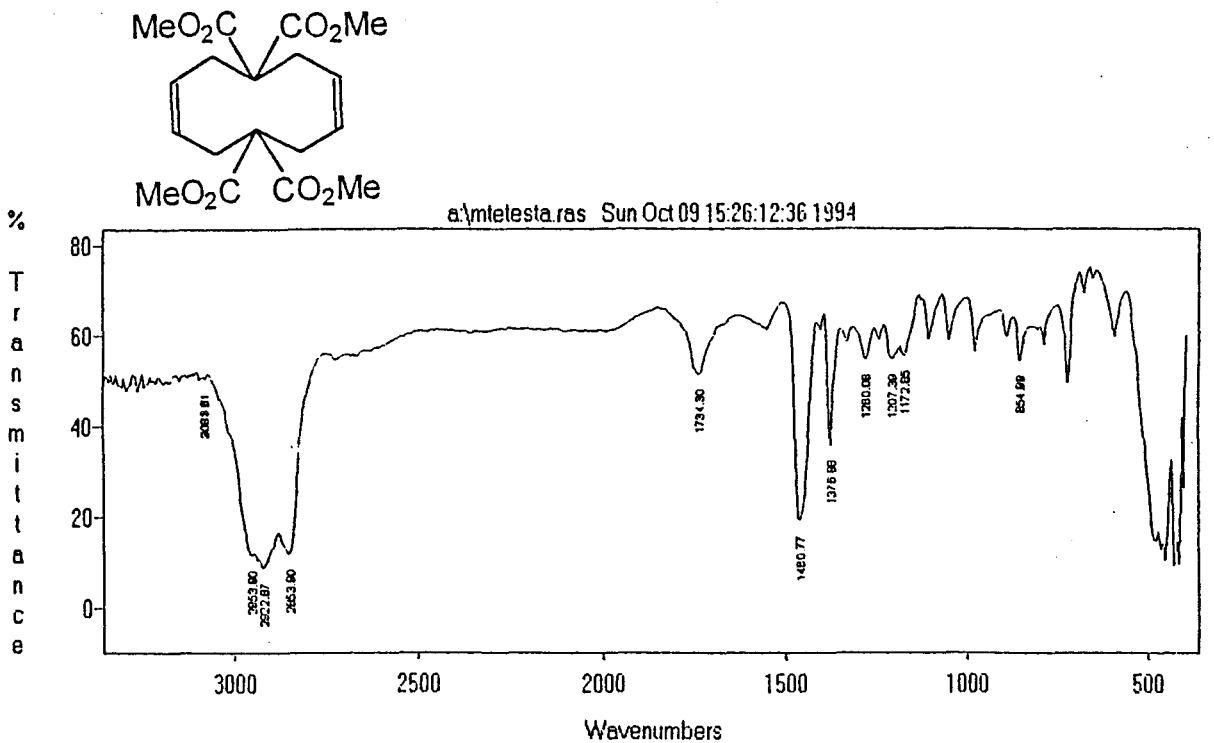
FTIR of Dipentylmalonate (39)



^{1}H NMR of Dipentylmalonate (39)



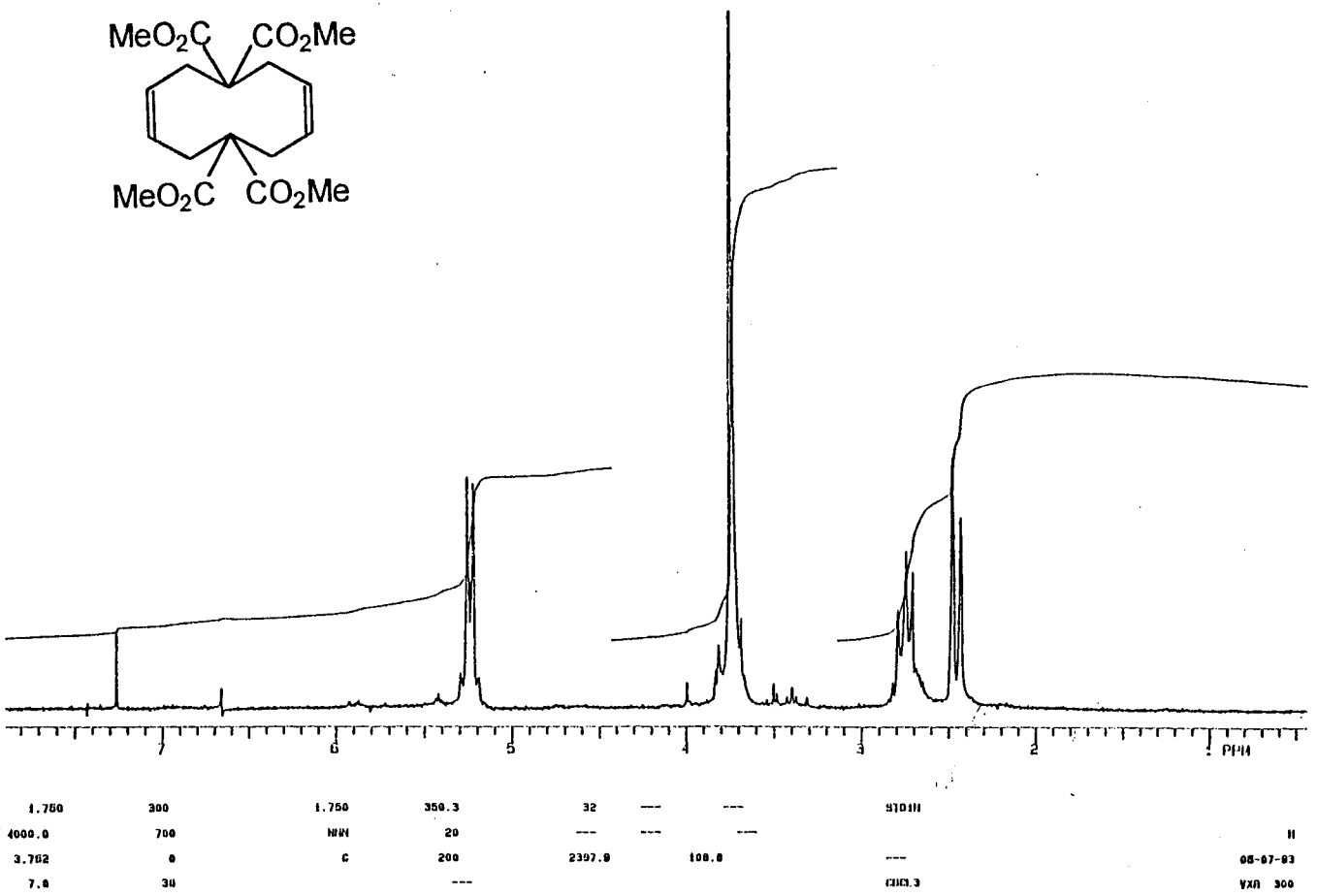
^{13}C NMR of Dipentylmalonate (39)



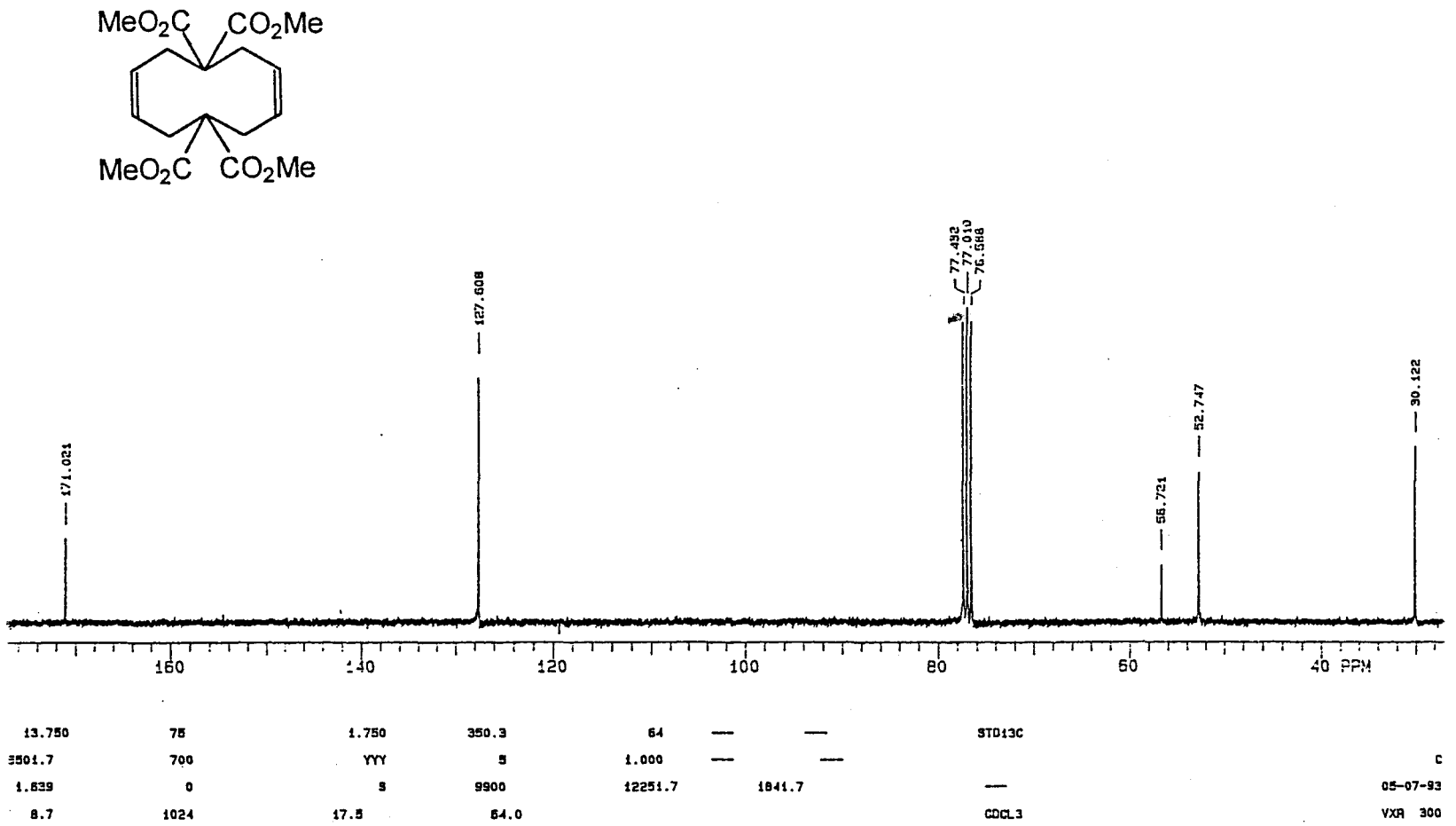
Peak Report
File: A:\MTETESTA.RAS
Title: a:\mtetesta.ras Sun Oct 09 15:26:12:36 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
854.99	54.37	1172.85	55.48	1207.39	54.74	1280.08	54.62
1376.88	35.62	1460.77	19.26	1734.30	51.46	2853.90	11.97
2922.87	9.11	2953.90	11.85	3081.91	50.75	3083.61	50.81

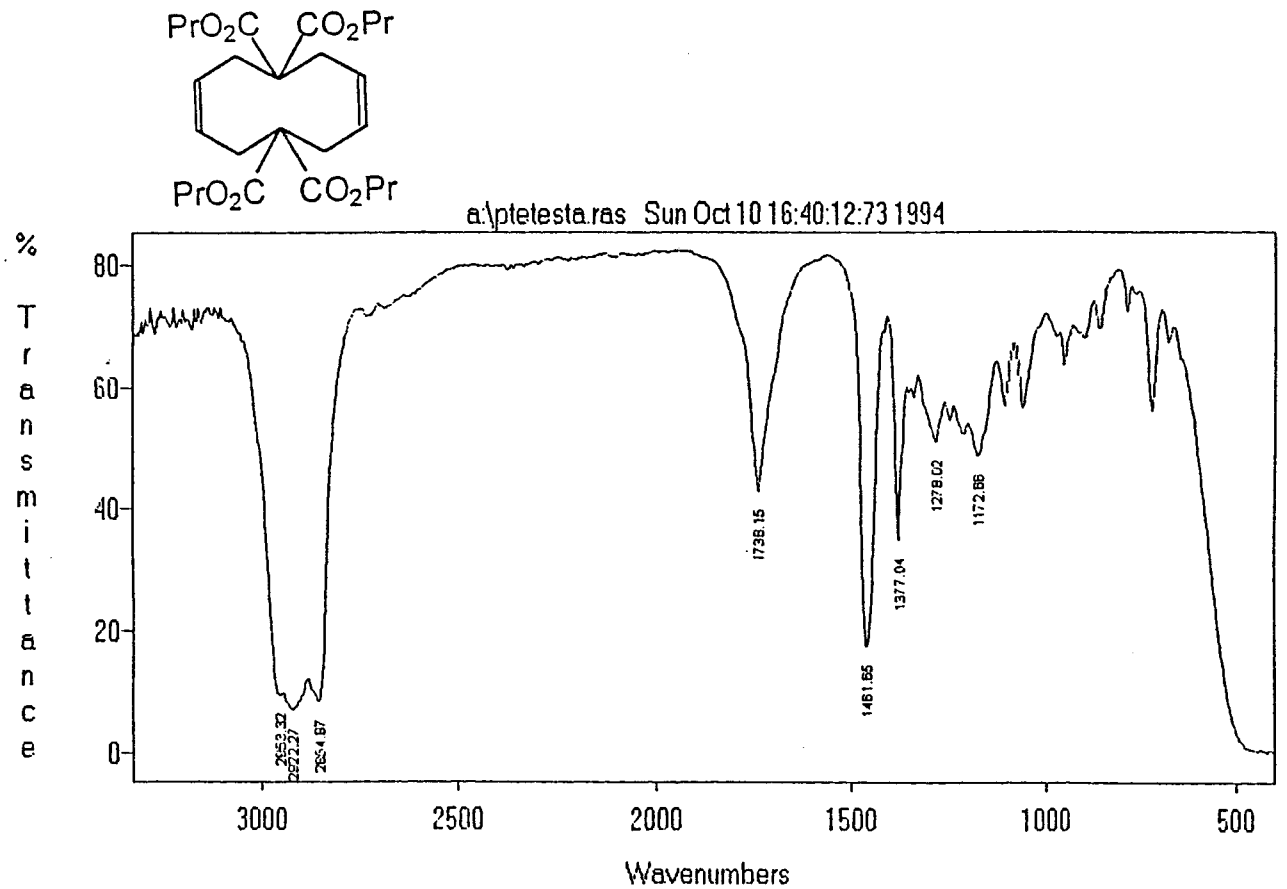
FTIR of Tetramethyl-*cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate (31)



^{1}H NMR of Tetramethyl-*cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate (31)



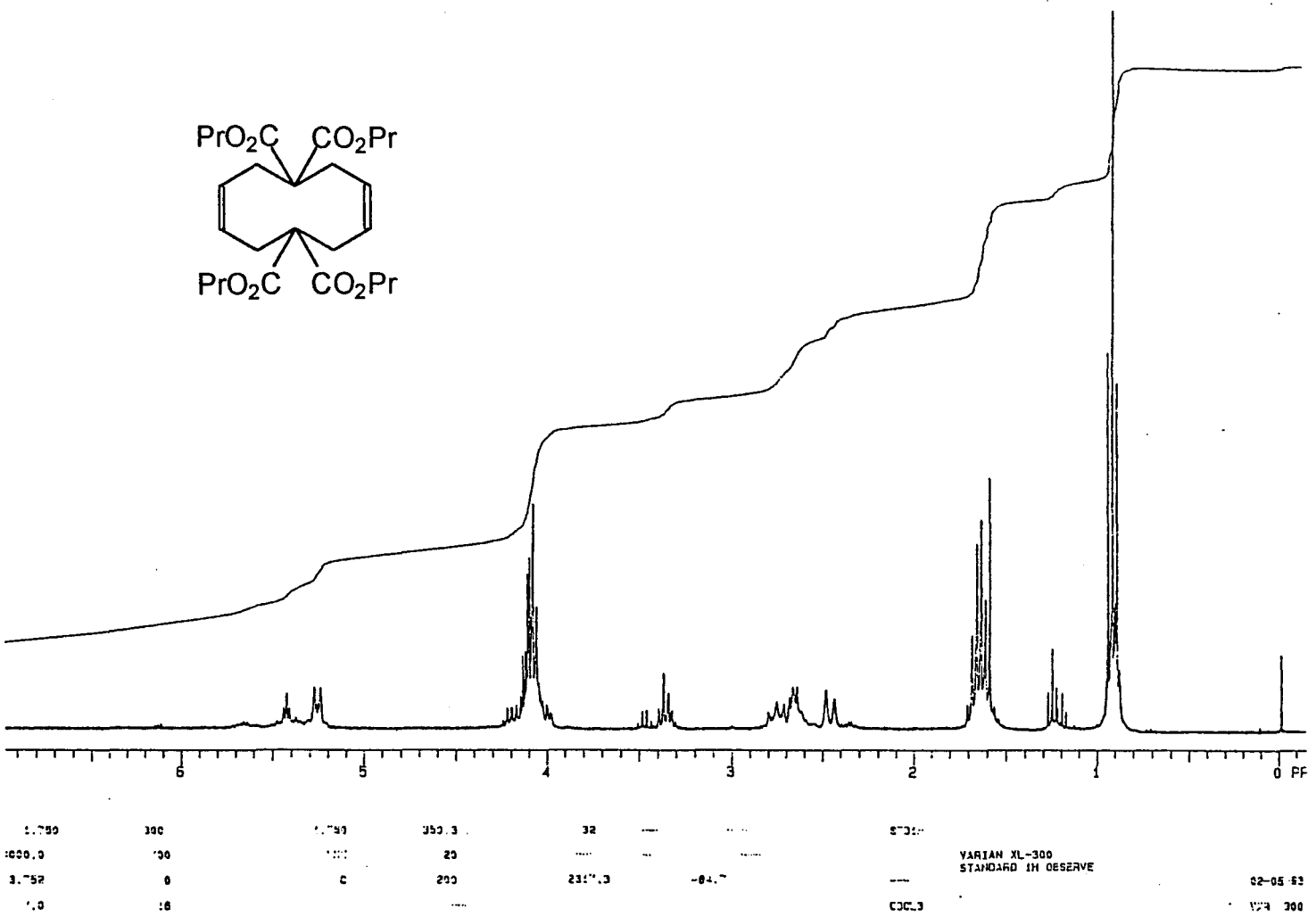
^{13}C NMR of Tetramethyl-*cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate **(31)**



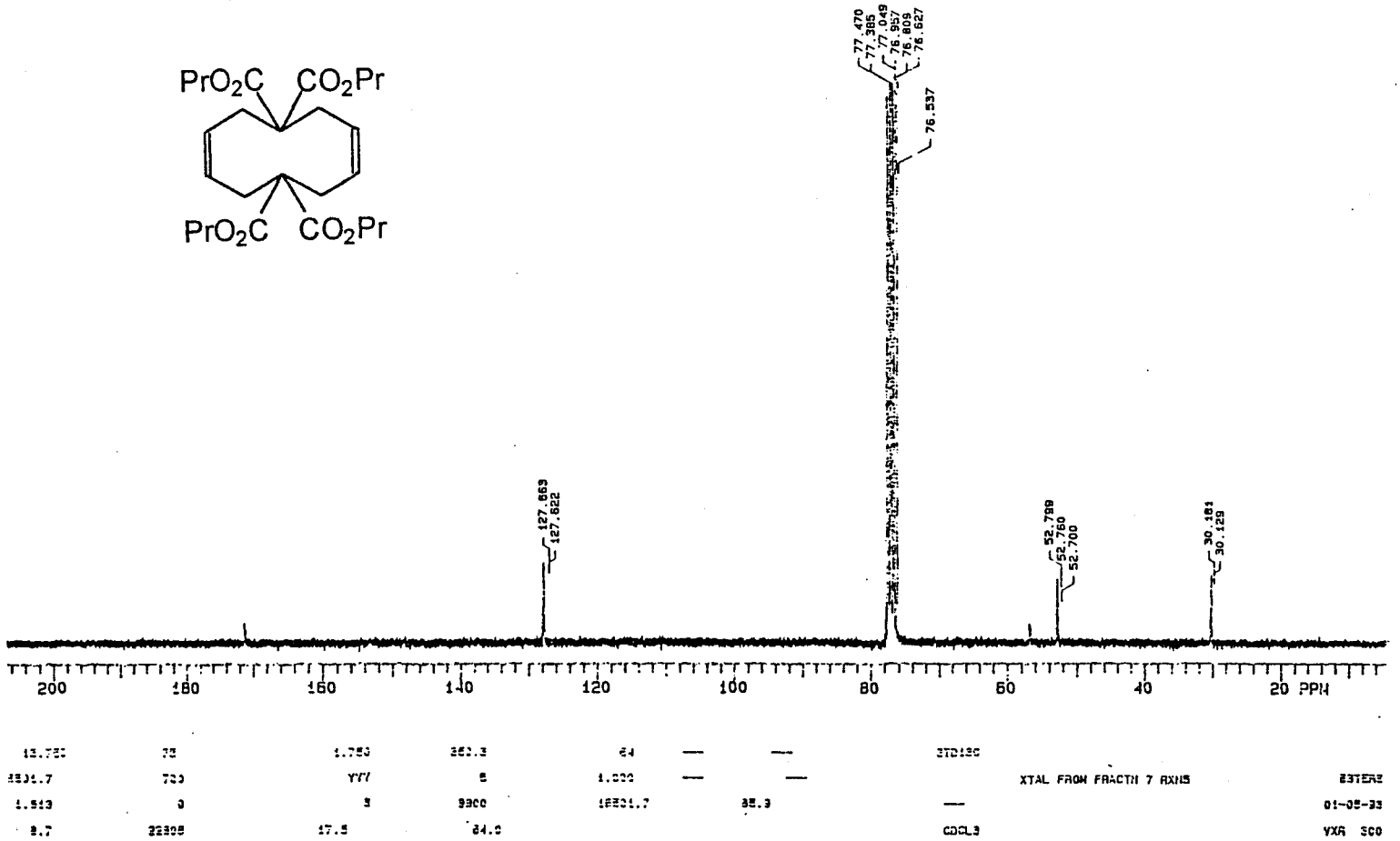
Peak Report
File: A:\PTETESTA.RAS
Title: a:\ptetesta.ras Sun Oct 10 16:40:12:73 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
1172.66	48.61	1278.02	50.98	1377.04	34.99	1461.65	17.50
1738.15	42.89	2854.87	8.42	2922.27	7.14	2953.32	9.47

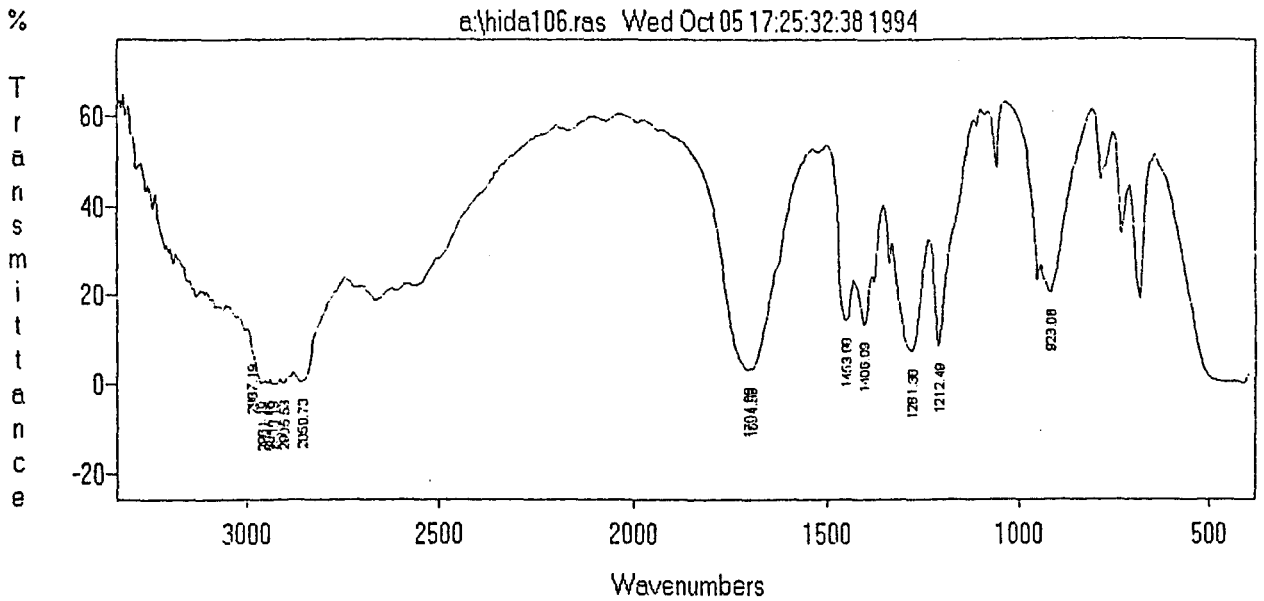
FTIR of Tetrapropyl-*cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate (36)



^{1}H NMR of Tetrapropyl-*cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate (36)



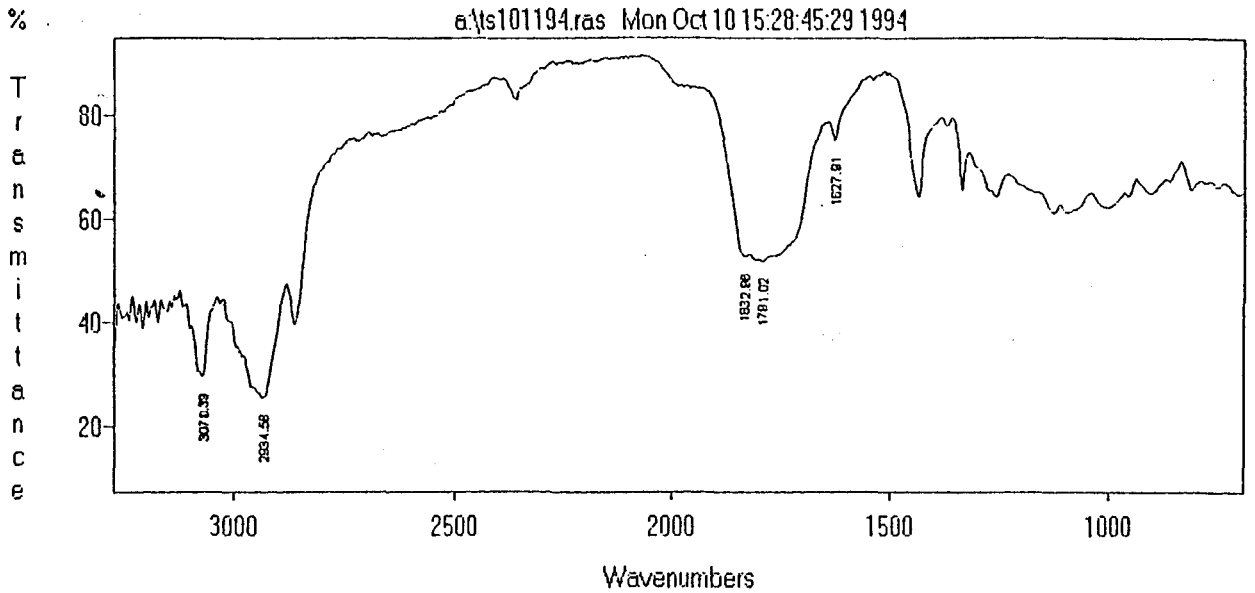
^{13}C NMR of Tetrapropyl-*cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate **(36)**



Peak Report
File: A:\HIDA105.RAS
Title: a:\hida106.ras Wed Oct 05 17:25:32:38 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
923.06	20.47	1212.49	8.24	1281.36	7.22	1406.09	13.05
1453.98	14.07	1694.56	3.24	1704.08	3.14	2859.73	0.50
2905.53	0.31	2933.19	0.00	2945.65	0.28	2961.19	0.16
2987.19	8.24						

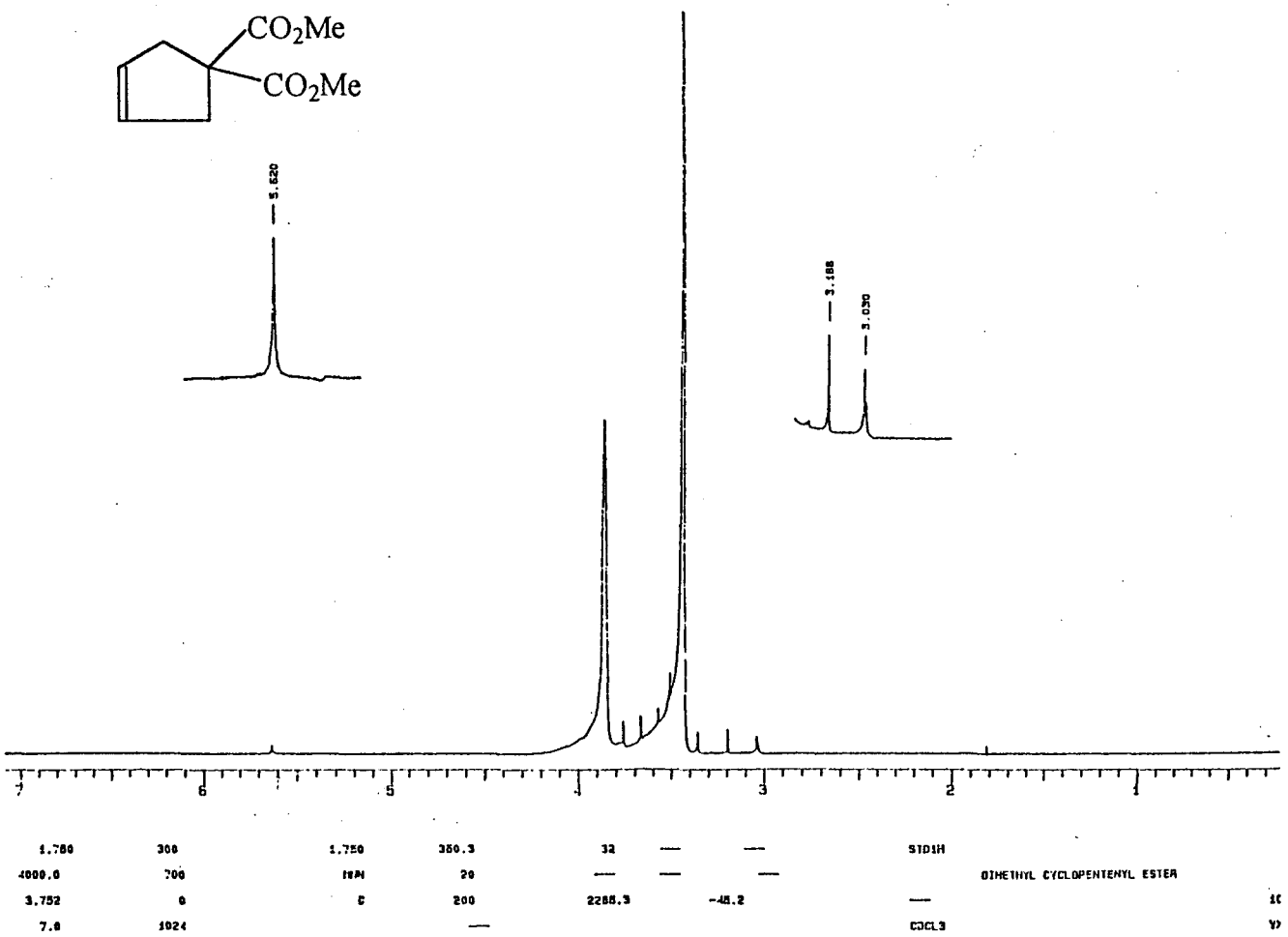
FTIR of Cyclopent-3-ene-1,1-diacid (11)



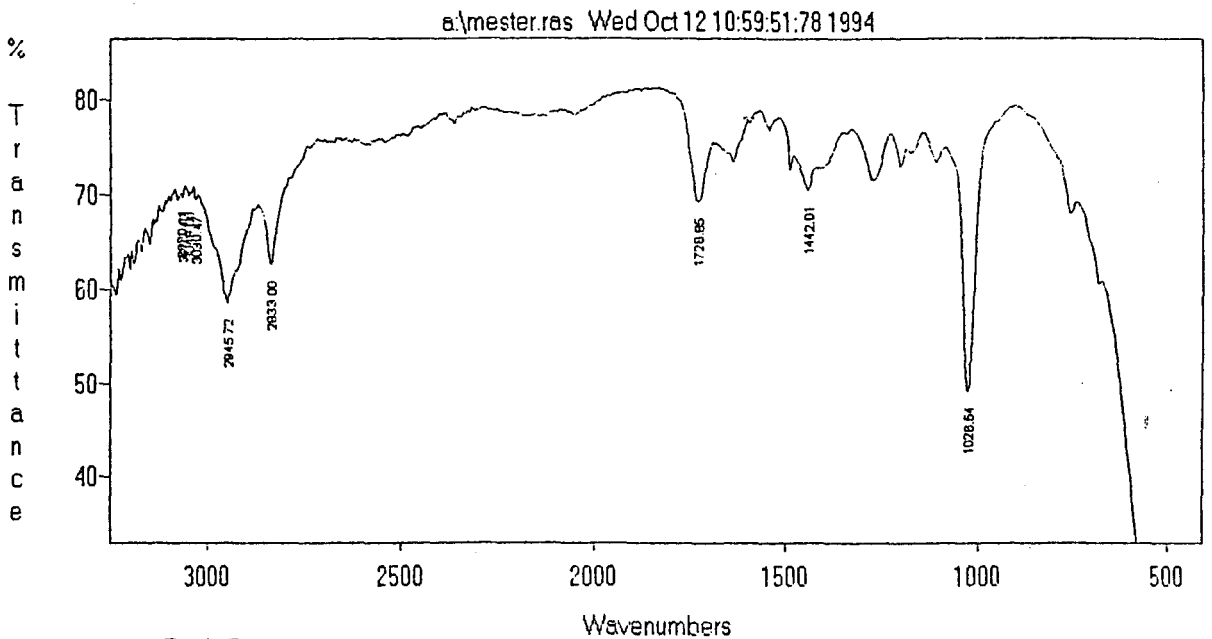
Peak Report
File: A:\TS101194.RAS
Title: a:\ts101194.ras Mon Oct 10 15:28:45:29 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
1627.91	75.25	1791.02	51.96	1832.96	52.73	2934.58	25.53
3070.11	29.77	3071.39	29.66				

FTIR of Cyclopent-3-ene-1,1-diacid chloride (47)



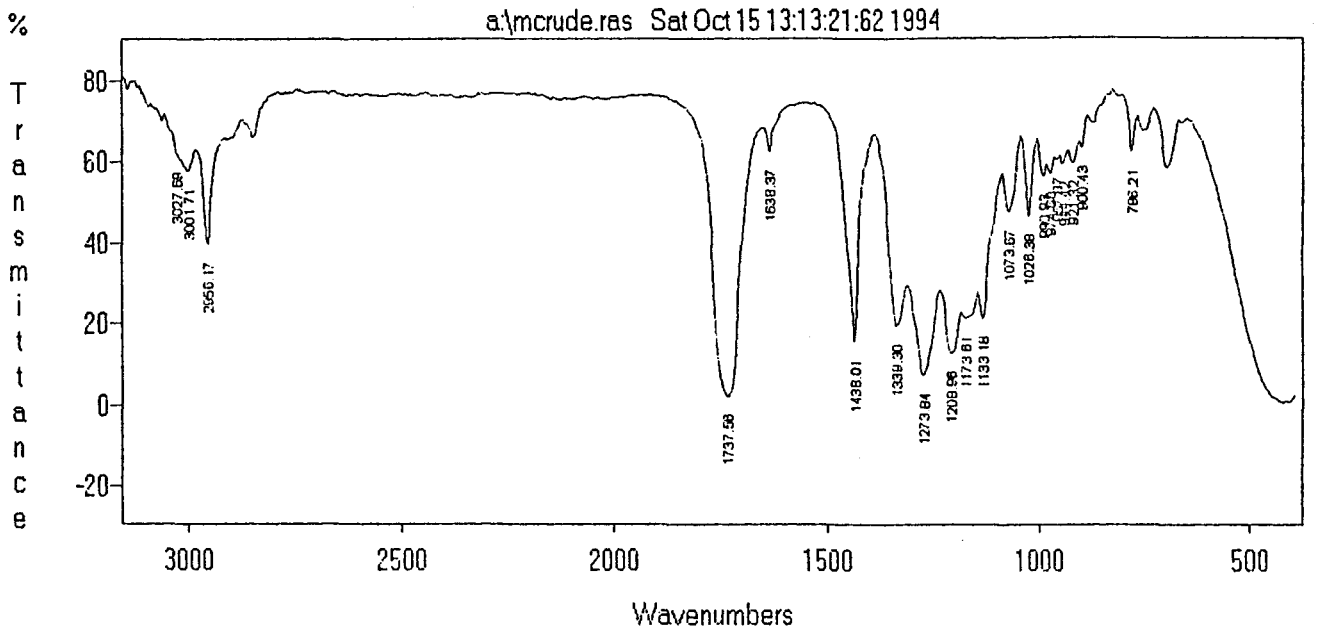
^{1}H NMR of Dimethyl cyclopent-3-ene-1,1-dicarboxylate (**29**)



Peak Report
File: A:\MESTER.RAS
Title: a:\mester.ras Wed Oct 12 10:59:51:78 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
1026.54	49.20	1442.01	70.53	1728.85	69.30	2833.00	62.57
2945.72	58.68	3030.47	69.49	3049.00	70.00	3065.42	69.70
3070.11	70.22						

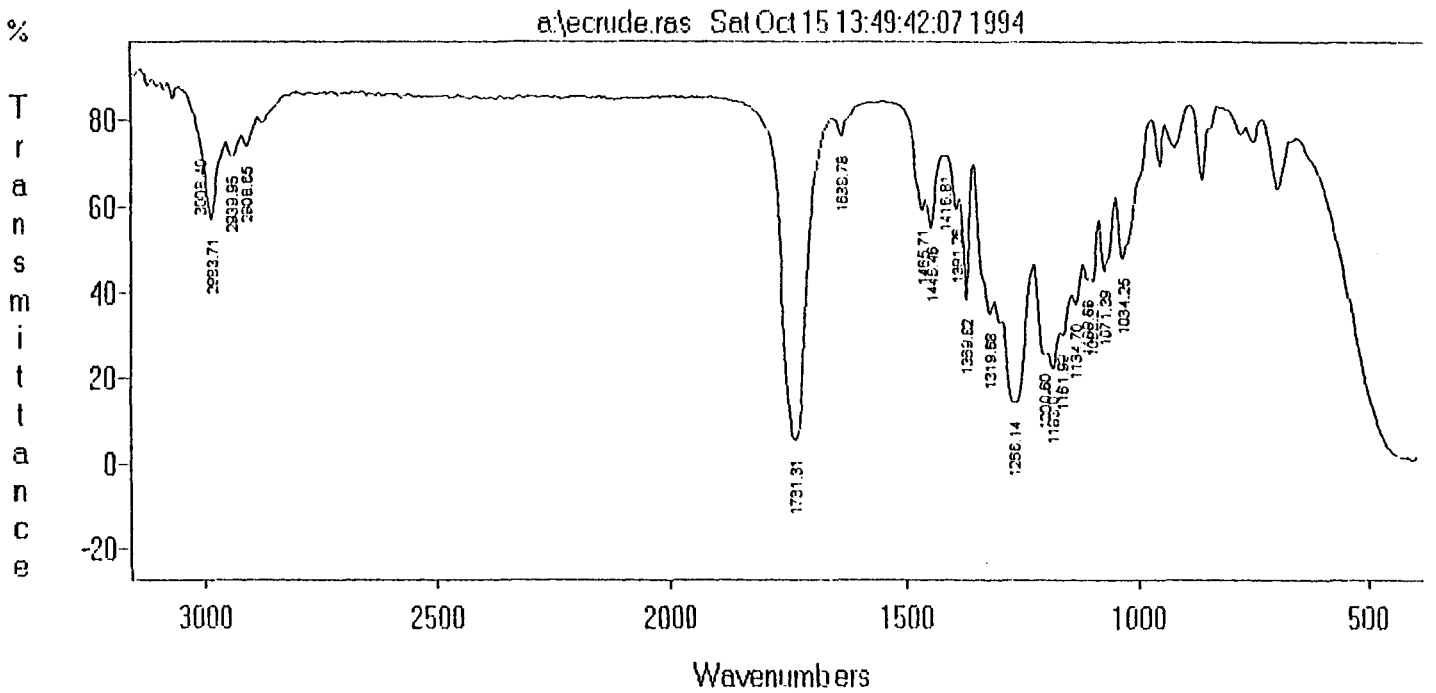
FTIR of Dimethyl cyclopent-3-ene-1,1-dicarboxylate (**29**)



Peak Report
File: A:\MCRUDE.RAS
Title: a:\mcrude.ras Sat Oct 15 13:13:21:62 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
786.21	62.58	900.43	63.31	921.32	59.83	944.42	59.43
957.87	60.58	974.68	57.01	990.93	56.42	1026.38	46.80
1073.67	47.82	1133.18	21.44	1173.61	21.57	1208.96	13.03
1273.84	7.67	1339.30	19.48	1438.01	15.82	1638.37	62.62
1737.56	2.32	2956.17	39.61	3001.71	57.96	3027.69	62.08

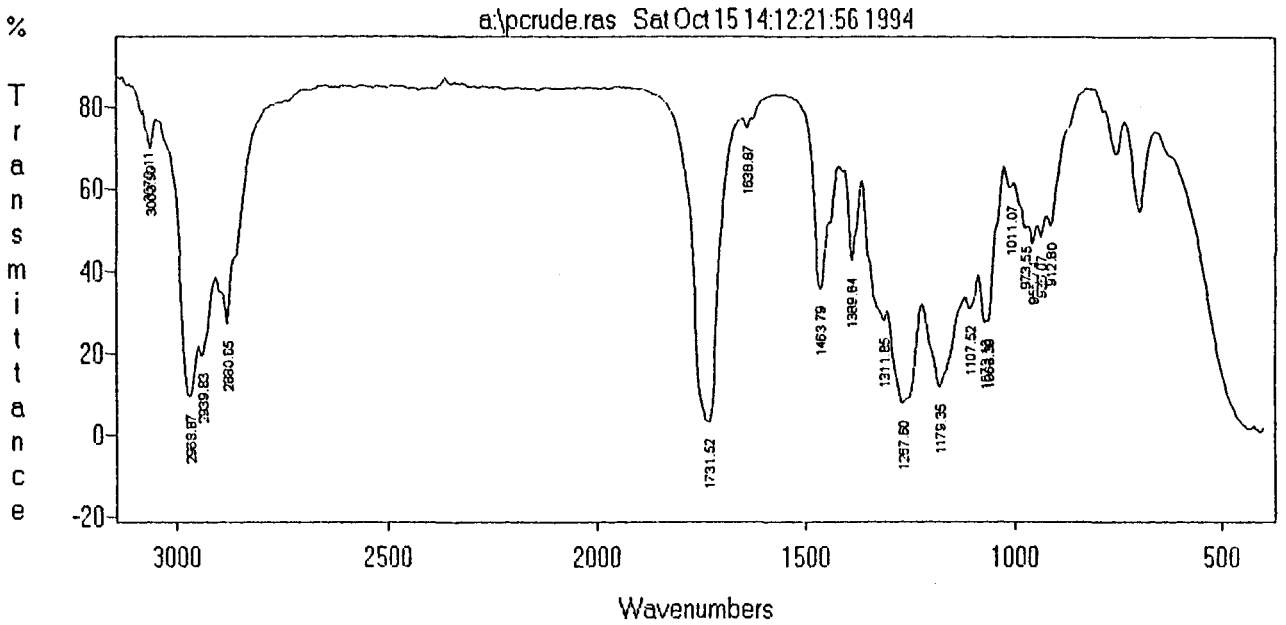
FTIR of Crude Reaction Mixture from Dimethyl malonate Cyclization



Peak Report
File: A:\ECRUDE.RAS
Title: a:\ecrude.ras Sat Oct 15 13:49:42:07 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
1034.25	47.90	1071.39	45.15	1098.21	42..65	1109.66	43.04
1134.70	37.29	1161.99	30.23	1183.01	22..26	1200.60	25.59
1266.14	14.46	1319.68	35.14	1369.82	38..43	1391.26	59.54
1416.81	71.76	1446.46	55.12	1465.71	59..26	1638.78	76.30
1731.31	5.65	2908.65	73.90	2939.95	71..73	2983.71	57.22
3008.40	75.49						

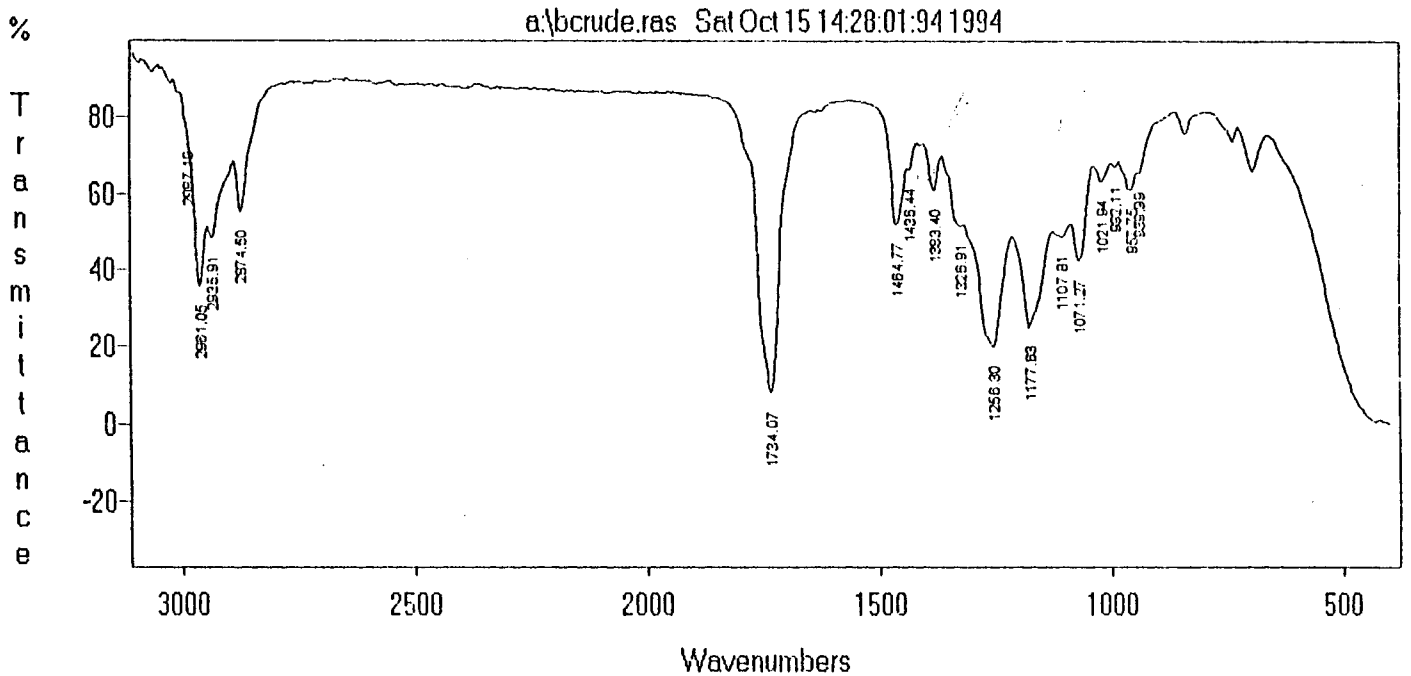
FTIR of Crude Reaction Mixture from Diethyl malonate Cyclization



Peak Report
File: a:\pcrude.ras
Title: a:\pcrude.ras Sat Oct 15 14:12:21:56 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
912.80	50.91	936.07	48.12	955.74	46.61	973.55	50.25
1011.07	60.15	1063.39	27.47	1072.13	27.24	1107.52	30.62
1179.35	11.48	1267.60	7.67	1311.85	27.85	1389.64	42.55
1463.79	35.74	1638.87	74.86	1731.52	3.15	2880.65	27.35
2939.83	19.33	2968.87	9.53	3063.99	69.97	3070.11	73.21

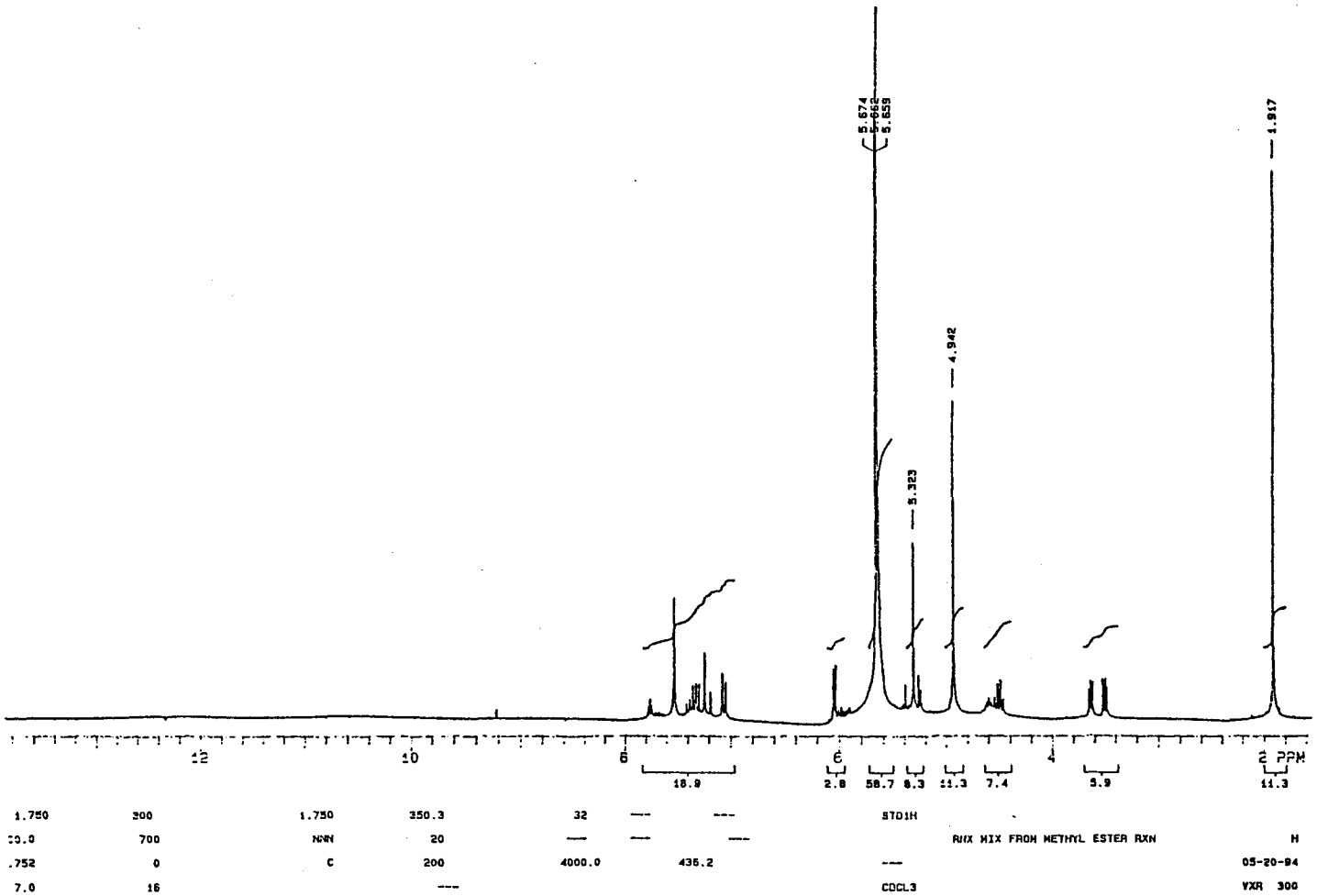
FTIR of Crude Reaction Mixture from Dipropyl malonate Cyclization



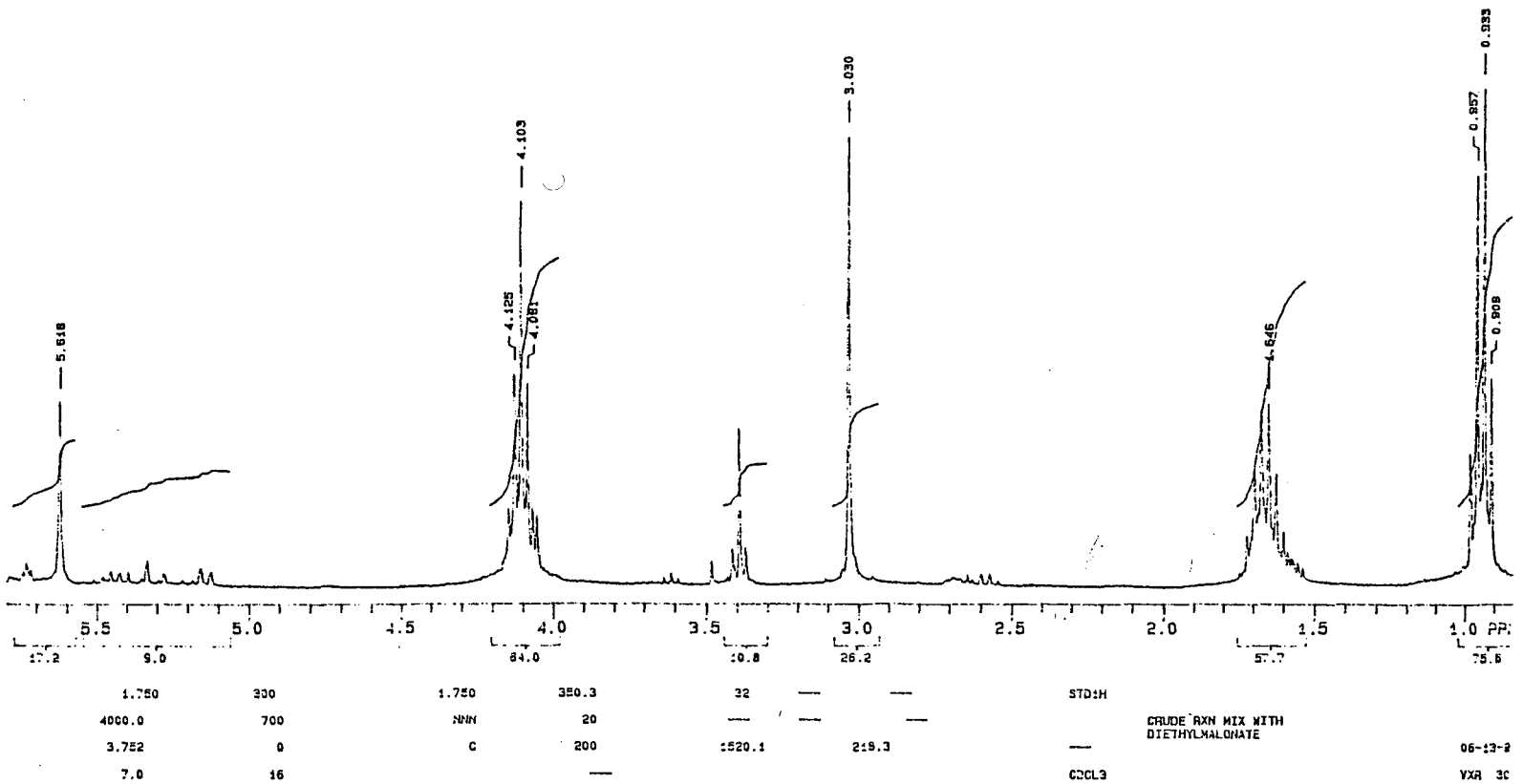
Peak Report
File: A:\BCRUDE.RAS
Title: a:\bcrude.ras Sat Oct 15 14:28:01:94 1994

cm-1	%T	cm-1	%T	cm-1	%T	cm-1	%T
939.99	65.80	957.75	61.51	992.11	67.33	1021.94	63.60
1071.27	42.60	1107.81	48.68	1177.63	25.20	1256.30	19.96
1326.91	51.78	1383.40	61.37	1436.44	66.66	1464.77	52.15
1734.07	8.30	2874.50	55.52	2935.91	48.49	2961.05	35.68
2987.19	76.03						

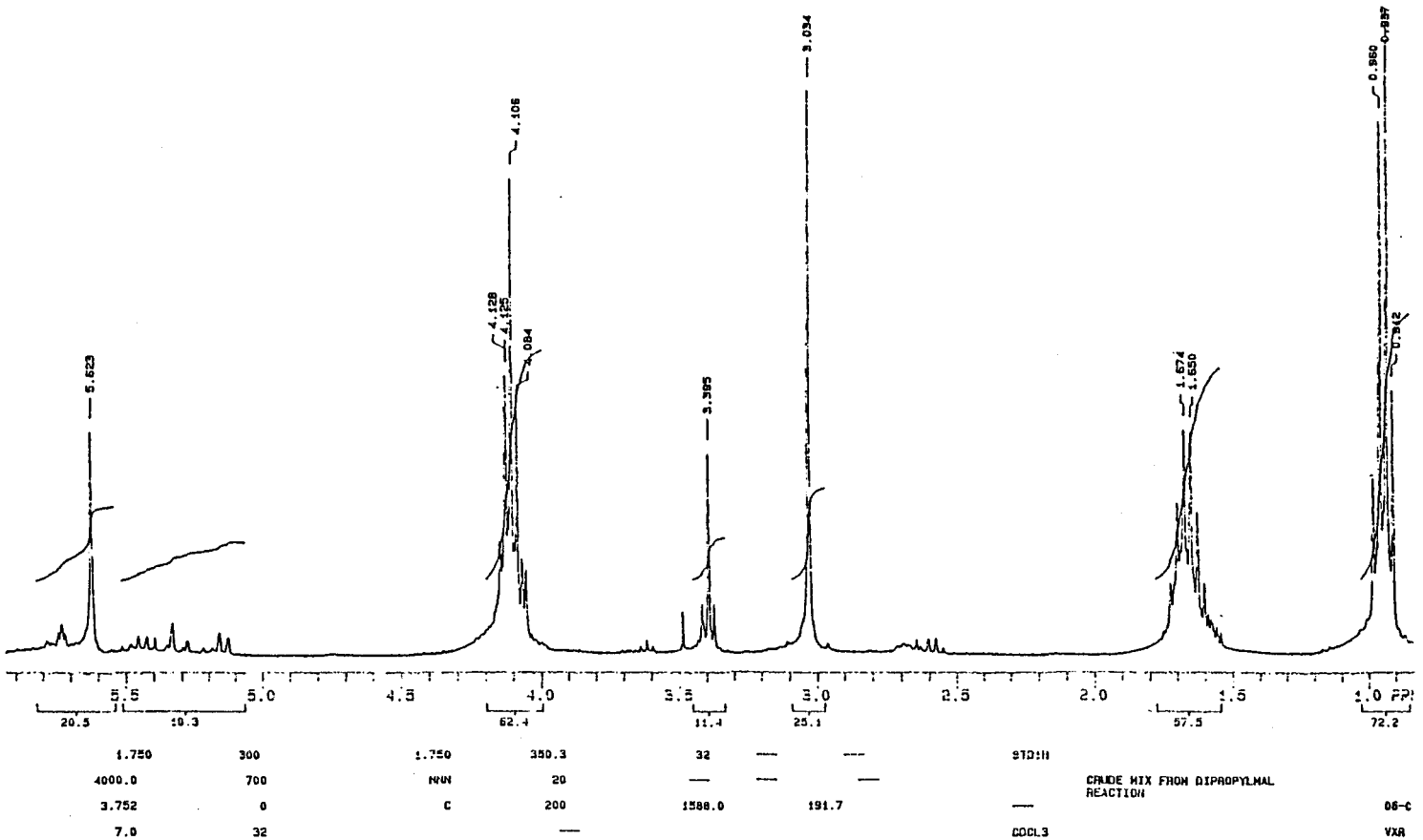
FTIR of Crude Reaction Mixture from Dibutyl malonate Cyclization



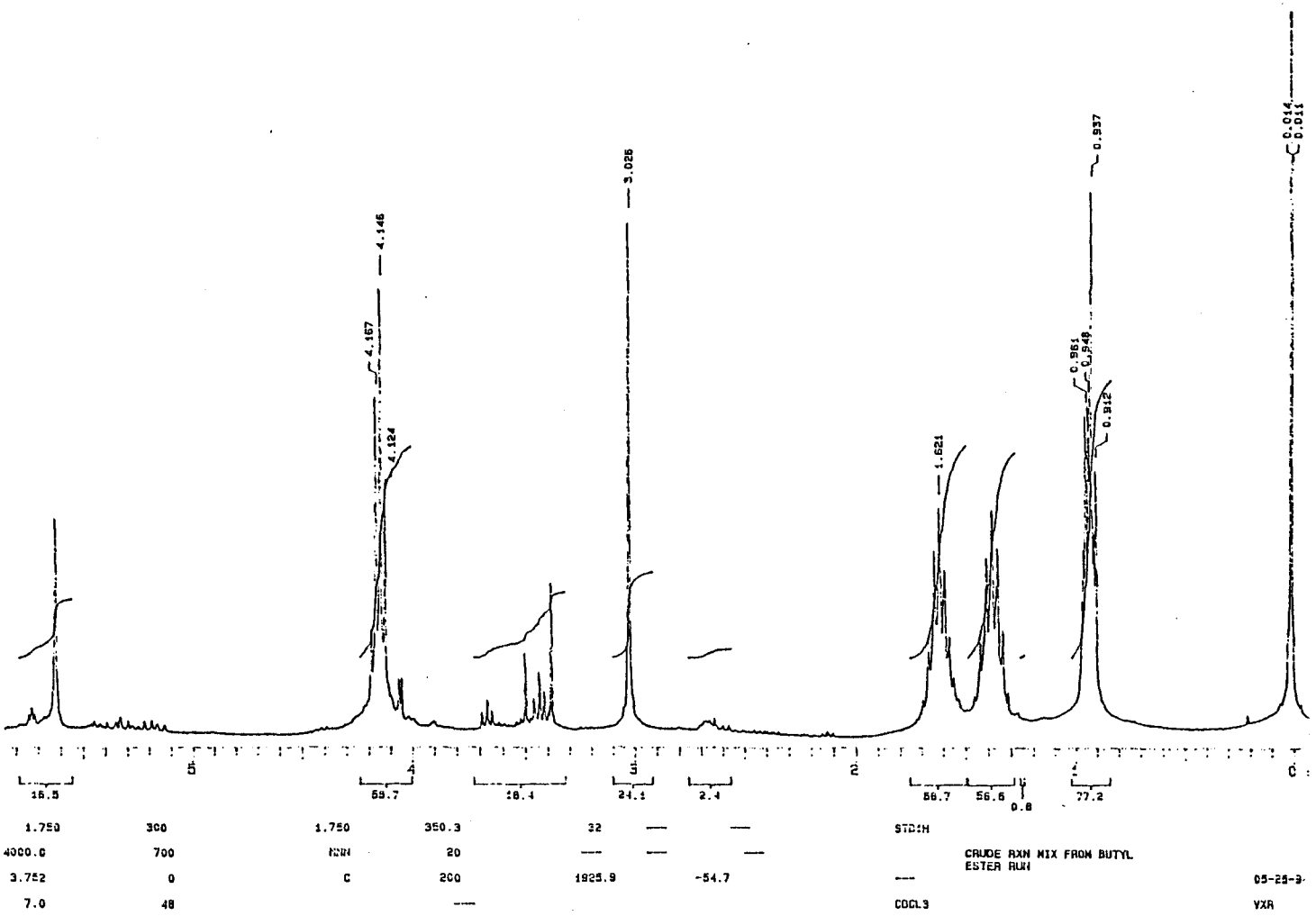
^{1}H NMR of Crude Reaction Mixture from Dimethyl malonate Cyclization



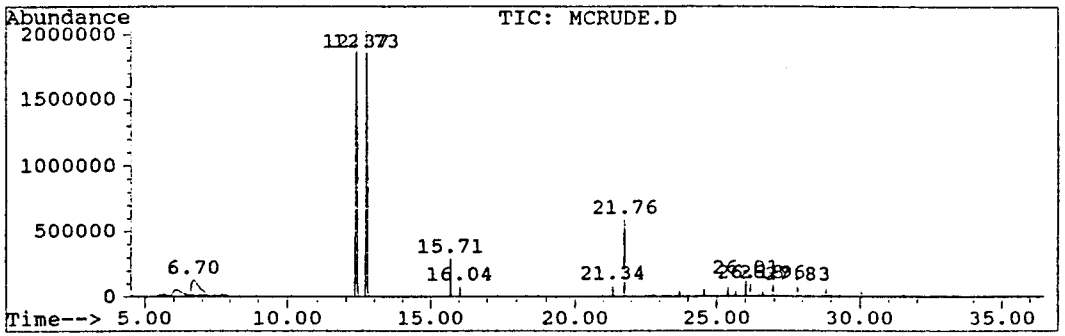
^{1}H NMR of Crude Reaction Mixture from Diethyl malonate Cyclization



^{1}H NMR of Crude Reaction Mixture from Dipropyl malonate Cyclization

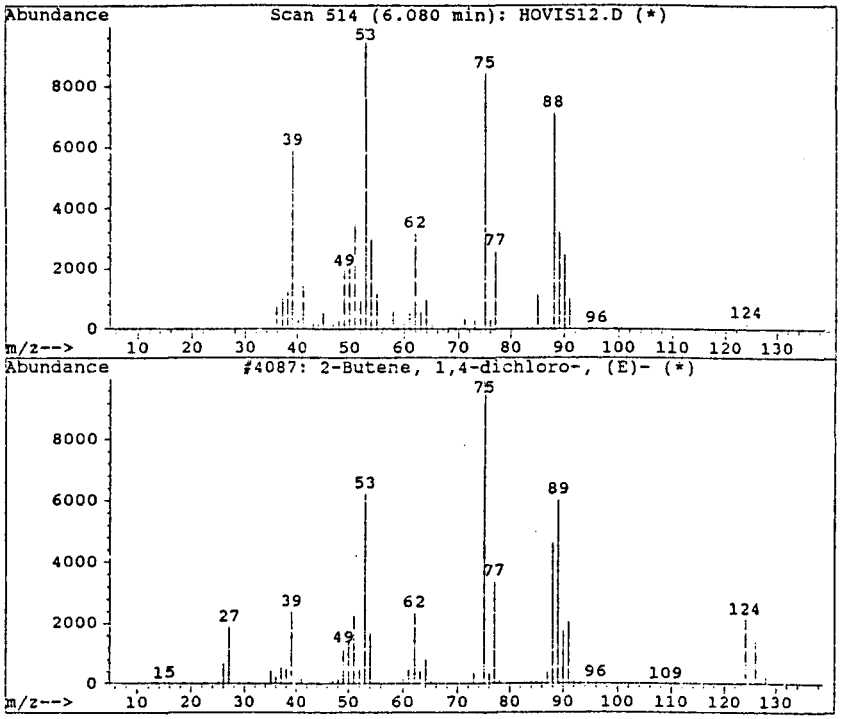


^{1}H NMR of Crude Reaction Mixture from Dibutyl malonate Cyclization

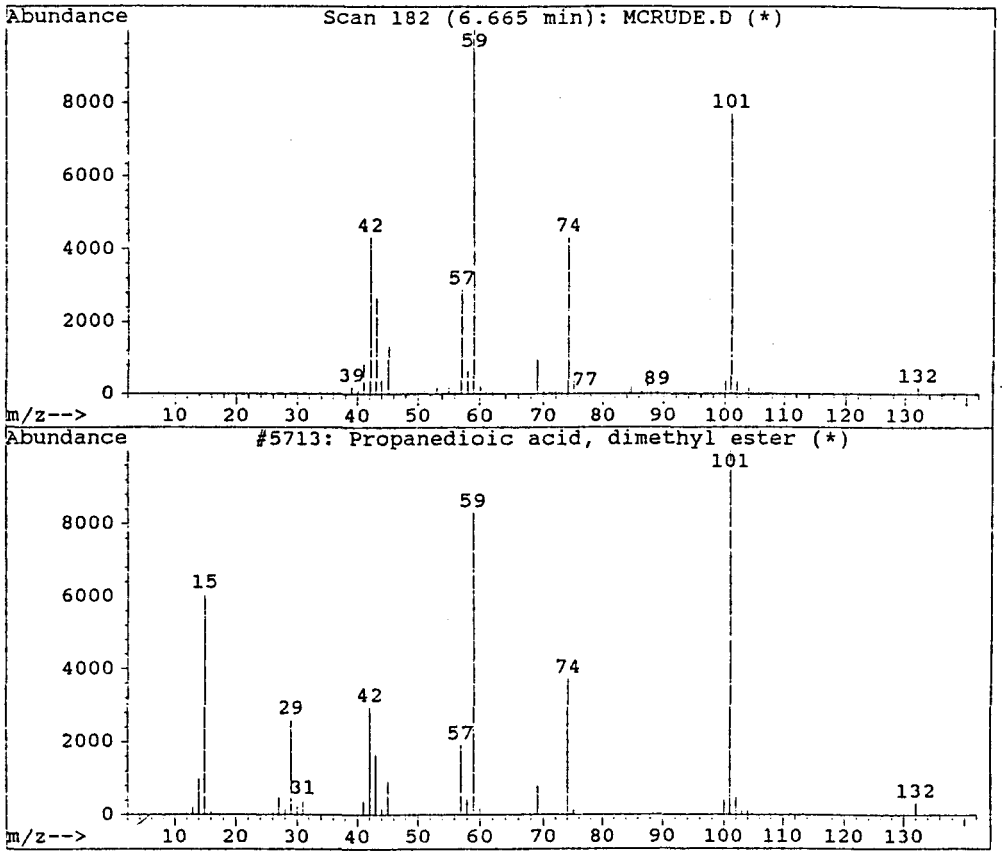


Retention Time	Area	Area %	Ratio %
Total Ion Chromatogram			
6.702	23155095	14.344	37.613
12.366	61561087	38.137	100.000
12.731	53700778	33.267	87.232
15.706	4512975	2.796	7.331
16.036	1144834	0.709	1.860
21.341	1103868	0.684	1.793
21.763	10008774	6.200	16.258
26.013	1764788	1.093	2.867
26.178	1406968	0.872	2.285
26.956	1505602	0.933	2.446
27.827	1558171	0.965	2.531

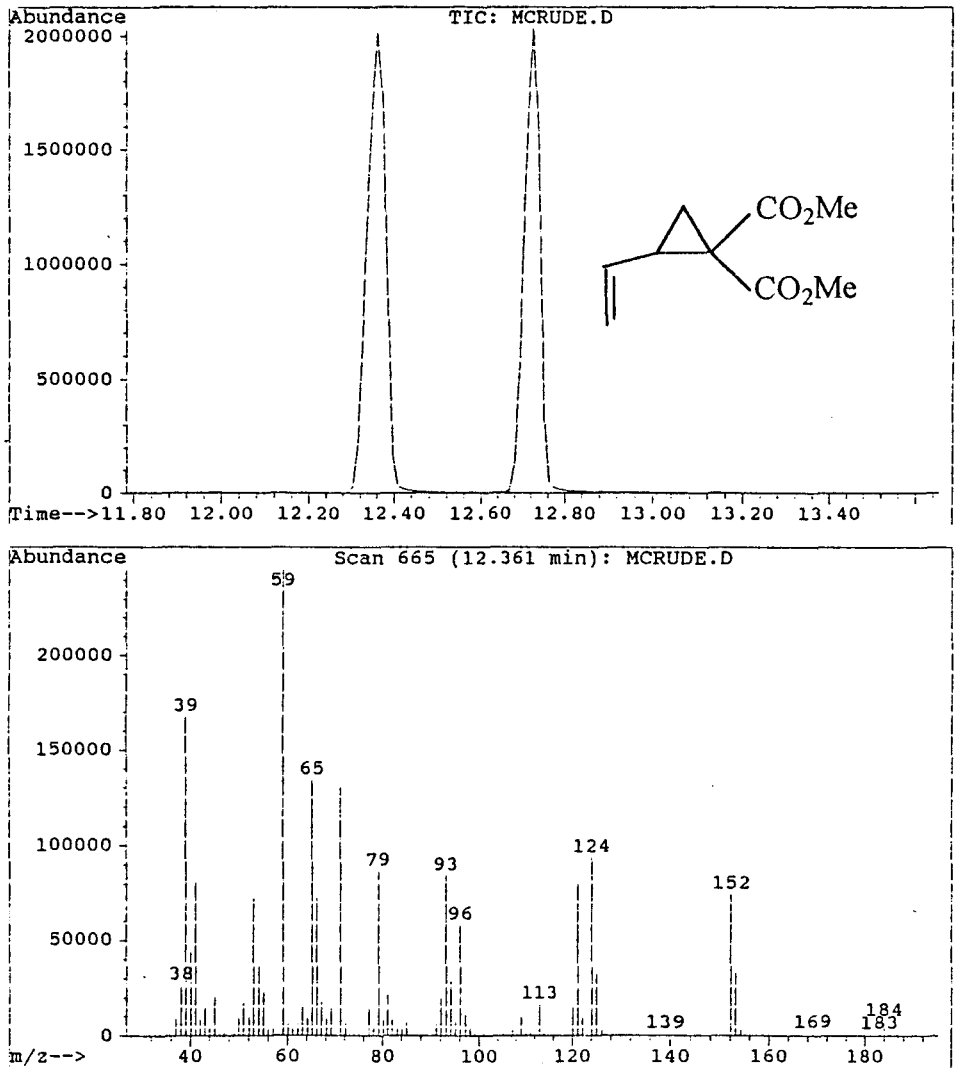
GC/MS Data for the Reaction of Dimethylmalonate with *cis*-1,4-dichloro-2-butene



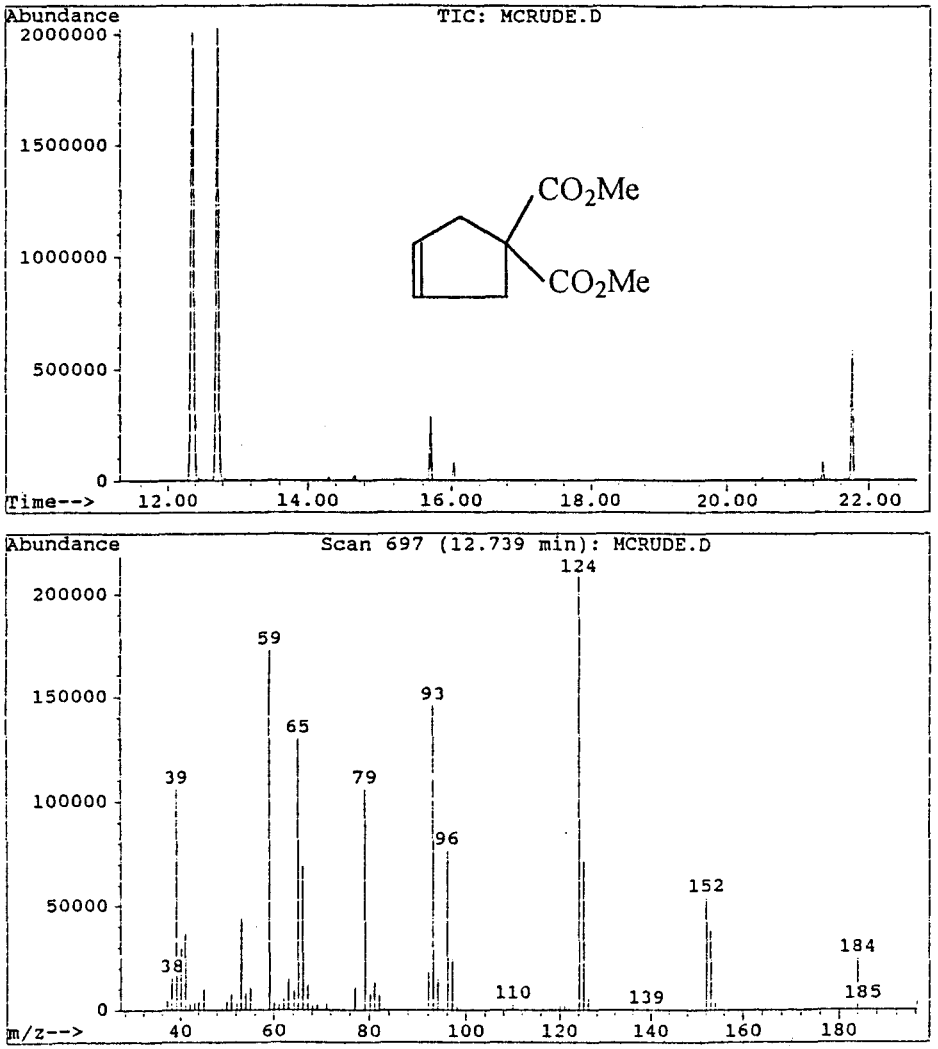
GC/MS Data for *cis*-1,4-dichloro-2-butene (2)



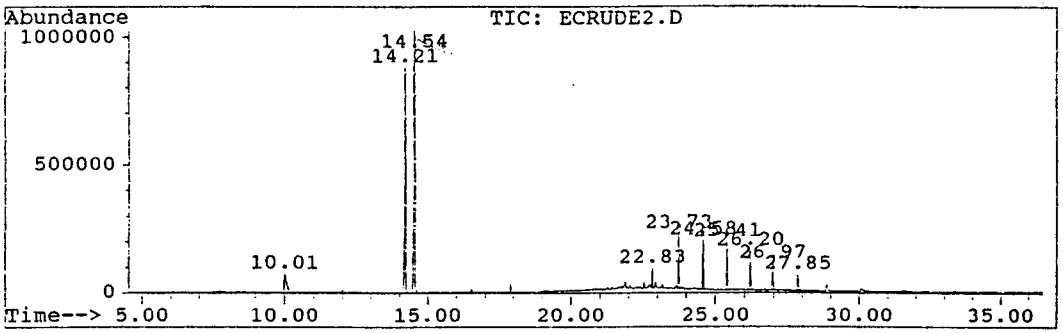
GC/MS Data for Dimethylmalonate



GC/MS Data for Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**30**)

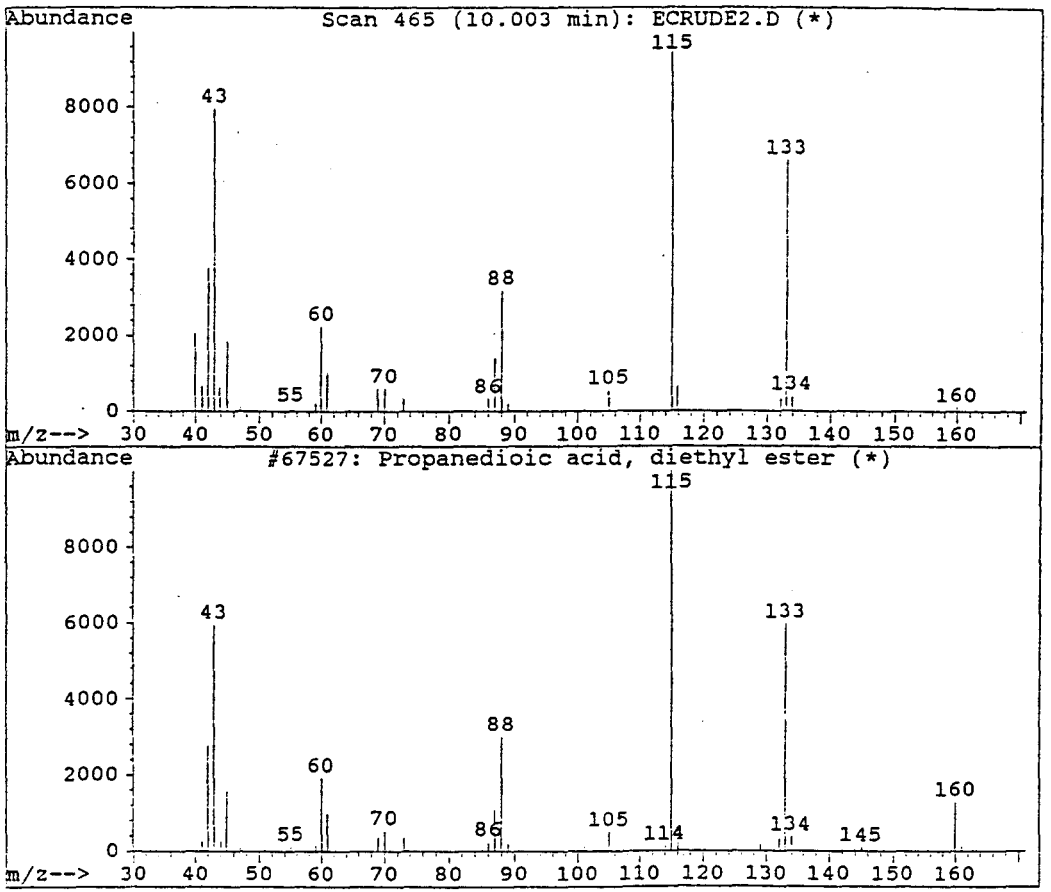


GC/MS Data for Dimethyl-cyclopent-3-ene-1,1-dicarboxylate (**29**)

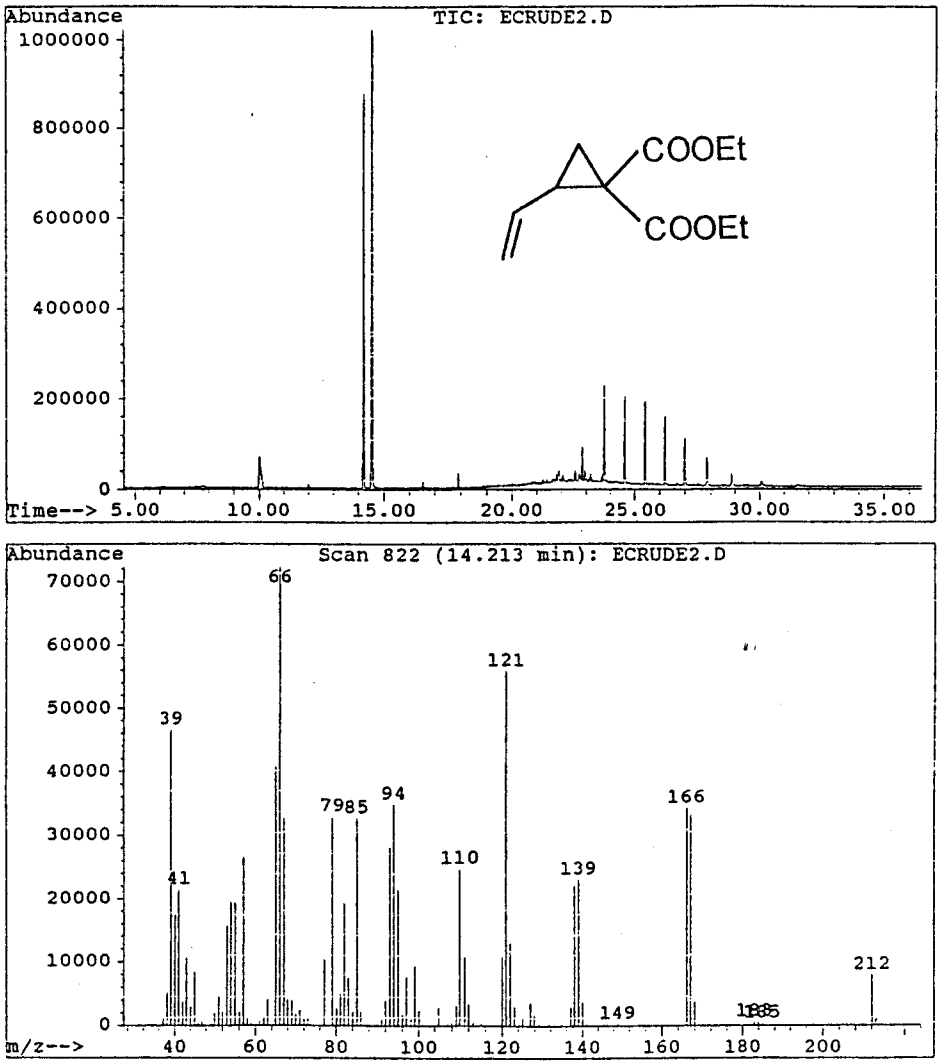


Retention Time	Area	Area %	Ratio %
Total Ion Chromatogram			
10.009	4036971	6.045	15.516
14.211	19614662	29.373	75.389
14.540	26018010	38.963	100.000
22.834	1378627	2.065	5.299
23.731	3649164	5.465	14.026
24.584	3057952	4.579	11.753
25.406	3003453	4.498	11.544
26.196	2635309	3.946	10.129
26.975	1944377	2.912	7.473
27.848	1438528	2.154	5.529

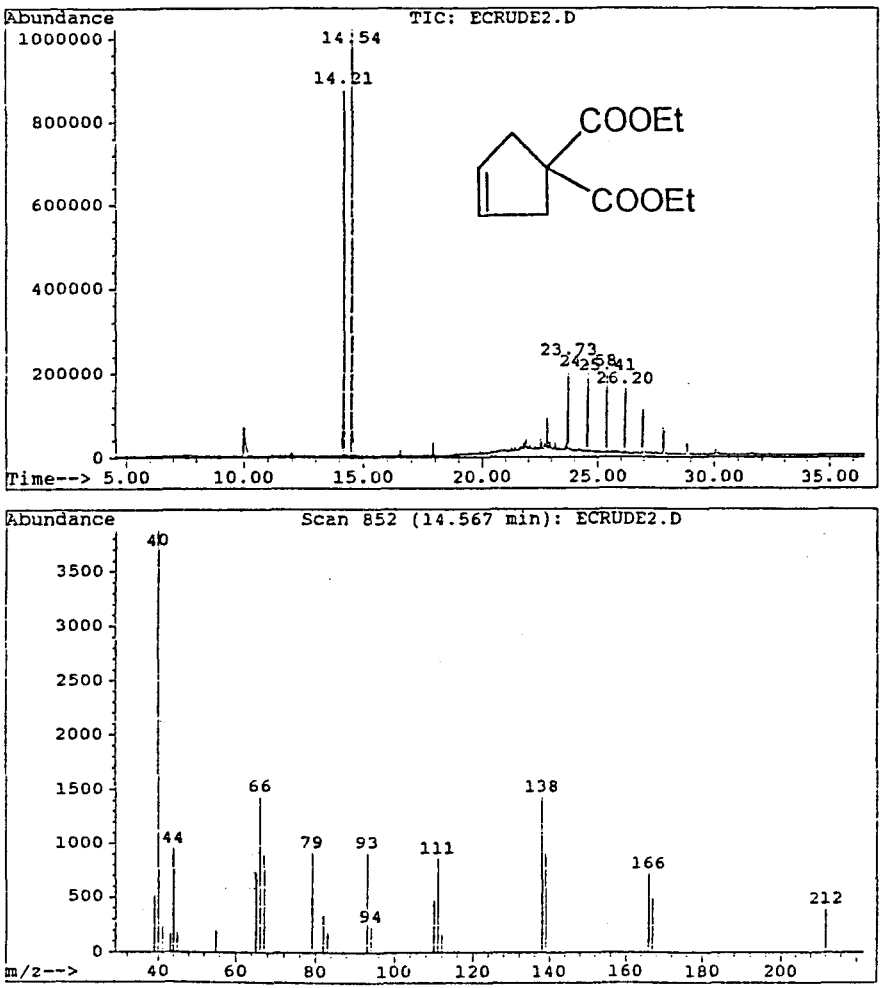
GC/MS Data for the Reaction of Diethylmalonate with *cis*-1,4-dichloro-2-butene



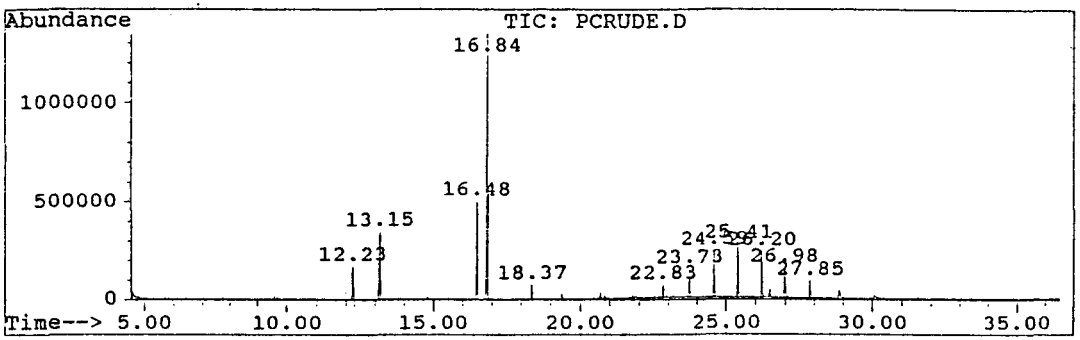
GC/MS Data for Diethylmalonate (3)



GC/MS Data for Diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**6**)

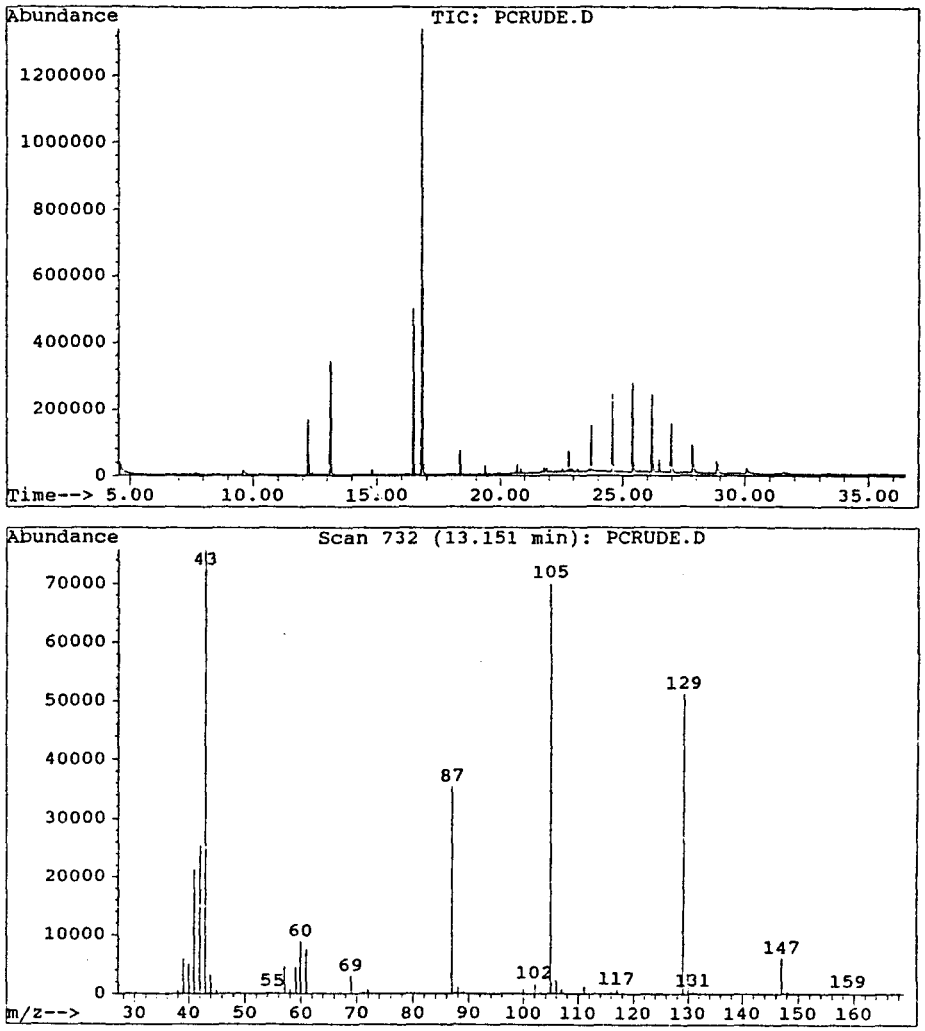


GC/MS Data for Diethyl-cyclopent-3-ene-1,1-dicarboxylate (5)

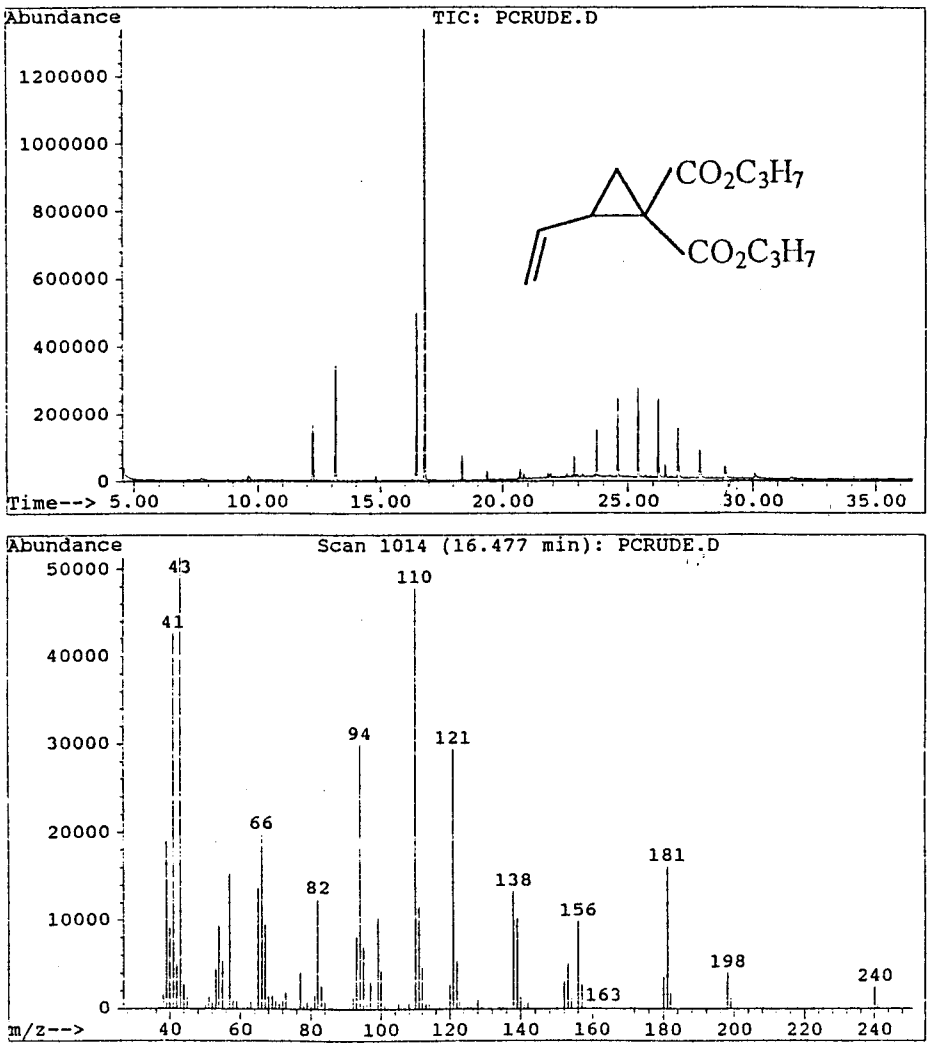


Retention Time	Area	Area %	Ratio %
Total Ion Chromatogram			
12.227	4147125	5.761	14.130
13.151	7380622	10.253	25.147
16.484	8598518	11.945	29.297
16.836	29349942	40.774	100.000
18.366	974697	1.354	3.321
22.833	1072930	1.491	3.656
23.728	2564051	3.562	8.736
24.585	3906719	5.427	13.311
25.409	4400241	6.113	14.992
26.198	4055745	5.634	13.819
26.979	3220929	4.475	10.974
27.852	2310794	3.210	7.873

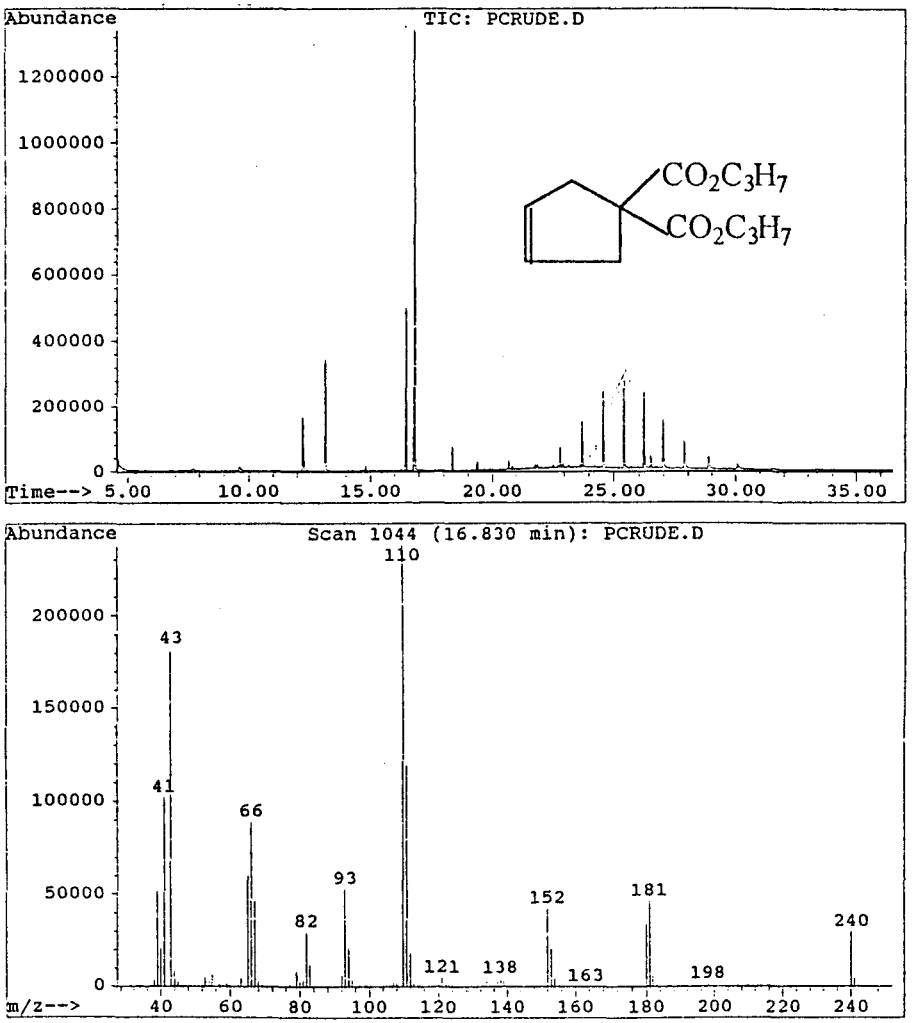
GC/MS Data for the Reaction of Dipropylmalonate with *cis*-1,4-dichloro-2-butene



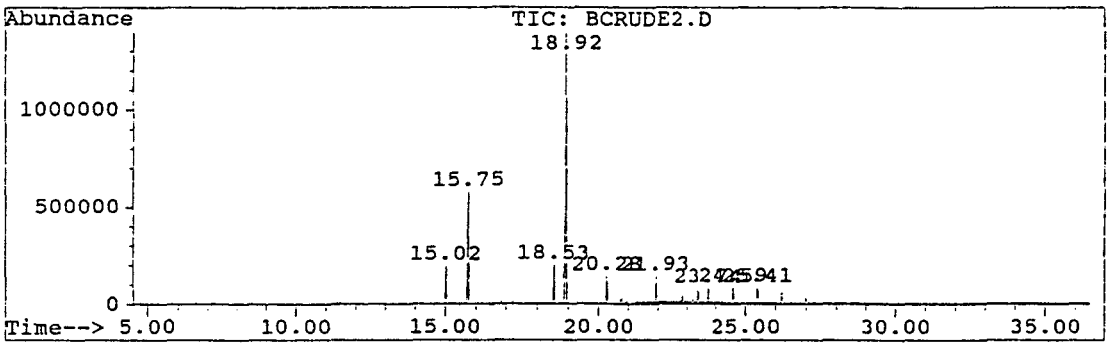
GC/MS Data for Dipropylmalonate (35)



GC/MS Data for Dipropyl 2-vinylcyclopropane-1,1-dicarboxylate (38)

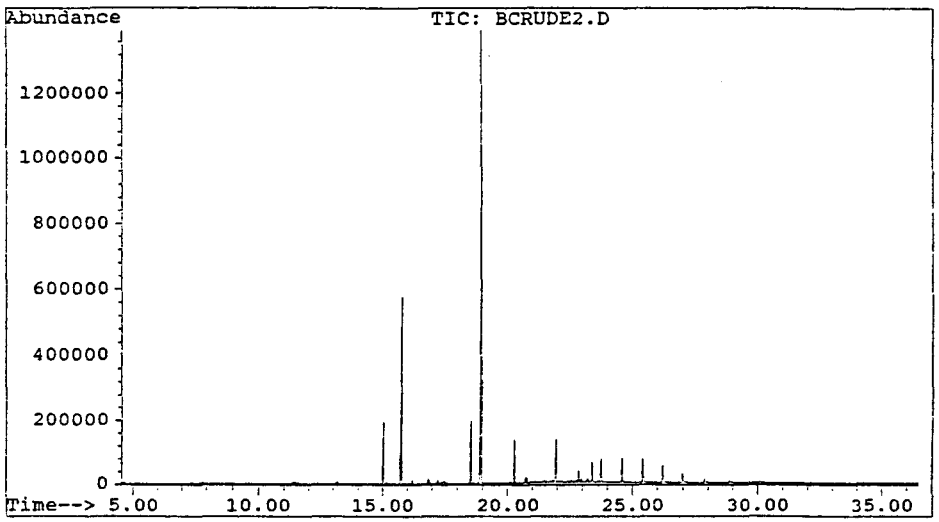


GC/MS Data for Dipropyl-cyclopent-3-ene-1,1-dicarboxylate (**37**)



Retention Time	Area	Area %	Ratio %
Total Ion Chromatogram			
15.023	2816527	5.363	9.611
15.752	9192906	17.504	31.371
18.534	2905434	5.532	9.915
18.924	29304013	55.796	100.000
20.281	1862048	3.545	6.354
21.933	2314808	4.407	7.899
23.736	1168567	2.225	3.988
24.592	1501784	2.859	5.125
25.415	1453805	2.768	4.961

GC/MS Data for the Reaction of Dibutylmalonate with *cis*-1,4-dichloro-2-butene


Abundance
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200000
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Time--> 5.00
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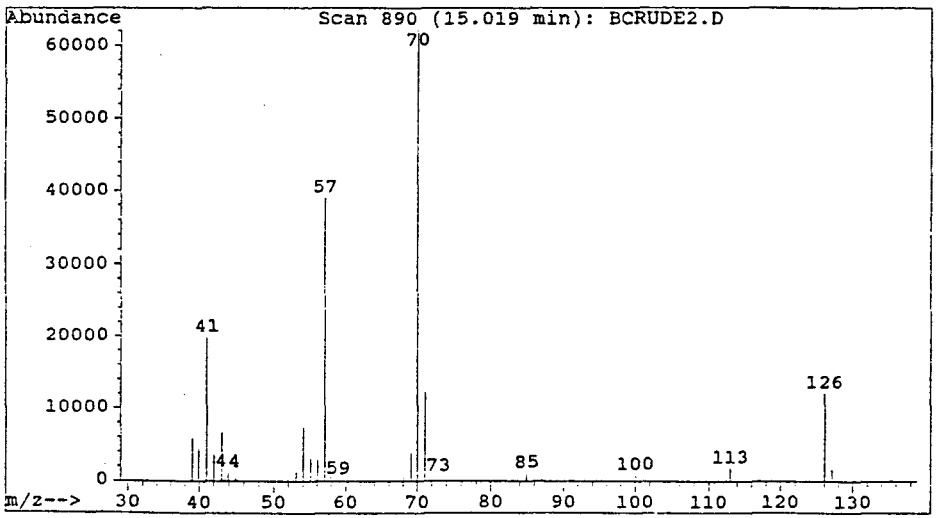
15.00
20.00
25.00
30.00
35.00


Abundance
Scan 890 (15.019 min): BCRUDE2.D
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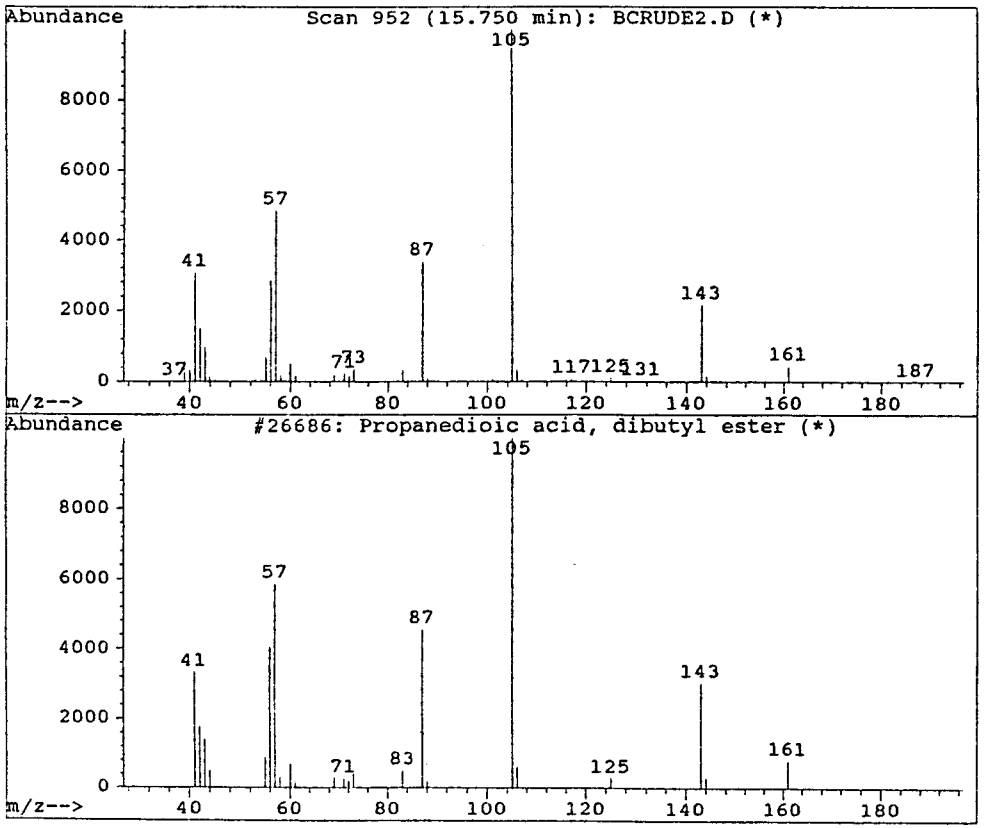
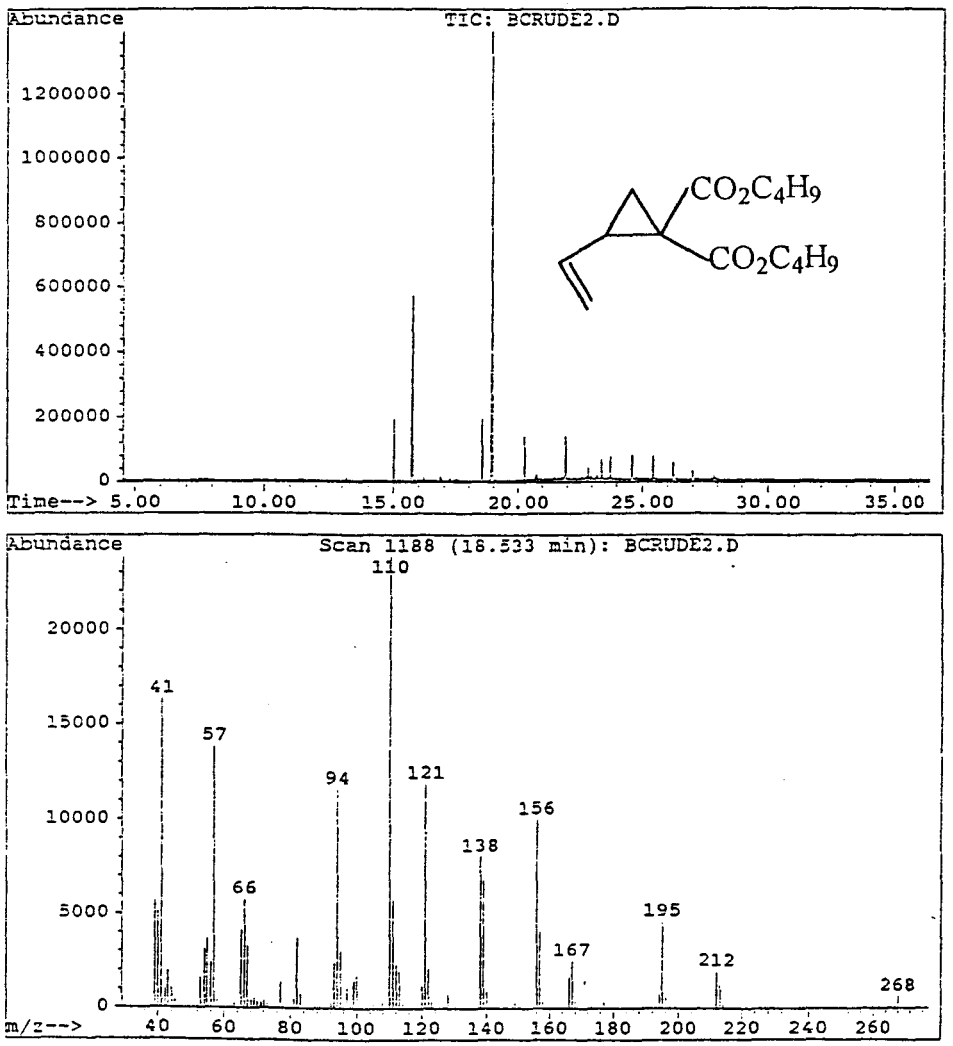
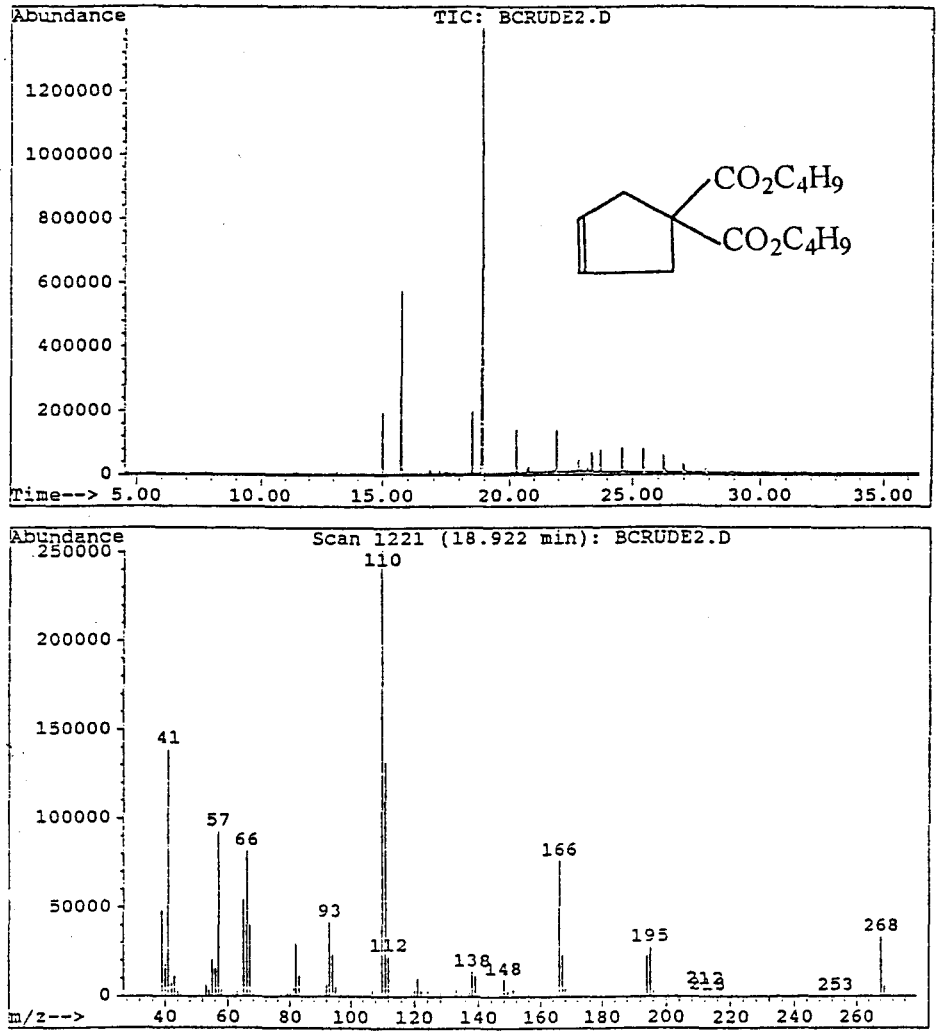
50000
40000
30000
20000
10000
0
70
57
41
126
44
59
73
85
100
113
m/z-->
30
40
50
60
70
80
90
100
110
120
130



GC/MS Data for Dibutylmalonate (43)



GC/MS Data for Dibutyl 2-vinylcyclopropane-1,1-dicarboxylate (**46**)



GC/MS Data for Dibutyl-cyclopent-3-ene-1,1-dicarboxylate (45)

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VITA

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He obtained his secondary education at Ozolua Grammer School, Ologbo, Edo state, Nigeria, before immigrating to the U.S. in 1982.

In June 1988, he obtained a B.S. degree in Chemistry from DePaul University, Chicago. He subsequently joined Tomoegawa (U.S.A.), Inc., a toner manufacturing company where he worked as a quality control inspector.

In September 1989, he joined the Chemistry department at Loyola University as a full time lab equipment/supply coordinator. In the Spring of 1990, he began the quest for an M.S. degree in chemistry on part-time. He participated in the Loyola University Sigma XI graduate student forum in May 1993. In October 1993, he also participated in the Amoco University poster session, and at the Annual Loyola University St. Albert's Day forum.

Hovis Imade is currently a member of the American Chemical Society.

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The final copies have been examined by the director of the thesis and the signature which appears below verifies the fact that any necessary changes have been incorporated and that the thesis is now given final approval by the committee with reference to the content and form.

The thesis is, therefore, accepted in partial fulfilment of the requirements for the degree of Master of Science.

1 December 1994
Date


Director's Signature