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The Synthesis and Characterization of Two All-Aliphatic Sterically Hindered Diesters of α,α,α',α'-Tetramethyladipic acid

by

Ronald L. Willson

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Approved by William B Martin, Jr

Approved by Lawrence McGahey

Approved by Keeran C Weiss

Date 5/31/89

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Thanks to all of the chemistry majors in the class of 1989 whose friendship and support have made this project and my time at Union so enjoyable.

Contents

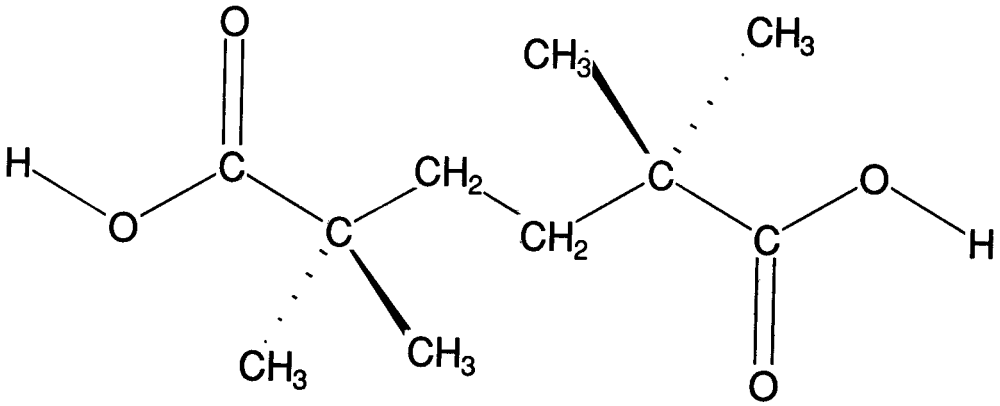
Abstract

Willson, Ronald L. Synthesis and Characterization of two All-Aliphatic Sterically Hindered Diesters of α,α,α',α'-Tetramethyladipic acid, Department of Chemistry, Union College, March, 1989

The bis-*t*-butyl- and bis-neopentyl glycol- diesters of α,α,α',α'-tetramethyladipic acid were synthesized via their diacid chlorides. α,α,α',α'-Tetramethyladipic acid was first prepared by a free radical coupling reaction of pivalic acid because it is not commercially available. The products of all syntheses were characterized by NMR and infrared spectra.

Fig. 1

α,α,α',α'-tetramethyladipic acid



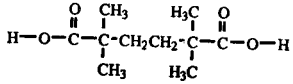
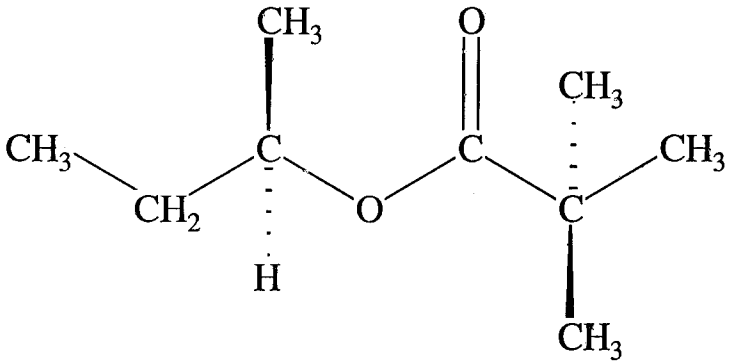


Fig. 2

sec-butyl pivaloate



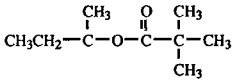
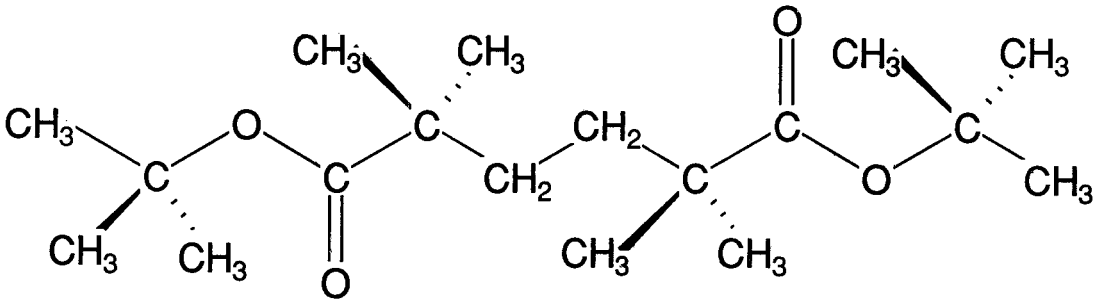


Fig. 3

bis-*t*-butyl α,α,α',α'-tetramethyladipoate



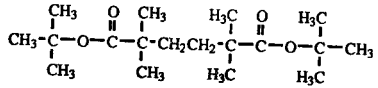
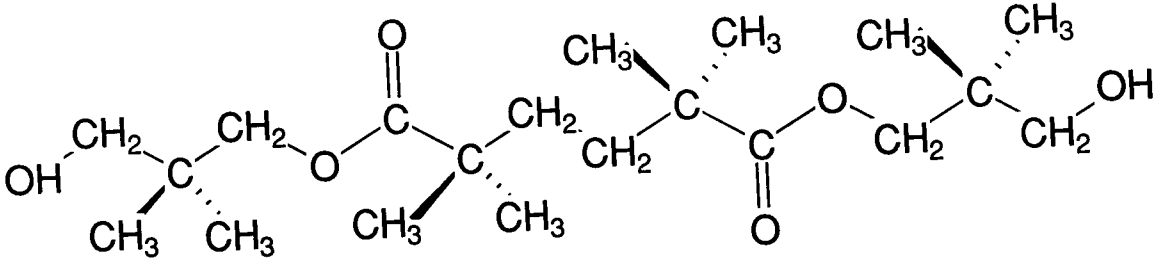
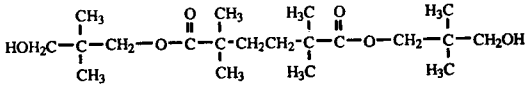


Fig. 4

bis-neopentyl glycol α,α,α',α'-tetramethyladipoate





Introduction

Polymer chemistry has become the leading field in research and industrial chemistry today. The primary reason for the extensive use of polymer chemistry is that polymers have been shown to be numerous and diverse not only in chemical and physical structure but in function as well. A myriad of different polymers demonstrating different properties and functions have been synthesized and polymers have become a part of the daily lives of everyone. From our trash bags to our clothing, polymers have become indispensable. Staudinger is generally credited as being the father of polymer chemistry although a foreshadowing of his ideas can be traced through older literature. In 1920 Staudinger proposed the chain formulas accepted today, but it wasn't until the 1930's that these ideas began to experience widespread acceptance. By the 1930's Carothers began synthesizing polymers using well-established methods and reactions of organic chemistry such as esterification and amidation to form the first polyesters and polyamides. Soon the multitude of chain types were being characterized by physical chemists such as Kuhn, Guth, and Herman Mark. Mark, like Staudinger is one of the "fathers" of polymer chemistry leading the way in the development of polymer science.

The goal of this thesis work was the synthesis of sterically hindered di- and polyesters. For the purpose of this study, esters which are very hindered will be considered to be those with tertiary alkyl groups α to the carbonyl carbons of the acids or tertiary alkyl groups α or β to the oxygens of the alcohols. The reason for the interest in

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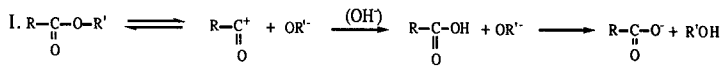
sterically hindered substances is that they have very low saponification rates. Since the saponification rates of the very hindered esters are so low,[1,2,3] it is reasonable to assume that the same would be true of polyesters possessing similar steric characteristics.

Saponification mechanisms:

Ester saponification rates and mechanisms have been well documented in the past. Four different types of base hydrolysis as proposed by Ingold[4] are as follows:

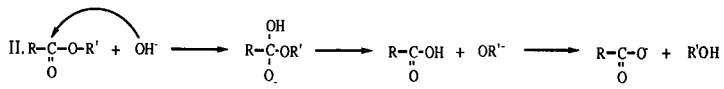
$B_{ac}1$

The base catalyzed 1st order acyl cleavage is the only mechanism that hasn't been observed. It involves an S_N1 mechanism where the acyl C-O bond breaks leaving the carbonyl cation and an OR' anion (eq. I).



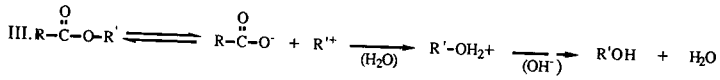
$B_{ac}2$

This is the classical mechanism for saponification and is observed almost exclusively. It is characterized by the formation of a tetrahedral intermediate resulting from a nucleophilic attack at the carbonyl carbon by a hydroxide ion (eq. II).



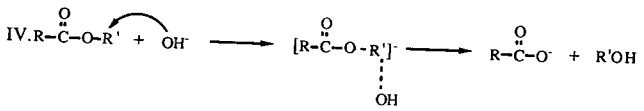
$B_{al}1$

This mechanism proceeds via an S_N1 pathway where the alkyl carbon-oxygen bond breaks forming a carbonium ion and the acid anion. The carbonium ion then combines with water and in the presence of a base loses a proton to form the alcohol. This mechanism has been shown to occur in esters in which R' is a tert-alkyl, allyl, or benzyl group[5] (eq. III).



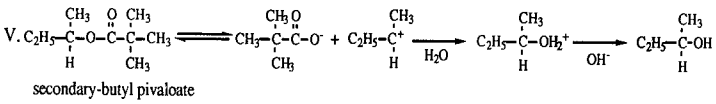
$B_{al}2$

This rare mechanism occurs in cases of extreme steric hindrance when the acyl carbon is blocked. The base attack occurs at the alkyl carbon transfering electrons to the COO^-, forming the acid anion and the alcohol. It has been observed in the cases of certain lactones, namely Malolactone and β-butyrolactone[6] (eq. IV).

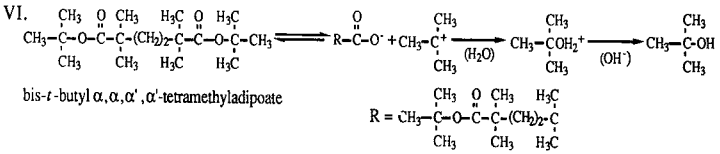


Regarding the esters synthesized in our work, the secondary-butyl pivaloate (Figure II), has been shown to undergo two of the aforementioned saponifications depending on the conditions. At temperatures below ~60°C it will saponify by the $B_{al}2$ mechanism, while at temperatures above ~100°C it will undergo base hydrolysis by the

$B_{al}1$ mechanism[7] (eq. V):



The bis-tertiary-butyl α,α,α',α'-tetramethyladipoate (Figure III) might be expected to undergo the $B_{al}1$ hydrolysis as follows (eq. VI).



Of the three observed saponifications, the bis-neopentyl glycol α,α,α',α'- tetramethyladipoate (Figure IV) would probably be expected to undergo the $B_{al}1$, if any (see discussion).

The *sec*-butyl pivaloate mechanisms are based on the findings of Walrath[7] and Watkins[8] who carried out various kinetic studies on the ester. The saponification mechanism of bis-*t*-butyl α,α,α',α'-tetramethyladipoate is speculative and based on the somewhat inconclusive data of Walrath who did kinetic and model studies on it. Walrath's conclusion was later disproved by Watkins who also did kinetic studies in bis-*t*-butyl α,α,α',α'-tetramethyladipoate and found that saponification did not occur ever after several months.

Thus, judging by data from the saponification studies mentioned above, it seemed that the two diesters would possess the desirable characteristic of very high stability in base. It should be noted that

there have been no direct studies on the bis-*t*-butyl α,α,α',α'-tetramethyladipoate or the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate or any reference to their synthesis. Of the three esters synthesized in this thesis, only the secondary-butyl pivaloate has been synthesized by others and has undergone saponification and model studies.

Esterification mechanisms:

Interest in the special properties which a polyester hindered to base attack might possess prompted an investigation to synthesize and study the esters mentioned above. Since the saponification of these sterically hindered esters is severely limited, one would assume that difficult esterification would logically follow.[1,2,6] The esterification of sterically hindered pivalic acid esters has been reported in the literature and several different procedures were found. Coopersmith, Ruthowski, and Fusco[1] proposed an acid catalyzed mechanism as (eq. VII):

VII. $R-\overset{O}{\overset{\|}{C}}-OH + H^+ \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH_2^+ + R'\text{-}OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{+}{O}(H)-R' + H_2O \xrightarrow[-H^+]{} R-\overset{O}{\overset{\|}{C}}-O-R'$

The acid is protonated (with either *para*-toluene sulfonic or sulfuric acid) to give the conjugated oxonium ion and the positive carbonyl carbon is attacked by the nucleophilic primary alcohol, undergoing a S_N2-like reaction and expelling the good leaving group water. The alcohol and acid are refluxed in the presence of the acid for up to 11 hours removing the water with an entrainer and a soxlet extracter over molecular sieves. With this method the methyl-, ethyl-, n-propyl-, n-butyl-, n-amyl-, hexyl-, and benzyl pivaloates were

formed. Using the common Fisher modification of this method, Bankowitz was able to prepare the tertiary-butyl pivaloate in 99.5% yields.[9]

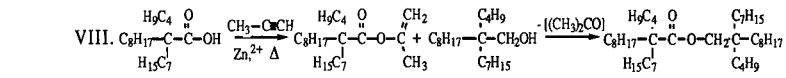
A similar acid catalyzed method for sterically hindered carboxylic acids is suggested by Newman.[2] He tried heating the carboxylic acid in 100% sulfuric acid and then pouring this mixture into the alcohol. Bankowitz[9] attempted the preparation of the tertiary-butyl pivaloate using this method and found no product.

A different approach was attempted by Bochkova, Proskuryakov, Puzitskii, Pirozhkov, and Eidus.[10] They first formed the acid chlorides of "neo"-acids by boiling them in thionyl chloride and then adding to the alcohol in 10% excess. In doing so they as well as Bankowitz were able to synthesize the dipivalic ester of neopentyl glycol in good yields.[9] Walrath was able to produce tertiary-butyl pivaloate in yields of 70-80%.[7]

A variation on the acid chloride technique was proposed by Crowther et. al.[11] The acid chloride was combined with the lithium salt of the alcohol at room temperature. Sixty percent yields of tertiary-butyl pivaloate were reported with this method.[9]

Other pertinent syntheses of sterically hindered esters employ different techniques. Parish and Stock[12] prepared pivaloyl napthalate in 93% yield by first reacting *in situ* the mixed anhydride of trifluoroacetic acid and carboxylic acid, followed by the alcohol. Pfeffer et. al.[13] reacted alkyl halides with acid in ethanol and hexamethylphosphoramide to produce esters such as methyl 2-methyl-2-propylpentanoate in 98% yield. Rothman et.al.[14] were able to produce sterically hindered esters by transesterification through the use of isopropenyl ester

intermediates. Bankowitz was able to perform the reaction with 2-butyl-2-heptyldecanol and Rothman's test compound, 2-heptyldecanoic acid, to form the ester in 95% yield as shown in the following (eq. VIII):



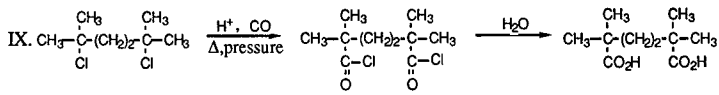
Again, the synthesis of sterically hindered pivalic acid esters (especially the *t*-butyl and neopentyl glycol ones) was sought because of their relative similarity to the esters of α,α,α',α'-tetramethyladipic acid and of the absence of references to any esters of the same.

Synthesis of dicarboxylic acids:

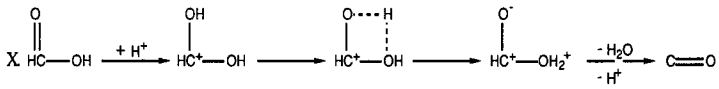
The preparation of α,α,α',α'-tetramethyladipic acid (2,2,5,5-tetramethylhexanedioic acid) is one for which there are several references in the literature. They date as far back as the 1950's but most are of a more recent nature, from the 1970's to the present. The reactions are basically of two types: 1) a carbon monoxide/acid catalyzed system reacted with alkyl halides, diols, or dienes; and 2) free radical coupling reactions.

Friedman[15] patented his process of reacting the di- or poly-tertiary halides with CO while in contact with acid catalysts to produce di- or polycarboxylic acids. The chains on the halides were alkyl chains or rings. Friedman prepared dihalides by treating the corresponding diols or dienes with HX, where X is F, Cl, or Br. The catalysts used were mineral acids (HF or H_2SO_4) and the CO pressure was about 1atm. to 1000psi with temperatures of 10-40°C and contact times

of 1 to 10 minutes. Tetramethyladipic acid was prepared in appreciable amounts (38%) by reacting 2,5-dichloro-2,5-dimethylhexane with anhydrous HF and 800psi carbon monoxide and then H_2O:



Essentially the same technique was employed by Schauerte and Koch[16] who reacted dienes and diols to produce 2,2,5,5-tetramethyl-hexanedioic acid. However, they used a formic acid as well as the carbon monoxide synthesis. The mechanism* for the formic acid reaction would probably be akin to that of the carbon monoxide one due to the possible dehydration of the formic acid in the presence of a strong acid as follows (eq. X):



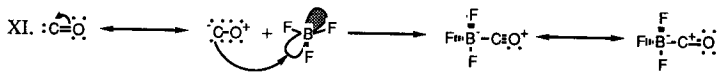
In the synthesis of α,α,α',α'-tetramethyladipic acid, though, the amount of product formed, whether starting from the diol or the diene, was less if run by the formic acid technique. The more successful method was carbon monoxide under pressure. It was noted that dienes branched at the double bonds (like 2,5-dimethyl-1,5-hexadiene, the reactant which would be used for synthesizing α,α,α',α'-tetramethyladipic acid) were more inclined to polymerize than

*The mechanism discussed is speculative as the literature in question was unavailable at the time of this writing.

the corresponding diols. As a result, the preferred method to synthesize the acid according to Schauerte and Koch is the reaction of the diol in the CO system.

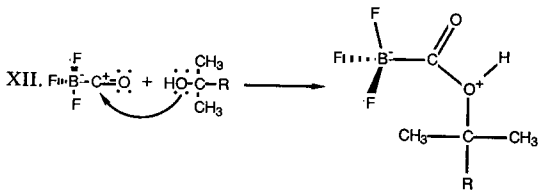
Tanomura and Kau[17] prepared the acid in much the same way by reacting 2,5-dimethyl-2,5-hexanediol with BF_3 and CO in the presence of acid at 6 hours, 150°C, and high pressure. A logical mechani m* for this reaction has the BF_3 Lewis acid sharing an electron pair from the carbon of CO of the proper resonance form (eq. XI).

XI.



From this point the positive carbon of the boron tetrahedral intermediate is attacked by the alcohol OH to form the species which will rearrange to the acid (eq. XII).

XII.



A three membered ring forms and as the alcohol oxygen loses its positive charge by donating a proton, the carbonyl carbon slides over to the alcohol carbon causing the alcohol oxygen to break away from the alcohol carbon (eq. XIII).

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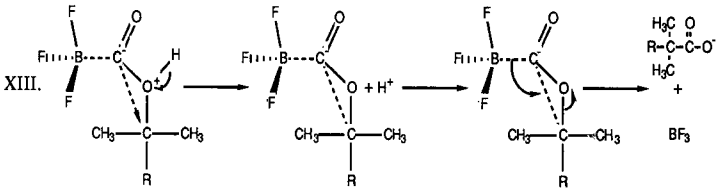
*The mechanism discussed is speculative as the literature in question was unavailable at the time of this writing.

XIII. 

In the correct proportions this reaction will presumably occur with all alcohol groups. Although it may be difficult to envision a tertiary alcohol attacking the positive carbon in a nucleophilic fashion, at high temperatures and pressures such activity has been noted.

Coffman, Lipscomb and Jenner[18] were among the first to synthesize this diacid and they did it by coupling pivalic acid with Fenton's reagent. This same coupling technique was used by Takebayashi and Sagane[19] who used the reaction to form a variety of α,α,α',α'- substituted dicarboxylic acids including propionic, isobutyric, and pivalic. It is this coupling mechanism that is the preferred one for our work for a variety of reasons which will be discussed later.

Experimental

Materials

All chemical compounds used in this work were purchased from the Aldrich Chemical Corp. except the pivalic acid (2,2-dimethyl-propanoic acid) which was supplied by Eastman Organic Chemicals, the pivaloyl chloride which was supplied by White Chemical Corp., and the gases which were supplied by Union Carbide Chemical Corp. All chemicals were of reagent grade.

I) Synthesis of *sec*-butyl pivaloate

Pivaloyl chloride was obtained from Aldrich Chemical Co. and distilled at 107°C. A mixture of ether and 2.818 g. of pivaloyl chloride was charged in a round bottomed flask fitted with a cooled condenser and a drying tube. The pivaloyl chloride/ether mixture was stirred and a mixture of secondary butanol, 1.731 g., and 10% excess of pyridine, 2.033 g., (dried over molecular sieves) was added dropwise. The temperature rise was noticeable but stayed below the boiling point of the ether. After the addition the reaction was refluxed at the diethyl ether boiling point for two hours and then allowed to cool to room temperature.

The reaction mixture was then washed with cold deionized water to remove the unreacted alcohol and the pyridine and pyridine·hydrochloride. Also the unreacted acid would be expected to be partially soluble in the water. The aqueous layer was discarded and the mixture was then washed with 5% NaOH solution to remove as the acid salt any acid or acid chloride present and the remaining

pyridine·HCl. It was next washed with 5% HCl solution to remove any remaining pyridine. Again the aqueous layer was discarded. The next washing was with 5% NaOH to insure the removal of any HCl salts and to neutralize the solution. The final washing was with water. The product after distilling off the ether was a clear, light yellow, pleasant smelling oil, which was then dried, weighed and characterized by NMR (see NMR III) and TLC. 2.89 g. were isolated for a 77% yield.

IIa) Synthesis of α,α,α',α'-tetramethyladipic acid

A free radical coupling was run using .2 mole (20.4 g.) of pivalic acid. The reaction vessel, a three-necked round-bottomed flask, was charged with 175 ml. of water and 3 ml. of concentrated sulfuric acid. A solution of 1.33 *M* $FeSO_4$ was prepared by dissolving .2 mole $FeSO_4$ (55.5 g. $FeSO_4 \cdot 7H_2O$) in 150 ml. of water with 11 ml. of concentrated sulfuric acid. Next a solution of 1.33 *M* H_2O_2 was prepared by adding 20.4 ml. of 30% H_2O_2 (density = 1.11 g/ml.) to 150 ml. of water. The ferrous sulfate solution remained sealed and the hydrogen peroxide solution was refrigerated until time of addition. The pivalic acid was warmed in a water bath to melt it (35.5°C = melting point) and added to the rapidly stirring reaction vessel to insure a large surface area. The system was put in an ice bath and was continuously and rapidly stirred while the solutions of 1.33 *M* $FeSO_4$ and 1.33 *M* H_2O_2 were added simultaneously and equivalently from suitably calibrated burets. The system wasn't allowed to exceed 30°C. The blue green solution of $FeSO_4$ turned yellow upon addition into the system and as the reaction continued the color of the system changed from yellow to brown. A

milky white, fatty solid formed and started to congeal by 50% addition. At the end of the addition (total time--15min.), large globules of the fatty solid were floating on the surface of the reaction solution covering a large proportion of the surface.

The work-up of the reaction commenced with a distillation of most of the water and co-distillation of the unreacted pivalic acid. The distillation system was a standard steam distillation system. Four-hundred and fifty milliliters of water and pivalic acid were steam distilled and set aside for weighing. The unreacted pivalic acid was calculated (using its water solubility also) to be approximately 15 g.

From this point the reaction solution was rinsed with 50 ml. of concentrated ammonium hydroxide and collected by gravity filtration. The filtrate was then acidified with concentrated HCl to induce precipitation and after neutralization the collected product was recrystallized in ethanol (about 2-3 ml./g.). 2.43 g. of α,α,α',α'-tetramethyladipic acid with a melting point of 181-183°C were isolated for a yield of 12% of theoretical. The filtrate mother liquor was evaporated to leave a brown oil that solidified over time.

IIb) Synthesis of α,α,α',α'-tetramethyladipic acid using .4 moles of pivalic acid

The above reaction was run using .4 mol. of pivalic acid (40.8 g.), 301 ml. of 1.33 *M* $FeSO_4$ solution with 22 ml. of H_2SO_4, and 301 ml. of 1.33 *M* H_2O_2. The reaction vessel was charged with 400 ml. of water and 6 ml. of H_2SO_4. Solutions and reagents were added and reaction

proceeded as before. Reaction temperature again remained well under 35°C and addition time was slightly over 15 minutes.

The unreacted pivalic acid was then removed by steam distillation (400 ml.) and again the unreacted acid was set aside for weighing. Unfortunately, the crude weight could not be determined as the mixture charred while attempting to separate it from the water by distillation. The white globules of crude tetramethyladipic acid turned beige after the distillation and were isolated and weighed: crude weight, 17.61 g.

Next, the α,α,α',α'-tetramethyladipic acid was rinsed with ~100 ml. of concentrated NH_4OH and this time filtered by suction filtration through diatomaceous earth to better remove the elusive Fe^{2+} and Fe^{3+} hydroxides. The eluent was then acidified with HCl to precipitate the carboxylic acid dissolved as the ammonium salt; the resulting solids were filtered by suction filtration. The acid was washed with excessive amounts of water until the washes were neutral. This was followed by recrystallization of the product in ethanol (2-3 ml./g.) after the product had air dried. The crystals were again dried after recrystallization, this time with suction. The filtrate from the recrystallization was allowed to evaporate leaving a considerable amount of crystals which formed during evaporation on the sides and bottom of the beaker as well as brown oil that appeared to be of the same composition as the oil from the first run. The weight of the oil was found to be 6.9 g. The white crystals melted between 188 and 190°C and weighed 9.28 g., a yield of 23%. The product was then further characterized by NMR and IR (NMR II and IR I) to confirm the formation of the desired product.

IIc) Synthesis of α,α,α',α'-tetramethyladipic acid from .8 moles of pivalic acid

The amounts of reactants were: .8 moles of pivalic acid, 602 ml. of 1.33 *M* $FeSO_4$ solution with 32 ml. of concentrated H_2SO_4, and 602 ml. of 1.33 *M* H_2O_2 solution. The reaction vessel, a 4000 ml. beaker, was initially charged with 800 ml. of H_2O and 12 ml. of H_2SO_4. To cut down on the premature oxidation of the $FeSO_4$, more effort was taken to remove oxygen from the system rather than merely preventing the casual contact of the solution with the air. Five-hundred and sixty-eight milliliters of water and 32 ml. of H_2SO_4 were added to a 1 liter volumetric flask which was then bubbled with nitrogen gas through a glass fritte for 20 minutes before addition of the ferrous sulfate. Upon addition the volumetric was immediately capped. The contents of the reaction vessel were treated similarly before the reaction was started. The reaction was carried out in the same manner as the other two; however it is to be noted that the center of the reaction solution did get warm ($35 < t < 45^oC$) during the simultaneous addition of the two solutions of reagents. Furthermore at the end of the reaction there was present considerably less than the expected amount of white fatty globules than had been observed in previous runs. It was these globules which had proven to be the desired product of α,α,α',α'-tetramethyladipic acid and as a result the system was set aside and isolation and purification were not continued.

III) Preparation of α,α,α',α'-tetramethyladipoyl chloride

The 2.43 g. of α,α,α',α'-tetramethyladipic acid from run Ia. was put in a 250 ml. three-necked round-bottomed flask fitted with a reflux condenser with a drying tube and a thermometer. To the vessel was added 3 times the molar amount of thionyl chloride, 4.28 g. This corresponds to a 1.5 times as many equvalents of thionyl chloride as acid. The reaction was heated to the boiling point of the thionyl chloride 79°C and allowed to reflux for 5 hours. The reaction proceeded smoothly and the expected odor and sight of HCl were present. After 5 hours the system was allowed to cool to room temperature and the reflux condenser was replaced with the apparatus necessary for distillation. The excess thionyl chloride (not very much) was distilled at 79°C. In order to minimize the decomposition that would occur from exposure to the moist air, the acid chloride was not isolated. Instead, the product was left in the 250 ml. round-bottom and the system rearranged for reflux in preparation for the first α,α,α',α'-tetramethyladipic acid ester synthesis.

IV) Preparation of bis-*t*-butyl α,α,α',α'-tetramethyladipoate

To the 2.43 g. of α,α,α',α'-tetramethyladipoyl chloride from the last synthesis was added a 10% excess of pyridine, 2.1 g. and a 10% excess of *t*-butanol, 1.96 g. The system was refluxed for 4 hours at 82°C, the boiling point of the alcohol.

At the completion of the reaction thin layer chromatography indicated the presence of more than the expected four components, possibly as many as six. The work-up commenced with the reaction

mixture being dissolved in 500ml. of water to dissolve the pyridine, pyridine·HCl, and the *t*-butanol, with the product and any other esters remaining in an oil. Next the oil was washed with a 5% NaOH solution to dissolve any monoester which might have formed. This mixture was then extracted with ether five times to dissolve any remaining diester. The combined ether layers and extracts were then rinsed with water to neutralize them. The ether was separated and dried with $MgSO_4$. After overnight evaporation, .186 g. of oil was left which was characterized by IR and NMR (see NMR V and IR III). The NaOH solution was acidified with HCl (pH ~1) and white solids precipitated. These solids were then characterized (see NMR IV and IR II). The melting point of the crystals was found to be 175-180°C and thin layer chromatography indicated two components.

Va) Preparation of bis-neopentyl glycol α,α,α',α'-tetramethyladipoate

Firstly, the acid chloride was produced by reacting 2.23 g. of α,α,α',α'-tetramethyladipic acid from run IIb. with twice as many moles of thionyl chloride (2.63 g.) and twice as much pyridine (1.75 g.). The acid and pyridine were charged into the same type of apparatus as was used for the first acid chloride preparation. The thionyl chloride was slowly added dropwise taking care not to add so fast that vapor escaped out through the drying tube and waiting long enough in between drops for the vapor to clear. The mixture was then refluxed for 2 hours at 70°C. After cooling, the mixture was poured into a beaker and covered with parafilm.

A second reflux apparatus was set up and into it was charged

four times the molar amount of neopentyl glycol, 4.6 g. and enough dimethoxyethane to solvate it. The acid chloride was then added dropwise to the excess of neopentyl glycol and after addition the system was refluxed at the dimethoxyethane boiling point, 84°C, for 2 hours. During the reaction the mixture turned a light orange.

To work-up the product the reaction mixture was first concentrated by removing the dimethoxyethane solvent with the rotovap. Next, the mixture was rinsed with about 500 ml. of H_2O to remove the remaining dimethoxyethane, pyridine, and pyridine·HCl. The aqueous solution was then washed five times with 10-15 ml. of ether each time to pull any entrained ester out of the water. The ether was then rinsed with water to remove any pyridine·HCl that might have come over. The organic solution was then dried with $MgSO_4$. The ether was evaporated and left 1.756 g. of fruity smelling, orange oil with similarly orange needles. TLC with silica plates and various solvents indicated the solid and liquid were of different composition. Further characterization was made with NMR and IR (NMR VI and IR IV).

Vb) A Second preparation of bis-neopentyl glycol α,α,α',α'-tetramethyladipoate

The apparatus was set up as before except that an all glass system was used to try to minimize any contamination from non-glass components which could color the reaction mixture. α,α,α',α'-Tetramethyladipic acid (2.52 g.) was mixed with 2.17 g. of pyridine in a 250 ml. three-necked round bottom flask. A four mole excess of thionyl chloride (5.93 g.) was again added dropwise and the

system was refluxed at 70°C for 7 hours. This time the excess thionyl chloride was distilled off under a vacuum to insure that a high percentage of it was removed. It is to be noted that when the vacuum was broken at the end of the distillation the incoming air was pulled through a large drying tube to maintain the moisture-free environment. The acid chloride was again added dropwise to the 5.18 g. of neopentyl glycol. However, this time the solvent was pyridine, not dimethoxyethane. The reactants were refluxed at the boiling point of pyridine (115°C) for 24 hours. The mixture again turned color although this time it turned a darker brown, indicating the previous lack of an all glass system probably had nothing to do with the formation of the color.

Most of the pyridine catalyst/solvent was removed with the rotovap and the mixture was then diluted with three times as much water to dissolve the remaining pyridine and pyridine·HCl. The water solution was then rinsed three times with 80 ml. of ether and the layers were separated. Evaporation of the ether left 1.14 g. of product identical in appearance and odor to that of the first run, although it was more crystalline. The aqueous was allowed to evaporoate, and later it was again diluted with fresh water, rinsed with ether, and the layers separated. The remains after the ether evaporation was a fruity smelling, light yellow, crystalline solid of weight .708 g. This solid also has the same pleasant, fruity odor as does the product of the previous run. The solid from the first ether extraction and the second were characterized by NMR and IR (NMR VII and VIII and IR V). Each melted between 110 and 120°C.

Discussion

Dicarboxylic acid Syntheses

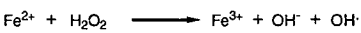
The dicarboxylic acid chosen for synthesis was α,α,α',α'-tetramethyladipic acid (2,2,5,5-tetramethylhexanedioic acid by IUPAC nomenclature). The reason for this choice is that tetramethyladipic acid is very sterically hindered and can be synthesized in fair amounts. The synthesis of α,α,α',α'-tetramethylsuccinic acid (2,2,3,3-tetramethylbutanedioic acid) which differs only by two methylene groups in the backbone, was considered and its synthesis was found to have been attempted by Coffman et. al.,[18] by coupling isobutyric acid. The synthesis was unsuccessful, however, producing instead α,α'-dimethyladipic acid. Another logical choice is diethylmalonic acid which is commercially available and similarly hindered. Its esterification by Bankowitz[9], however, was quite unsuccessful; at the stage of forming the acid chloride it decarboxylated. It was decided, then, to synthesize the α,α,α',α'-tetramethyladipic acid.

The method of Coffman et. al.[18] was chosen for the synthesis of α,α,α',α'-tetramethyladipic acid due to its relative simplicity when compared to the syntheses by the carbon monoxide method. The carbon monoxide syntheses require equipment and facilities unavailable to us. Furthermore, exposure to the extremely caustic chemicals and the high pressures required for syntheses of this type make them unsuitable for our purposes.

The method of Coffman et. al. is a free radical pivalic acid

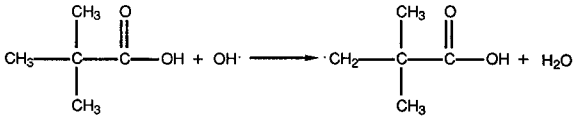
coupling reaction using Fenton's reagent (ferrous sulfate and hydrogen peroxide) as the initiator. Iron in the divalent form cleaves the hydrogen peroxide reducing one OH to a hydroxide ion, while the other forms a free radical (eq. XIV).

XIV. initiation:



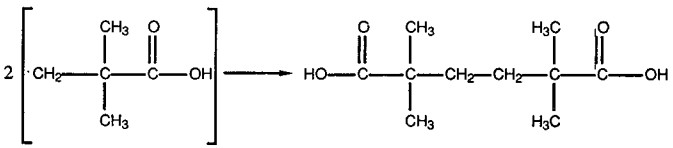
The hydroxide free radical is now able to abstract a hydrogen from the pivalic acid forming a pivalic acid free radical and water (eq. XV).

XV. propagation:



It is the coupling of two pivalic acid free radicals in the termination step which forms α,α,α',α'-tetramethyladipic acid (eq. XVI).

XVI. termination:



This reaction is not expected to result in a mixture of products because pivalic acid can only form one free radical of the type to make a dicarboxylic acid since all its alkyl hydrogens are equivalent. Thus, it doesn't matter which hydrogen is abstracted, the same free radical is always formed.

The yield of the first synthesis of the acid using .2 moles of pivalic acid was only 12%. The amount of unreacted pivalic acid isolated was .146 moles meaning that only .054 moles, or 27% did react. The yield of the reaction based on the .054 moles of pivalic acid which did react is 44.5%. Coffman reports obtaining a 37% yield, but doesn't note how much pivalic acid went unreacted.

Since pivalic acid forms a primary free radical, it is difficult to effectively increase the yield. A primary free radical is more unstable than either a secondary or tertiary free radical and it is known that increased molecule reactivity is favored by a more stable free radical while increased radical reactivity is favored by a less stable free radical. Thus, the formation of the radical is expected to be considerably slower than the termination step in this reaction because a primary free radical is formed. Once the radical is formed however, it is sure to react with something. Thus, this synthesis has an obstacle and it is the reactivity of pivalic acid by a free radical mechanism.

The second synthesis using .4 moles of pivalic acid gave better results, giving a yield of 23% of theoretical, almost twice that of the first synthesis. Although the unreacted pivalic acid/water mixture couldn't be separated for weighing (it charred during distillation), there did exist a considerable amount of unreacted pivalic acid judging from the amount of sludge which formed after the excess water and unreacted pivalic acid was distilled following the reaction.

The third synthesis resulted in what seemed to be a much smaller amount of product than expected. The temperature of the reaction system is certainly suspect in this result. The temperature of the reaction mixture rose above the recommended maximum of 35° to

approximately 40 or 45°C. Hydrogen peroxide is prone to decompose by disproportionation to H_2O and O_2 and the rate of decomposition would be accelerated by the rise in temperature which occured as the reaction proceeded. This increased decomposition of the H_2O_2 would in turn result in a lower yield.

Another variable that would affect yields is the agitation of the reaction solution. As mentioned above it is in the best interest of the experimenter to see that the OH free radicals have as many productive collisions with pivalic acid molecules as possible. Coffman reports that their reaction was "vigorously agitated." Our mixtures were rapidly stirred with as big a stirring bar as available. In the last synthesis the stirring was probably not as efficient as it could have been; a 2 inch magnetic stirring bar was used in a 4 liter beaker. Because the peroxide is not very stable other methods should be investigated to maximize its contact with the acid before decomposition.

According to Coffman, the concentration of pivalic acid in the reaction mixture is directly proportional to yield of product formation. In our syntheses, the concentration of pivalic acid was the same in each of the synthesis and equal to the highest concentration Coffman used ($\sim.5M$). Thus the concentration of the pivalic acid would not be expected to have resulted in variations in our product yields.

The product isolated in the first two syntheses contained, besides white crystals, a dark brown oil that solidified over time. This oil, although not characterized, smelled of pivalic acid and most likely obtained most of its color from the iron hydroxides which filtration failed to remove completely. It undoubtedly contained tetramethyladipic acid as well, and as a result removal of the iron to

minimize the amount of brown oil formed is of great importance. Thus, in the second synthesis, the product was filtered by vacuum filtration through diatomaceous earth with considerably better results as seen not only in appearance of the crystals, but in the melting points as well. There also seemed to be (judging from appearances), a smaller percentage of brown oil in the second synthesis. The melting point of the product of the first synthesis was 180-183°C and 188-190°C for the second. As compared to the literature value of 190°C, the product from the second synthesis is clearly of higher purity.

Further characterization was made by NMR and IR (NMRs II and IR I, see also Fig. 5). Product from the second synthesis was used because of its higher purity. The solvent used was deuterated acetone. The reason for this was the lack of other suitable solvents which would have no conflicting NMR absorptions and would dissolve tetramethyladipic acid. As a result, the NMR shows a large multiplet at 2ppm. This is due to exchange of the deuterium atoms with the protons of tetramethyladipic acid which are present in solution. The equivalent methylene protons show a singlet at 1.5ppm and the equivalent methyl protons show a singlet at 1.15ppm, the same chemical shift that pivalic acid exhibits in the literature and in NMR Ia. The relative peak heights of these two singlets match the expected 1:3 ratio. The carboxyl hydrogen isn't shown as it would be expected to appear between 10 and 12ppm. The slight downfield shift of each is due to the inductive effect of the carboxyl group.

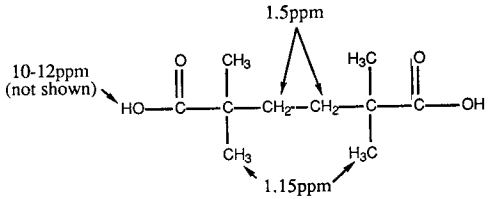


Fig. 5.-Peak assignments for NMR II.

The ^{13}C NMR (NMR IIb and c) also appear to support α,α,α',α'-tetramethyladipic acid formation. Two of the three peaks that appear correspond with those of spectrum Ic (pivalic acid in deuterated acetone). They are the methyl carbons at 30ppm and the quaternary carbons at 47ppm. The third peak then, would be expected to be that of the methylene carbons. This is plausible as the methylene carbons would be expected to absorb further downfield than the methyl carbons and further upfield than the quaternary carbons. The relative peak heights are also consistent; the methyl peak is the tallest and the quaternary carbon peak is the smallest. The carbonyl carbon might be the small peak at 184ppm judging from the similar peak which appears on the pivalic acid ^{13}C spectrum, although it is hard to distinguish it from the noise. The acetone shows the multiple peaks at 34-35ppm due to differences between the two methyl carbons as they exchange varying numbers of deuteriums with the acid protons present.

The IR (IR I) also shows the expected spectrum. A broad OH stretch is seen from 3500 to 2300cm^{-1}, strong carbonyl stretching at 1700cm^{-1}, and medium intensity methylene and methyl bending at 1470 and 1400cm^{-1}, respectively. The spectrum also has the characteristic absorptions of α,α'-dimethyladipic acid in the fingerprint

region, including a strong band at 1225cm^{-1} and an absorption between 950 and 870cm^{-1}.

Diester Syntheses

The saponification mechanisms of the esters synthesized would be expected to be of the alkyl-oxygen cleavage types since their hindered nature prevents the classical $B_{ac}2$ mechanism. As mentioned earlier, the mechanism of the *sec*-butyl pivaloate has been determined by kinetic studies.[7]

The mechanism for the saponification of the bis-*t*-butyl α,α,α',α'-tetramethyladipoate, although not directly studied, might be expected to be a $B_{al}1$ type. This choice is supported by the observation that the other plausible mechanism, the $B_{al}2$, can be ruled out because the methyl groups that prevent attack at the acyl carbon are also present on the alkyl carbon making attack there highly improbable. It is logical that data indicate that the *sec*-butyl pivaloate can show attack at the alkyl carbon at higher temperatures because it has only one methyl group leaving the oxygen partially accessible to base attack. Since the $B_{ac}1$ mechanism has never been observed, it would not be reasonable to expect it in this case.

Thus, due to the experimental findings of *t*-butyl pivaloate saponification mechanism[7] found in the literature, coupled with the relative similarity of *t*-butyl pivaloate to bis-*t*-butyl α,α,α',α'-tetramethyladipoate it is not unreasonable to expect a $B_{al}1$ type saponification for this diester. However, studies of *t*-butyl pivaloate by Watkins[8] suggest that this does not occur. His results indicate that

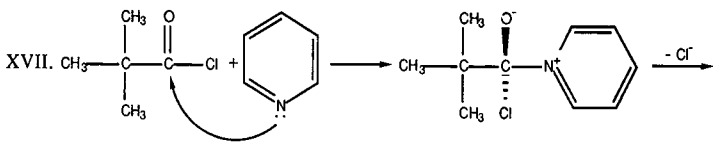
t-butyl pivaloate remained unsaponified even after several months, at up to 55°.

Speculation as to the saponification mechanism of the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate is particularly difficult. Although one might initially expect a $B_{al}1$ mechanism, because neopentyl glycol is a primary alcohol it forms an unstable carbocation. Furthermore, it is hindered to base attack at both the alkyl and acyl carbons. These two characteristics make saponification by any of the known mechanisms highly improbable.

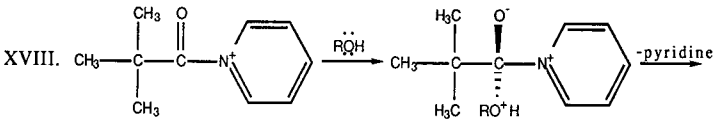
Thus, the saponification rates of the two diesters, although not yet proven, would appear to be effectively zero.

The first ester synthesized was that of *sec*-butylpivaloate. This was done to evaluate the esterification method chosen, that of Bochkova et. al.[10], as well as to develop familiarity with the reaction itself. The reason for this choice of synthesis was the aforementioned success reported by Bochkova and by Bankowitz[9], and also that by Walrath, who produced tertiary-butyl pivlaoate in yields of 70-80%.[7] Another reason the method was chosen is the relatively straightforward nature of the reaction compared to that of, for instance, Pfeffer[13], who also reported high yields of sterically hindered esters.

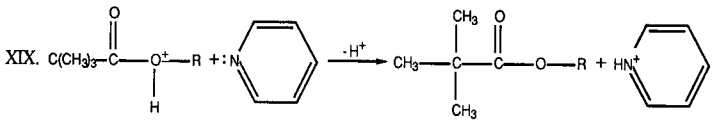
The mechanism of the acid chloride synthesis begins with the solvent and catalyst, pyridine, nucleophilically attacking the carbonyl carbon of the acid chloride, forming a tetrahedral intermediate (eq. XVII).



The chloride ion leaves and the double bond between carbon and oxygen reforms. The unbonded electrons on the alcohol oxygen then nucleophilically attack the carbonyl carbon in much the same way pyridine did initially (eq. XVIII).



At this point pyridine leaves and since it is basic, it will accept the proton on the positive oxygen to complete the ester formation (eq. XIX).



The *sec*-butylpivaloate was synthesized in 77% yield as mentioned earlier. The reaction ran well with a mild exotherm. The product isolated was characterized by proton and ^{13}C NMR (NMR IIIa and b) and compared with spectra in the literature.

The two NMRs show peaks corresponding to the hydrogens and carbons as shown below (Fig. 6):

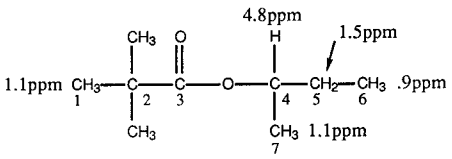
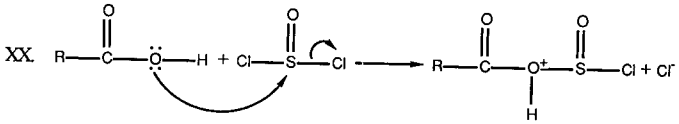


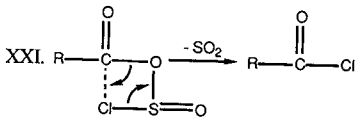
Fig. 6.-Peak assignments for NMR III.

The doublet at 1.1ppm is actually one-half of the doublet of the hydrogens on carbon 7 hidden by the large singlet of the methyl hydrogens of the pivalic acid. The spike at 1.25ppm is an impurity judging by its very small integration value (less than that of the single proton at 4.8ppm). Integration of the peaks gives reasonable values for the relative numbers of hydrogens. The ^{13}C NMR shows seven peaks at with values and assignments as follows: carbons 1, 27ppm; carbon 2, 39ppm; carbon 3, 179ppm; carbon 4, 72ppm; carbon 5, 29ppm; carbon 6, 10ppm; and carbon 7, 20ppm. The three peaks at 76-78ppm are $CDCl_3$ solvent signals. These assignments were made by comparing NMR Ib with a ^{13}C spectrum of pivalic acid and by using literature values for chemical shifts. Thin layer chromatography also supports the formation of the *sec*-butylpivaloate when R_f's were compared with a known sample.

The next reaction was the esterification of α,α,α',α'-tetramethyladipic acid with *t*-butanol. The acid was converted to the diacid chloride by reacting with thionyl chloride as described in the experimental section. The mechanism starts with the oxygen nucleophilically attacking the thionyl sulfur. This results in the loss of a chloride ion and a positive intermediate being formed (eq. XX).

XX. 

Next, this intermediate loses a proton and forms a cyclic structure as the chlorine bends around to attack the carbonyl carbon. Bond transfers occur resulting in a bond being formed between the carbonyl carbon and the chlorine and the sulfur and the oxygen. The sulfur and two oxygens then leave as SO_2 and the acid chloride is formed (eq. XXI).

XXI. 

Rather than risk the decomposition of any of the α,α,α',α'-tetramethyladipoyl chloride, it was decided that the product should be reacted immediately, without any characterization.

The products formed from the esterification of α,α,α',α'-tetramethyladipic acid and *t*-butanol were both an oil and a crystalline solid. The two α,α,α',α'-tetramethyladipic acid ester products possibie are the diester, bis-*t*-butyl α,α,α',α'-tetramethyladipoate and the monoester, *t*-butyl monohydrogen α,α,α',α'-tetramethyladipoate. A mixture of products was expected not only from the TLC results on the unpurified product mixture, but also from the fact that α,α,α',α'-tetramethyladipic acid would be able to form the anhydride when undergoing chlorination. The anhydride formation is initiated when one of the carboxyl groups sees a newly formed acid chloride group. The chlorine then removes the acidic hydrogen producing HCl

and the anhydride. This reaction would not appear to be unfavored as the anhydride forms a stable seven membered ring (Fig. 7).

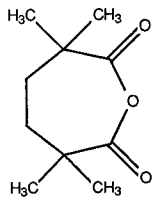


Fig. 7.- α,α,α',α'-tetramethyladipic anhydride

There was considerably more solid, .744 g., than oil, .186 g. The yields were low; there appears to be a large amount of unreacted acid mixed with the solid. The melting point of the solid was found to be 175-180°C which is lower than that of α,α,α',α'-tetramethyladipic acid and could be representitive of a mixture of the diacid and monoester. This speculation can be made since the diacid and the monoester both would have been dissolved in the 5% NaOH solution and not in the ether. However, the solid could also contain unreacted diacid and diester if the diacid pulled some of the diester with it into the ether. Then there is also the possibility that the solid could also contain a mixture of all three. Several TLC's in different solvents were run on the solid and it was found to contain two components, eliminating the possibility of a mixture of all three compounds.

The solid crystalline product appears by its spectrum NMR IV (see also Fig. 8, below), to be the monoester *t*-butyl monohydrogen α,α,α',α'- tetramethyladipoate. The IR (IR II) also indicates the presence of an acid-ester. However, the determination as to whether it is a

mixture of tetramethyladipic acid and diester or true monoester can't be made from the infrared spectrum.

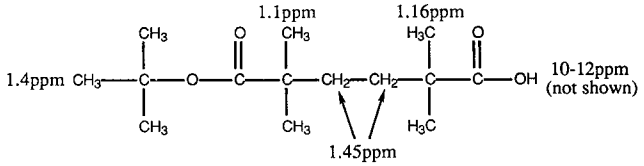


Fig. 8.-Peak assignments for NMR IV.

In NMR IVa, the *t*-butanol hydrogens appear at 1.4ppm which coincides with the literature value. The methyl protons close to the carboxyl group appear slightly farther downfield than those closer to the alcohol, 1.16 and 1.1ppm, respectively. The integration supports these peak assignments; the ratio of the integration of the alcohol protons to the two tetramethyladipic acid methyl proton peaks combined is approximately 9:12. The fact that the integration is less than 9:12 indicates that there is unreacted tetramethyladipic acid in the solid. The methylene protons, although they are slightly different, appear at the same chemical shift--1.45ppm. The carboxyl proton isn't seen and as before would be expected far downfield at approximately 10-12ppm. The large spike at 7.3ppm is due to chloroform; as was the case with tetramethyladipic acid and deuterated acetone, the acid hydrogen is apparently able to exchange with the deuterium of deuterated chloroform. There is also the possibility that the deuterochloroform is not 100% $CDCl_3$.

The oil product shows NMR spectra Va and b with peak assignments as shown below (Fig. 9):

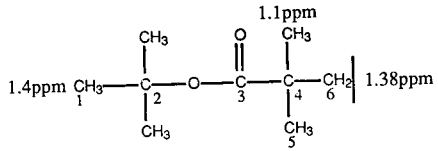


Fig. 9.–Peak assignments for NMR V.

The *t*-butanol protons appear at the same shift that they do in the monoester. Similarly, the tetramethyladipic acid methyl protons have the same chemical shift as those methyl protons closer to the alcohol in the monoester. The *t*-butanol hydrogens overlap the singlet of the tetramethyladipic acid methylene hydrogens which appear slightly further upfield than they did in NMR IIa, in which deuterated acetone was the solvent. The peak of the methylene protons can be seen, though, when the spectrum is expanded; they appear just to the right of the *t*-butanol hydrogens at 1.38ppm. The tetramethyladipic acid methyl hydrogens appear at 1.1ppm which is just about where they appeared earlier.

The ^{13}C spectrum (NMR Vb) denotes six different carbons as numbered above (Fig. 8). Carbons 4, 5, and 6 which appear at 42, 36, and 28ppm respectively, coincide very well with the same carbons on α,α,α',α'-tetramethyladipic acid (considering the difference in solvents). The most shielded *t*-butanol methyl carbons appear at 26ppm. The two most deshielded carbons, carbons 2 and 3, appear at 80 and 178ppm, respectively. They as well as carbon 4 show the smallest peaks as the lack of hydrogens results in the longest relaxation times. To insure correct ^{13}C peak assignment, an APT (attached proton test) spectrum was acquired (NMR Vc). An APT spectrum inverts the peaks of methine

and methyl carbons (those with odd numbers of protons) while leaving methylene and quaternary carbons unchanged. With this in mind, it was expected that carbons 1 and 5 would show inverted peaks and they did.

Infrared spectrum III shows very clearly that an ester is present. Strong carbonyl stretching is shown at $1725cm^{-1}$ and strong carbon-oxygen single bond stretching is seen from 1275 to $1100cm^{-1}$. Also present are adipic acid and *t*-butanol stretching in the fingerprint region.

One reason for the poor yields encountered in this synthesis could be that the reaction wasn't refluxed for a long enough period of time or at a high enough temperature. Another problem could be that if all of the thionyl chloride wasn't removed and the mixture was acidic, a fair amount of diester hydrolysis could be occurring and the reaction could be proceeding back to the left. Thus, the reaction should be attempted at higher and lower temperatures. Also, the system should be checked for acidity and/or the $SOCl_2$ should be distilled off under a vacuum to insure more complete removal.

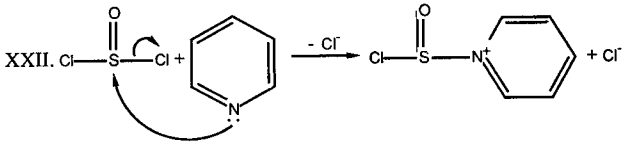
Similarly, poor yields would be expected if there weren't enough excess of *t*-butanol. By increasing the amount of alcohol in the reaction mixture one would be increasing the probability of diester formation over monoester formation as well as mono or diester formation over that of the anhydride. If the anhydride doesn't form to any great extent, however, there should be no reason why there wouldn't be a greater yield of diester under the proper conditions.

The next esterification attempted was that of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid with neopentyl glycol. Because neopentyl glycol

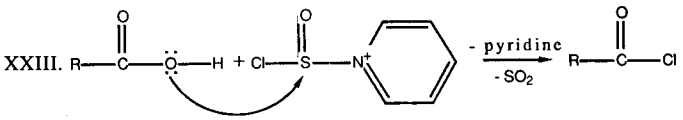
(2,2-dimethyl-1,3-propanediol) is difunctional, it should be able to react with a difunctional acid to eventually produce a polyester. The α,α,α',α'-tetramethyladipic acid formed in synthesis IIb was used for this reaction.

For this synthesis a different technique was tried. The acid chloride was produced by reacting the diacid dissolved in pyridine with the excess of thionyl chloride. This was attempted to try to maximize the amount of acid chloride formed because pyridine is thought to be a catalyst not only in the esterification reaction but in the acid chloride reaction as well.

The mechanism for the pyridine-catalyzed acid chloride reaction starts with an acid-base reaction between pyridine and thionyl chloride (eq. XXII).



This thionyl chloride-pyridine complex is thought to be more reactive than thionyl chloride alone because pyridine is a better leaving group than a chlorine. Thus, the reaction of the diacid with the thionyl chloride-pyridine complex would occur faster (eq. XXIII).



To confirm that this reaction would occur, it was first attempted

with acetic acid and ethanol. Before running the test reaction though, a small amount of thionyl chloride and pyridine were combined to see if they reacted to form the expected salt. They did, in fact, react to form a white crystalline salt so the reaction was attempted with acetic acid and ethanol. The acid was reacted with the thionyl chloride and pyridine, all three being of equal concentration. This was refluxed for several hours at 76°C and the ethanol was then added dropwise and this mixture was refluxed for two hours. The resulting mixture smelled strongly of pyridine and ethyl acetate indicating the reaction had proceeded. Thus, the same reaction was attempted with α,α,α',α'-tetramethyladipic acid and neopentyl glycol. It was hoped that the acid chloride mixture would be able to be reacted directly with the alcohol to esterify it. In this way, pyridine would be the solvent and the catalyst.

In this first synthesis of the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate, the acid chloride synthesis was carried out as descibed above but in the esterification, dimethoxyethane was used as the solvent. The product formed was a pleasant smelling orange oil weighing 1.76 g., and .01 g. of crystals. Thin layer chromatography was performed and the two were determined to be of differing compositions. The crystals melted in stages, from 125-130°C, then from 185-190°C. This suggests that the solid was a mixture of the two solid reactants, the first melting point corresponding to neopentyl glycol, the second to tetramethyladipic acid.

The oil was first characterized by NMR. The proton spectrum (NMR VIa) is not a simple as expected. The peaks exhibit a lot of second order splitting.

To interpret this spectrum, a spectrum was first run on neopentyl

glycol (see NMR IXa). The methyl protons are clearly present at .9ppm while the methylene protons absorb at 3.5ppm. That leaves the peak at 2.4ppm to represent the OH protons of the glycol. These assignments are certain as they are supported nicely by the integration values of 3:2:1 for the methyl, methylene, and hydroxide protons, respectively.

With these assignments in mind as well as the fact that the reaction was run with a large excess of the glycol, an interpretation of the spectrum can be made. The large peak at .86ppm can be assigned to the methyl protons of unreacted neopentyl glycol which wasn't removed from the diester by the separation scheme. If the large peak at 3.39ppm is assigned to the methylene protons and the absorption at 3.6ppm to the hydroxide protons, these three absorptions would account for the free neopentyl glycol in the solution. The integration supports these assignments. Reading from the plot, the integration values are 24:13:6 or 4:2.2:1. This can be looked upon as the ratio of the three types of glycol protons.

That would leave the remaining peaks due to the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate. The absorption at .94ppm is that of the glycol methyl protons. The broader absorption at 1.1ppm is almost certainly due to the tetramethyladipic acid methyl protons as they appear at the same chemical shift in the spectrum of α,α,α',α'-tetramethyladipic acid (NMR IIa). Therefore, the peaks between 1.28-1.5ppm most probably represent the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate methylene protons on carbon 8 (see Fig. 11) for the same reason. That leaves two absorptions, one group of peaks between 3.3-3.38ppm and the other at 4ppm. These would represent the glycol methylenes. The choice as to which is which was

made after consulting the Aldrich Library of NMR Spectra.[20] Compounds which most nearly approximated the system of a methylene group bonded to a carboxyl group with a β-hydroxymethylene were investigated. Although there were a few that contradicted, most compounds, including methyl-2,2-dimethyl-3-hydroxypropionate show the methyl or methylene bonded to the carboxyl group absorbing further downfield that the hydroxy-methyl or methylene. Therefore, the peaks appearing at 4ppm were assigned to the methylene hydrogens bonded to the carboxyl group and the peaks between 3.3-3.38ppm were assigned to the hydroxymethylene hydrogens.

A rationalization of the integrations was attempted to support the above assignments (see Fig. 10, below).

proton	CH_3 (NPG)	CH_3 (adipic acid)	CH_2 (adipic acid)	CH_2 (NPG)	hydroxyCH_2	OH
carbon (see Fig. 11)	3	7	8	4	1	
chemical shift (δ)	.86	1.1	1.3-1.5	4	3.3	8.05
integration	23	28	14	9	27	6
integration ratio	3.8	4.67	2.3	1.5	4.5	1
number of protons	4	5	2	2	4	1

Fig. 10.-Interpretation of integration values for NMR VIa.

Although the ratios don't all coincide with the expected ratios, they do give a sum total of 18 or 19 hydrogens (for one-half of the ester since it is symmetrical) which approximates the actual value which would be 19. Also note that the peak at 8ppm was assumed to be that of the glycol OH, which could appear at any variety of chemical shifts. A summary of the assignments for the neopentyl glycol

α,α,α',α'-tetramethyladipoate is shown in Fig. 11.

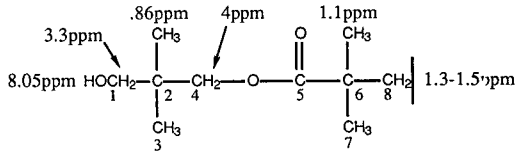


Fig. 11.-Peak assignments for NMR VI.

Infrared spectrum IV possesses all the characteristic absorptions of not only an ester but more specifically the spectrum shows stretching and bending due to adipic acid esters and neopentyl glycol as well. The general ester absorptions include: alcohol stretching from $3700\text{-}3000 cm^{-1}$ due to the free hydroxides on either end of the molecule, carbonyl-oxygen stretching from $1300\text{-}1100 cm^{-1}$, and carbon-oxygen stretching from $1075\text{-}100 cm^{-1}$. The absorptions specific to neopentyl glycol occur at 925 and $860 cm^{-1}$, these however don't support diester formation since it is known that the product mixture contains unreacted glycol. Those resembling the literature absorptions of α,α'-dimethyladipic acid methyl and methylene C-H stretches are seen at 1475 and $1375 cm^{-1}$.

The ^{13}C NMR of this product is shown by NMR VIb. Because of the different constitiuents present it is difficult to interpret. The total number of carbons expected from the both the diester and unreacted glycol is 11. This spectrum contains upwards of 25 peaks. Three regions of the spectrum can be seen: a methyl carbon region from 20-27ppm, a methylene carbon region from 60-75ppm, and a carbonyl region at 162ppm. These were determined from the 13C spectra of the pure glycol (NMR IXb) and α,α,α',α'-tetramethyladipic acid (NMR IId). To test

these classifications an APT spectrum was run (NMR VIc). Indeed the methyl peaks did invert while the ones classified as methylenes remained unchanged. To get a better idea of which carbons are attached to which hydrogens, a HETCOR, or heterogeneous nucleus correlation experiment was run (NMR VIf). It plots the carbon spectrum against the proton spectrum and correlates carbons with their hydrogens. A few results can be noted from this spectrum. First there is an interaction between what were said to be the glycol methyl protons and the carbon peaks at 22ppm. This is consistent with what the spectrum of pure glycol indicates (NMR IXb). Another interaction is seen between the tetramethyladipic acid methyls in the diester and the ^{13}C peak at 25ppm. This too, makes sense since the ^{13}C peak for the methyls of tetramethyladipic acid in NMR IIc appeared slightly further downfield at 30ppm in deuterated acetone. What was thought to be the CH_2-carboxyl hydrogens in the diester show an interaction with the group of methylene carbons at 68-70ppm.

It is important to note that the ^1H NMR spectrum of bis-neopentyl glycol $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipoate (NMR VIa) should contain only singlets. Because it is so complex it is unlikely that the multitude of splitting is due solely to interactions with unreacted neopentyl glycol. Rather it is the presence of byproducts such as monoester and ringed structures that are contributing to the spectra's complexity. This possibility can be inferred from the carbon spectrum which indicates that there could be more than one type of carbonyl carbon because there are two peaks at 161ppm and the multitude of methylene and other peaks. There also exists the possibility that the complexity of the spectra of bis-neopentyl glycol

α,α,α',α'-tetramethyladipoate could be due to interactions with itself; interesting interactions can be seen in the HCOSY spectrum of bis-neopentyl glycol α,α,α'α,'-tetramethyladipoate (NMR VId and e) between the hydroxy methylene protons and what were assumed to be the OH protons at both 3.6 and 8.05ppm. A COSY or homonuclear correlation experiment identifies interactions that occur between protons that aren't necessarily on adjacent carbons.

This synthesis was attempted again with approximately the same amounts of reactants. This reaction differed from the first in that pyridine was used not only as a catalyst in the acid chloride reaction, but also as the solvent in the esterification reaction. The esterification was also run at a higher temperature (115°C) for a considerably longer period of time, 24 hours.

The two ether extractions performed on the reaction mixture gave essentially the same product each time as indicated by the NMR and IR spectra (NMR VII & VIII and IR IV & V). The ^{1}H NMR spectra appear considerably "cleaner" than the spectrum of the first bis-neopentyl glycol α,α,α',α'-tetramethyladipoate ester synthesis. Moreover, it would appear that they do, in fact, differ from spectrum VI.

If the peaks are assigned as they were in NMR VI, one will notice that the two singlets that characterized the diol methyl protons are not present. Instead, the diol methyl protons appear as one singlet. Similarly, the multitude of peaks representing the methylene protons of the alcohol has become a large singlet. Also notable is the large relative increase in size of the deuterated chloroform peak at 7.3ppm. This is indicative of the presence of acidic protons which would be able to

exchange with the deuterium. In short, the spectra characterizing the products from the second synthesis of bis-neopentyl glycol α,α,α',α'-tetramethyladipoate are a combination of the spectra for neopentyl glycol and α,α,α',α'-tetramethyladipic acid.

The IR spectrum of this product (IR V) also differs from the spectrum of the original neopentyl glycol ester synthesis. When compared with the literature there is no doubt that it is a spectrum of neopentyl glycol with some carbonyl stretching ($1700cm^{-1}$) and carboxyl OH stretching ($3500\text{-}300cm^{-1}$) from unreacted α,α,α',α'-tetramethyladipic acid. There is no carbonyl-oxygen stretch characteristic of an ester as there was in IR IV. The lack of carbonyl-oxygen stretching indicates that no reaction occured.

Furthermore the two indentical ^{13}C NMR spectra (NMR VIIb and VIIIb) display the results of a neopentyl glycol ^{13}C NMR when compared to the spectrum taken of the pure neopentyl glycol used in the reactions (NMR IXb).

Thus, it is apparent that the reaction was unsuccessful. The most obvious reasons for this failure relate perhaps to the change in reaction conditions, i.e. the higher temperature and longer reflux time. Another very notable occurrence was the lack of solubility of the neopentyl glycol in the pyridine. When the experiment was run, the solution had to be agitated vigorously to keep the diol from settling to the bottom of the flask. This could have contributed to the lack of product formed.

Conclusions

In conclusion, α,α,α',α'-tetramethyladipic acid was synthesized in

fair yields using the redox coupling reaction of Coffman et. al.[18] It was found that the best yields were obtained when the reaction was kept below 30°C and the crude product was filtered by vacuum through diatomaceous earth instead of gravity filtration. It also seems beneficial to handle the ferrous sulfate heptahydrate solution in a manner that minimizes exposure to the air to prevent the oxidation of the ferrous ion to the ferric.

The esterification of the two diesters was successful although the yields were poor. It is quite possible that tetramethyladipic acid has the ability to form an anhydride during the acid chloride preparation. This would result in a mixture of products including the mono and diesters. The two successful esterification reactions were run for considerably shorter amounts of time and at a lower temperatures than the unsuccessful second synthesis of the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate.

The technique of reacting the solid diacid with thionyl chloride and pyridine appears to have been successful in forming the diacid chloride. However, it is unknown whether this mixture can be reacted directly to esterify or whether a different solvent is necessary, as only the first esterification with neopentyl glycol using dimethoxyethane as the solvent was successful.

The spectra of the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate proved to be quite complicated due in part to the presence of unreacted glycol but the possibility of intra- and intermolecular interactions also exists as well as the formation of different products.

Implications

Now that it has been shown that the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate can be synthesized the possibility exists for polymerization. The synthesis of such a sterically hindered polyester could have far reaching implications. Since the saponification rates of the tertiary-butyl esters synthesized here are effectively zero,[7,8,9] one would similarly expect the neopentyl glycol diester would show great stability in basic media. It is only when a polyester is finally synthesized can it be characterized and its possible functions and uses be determined.

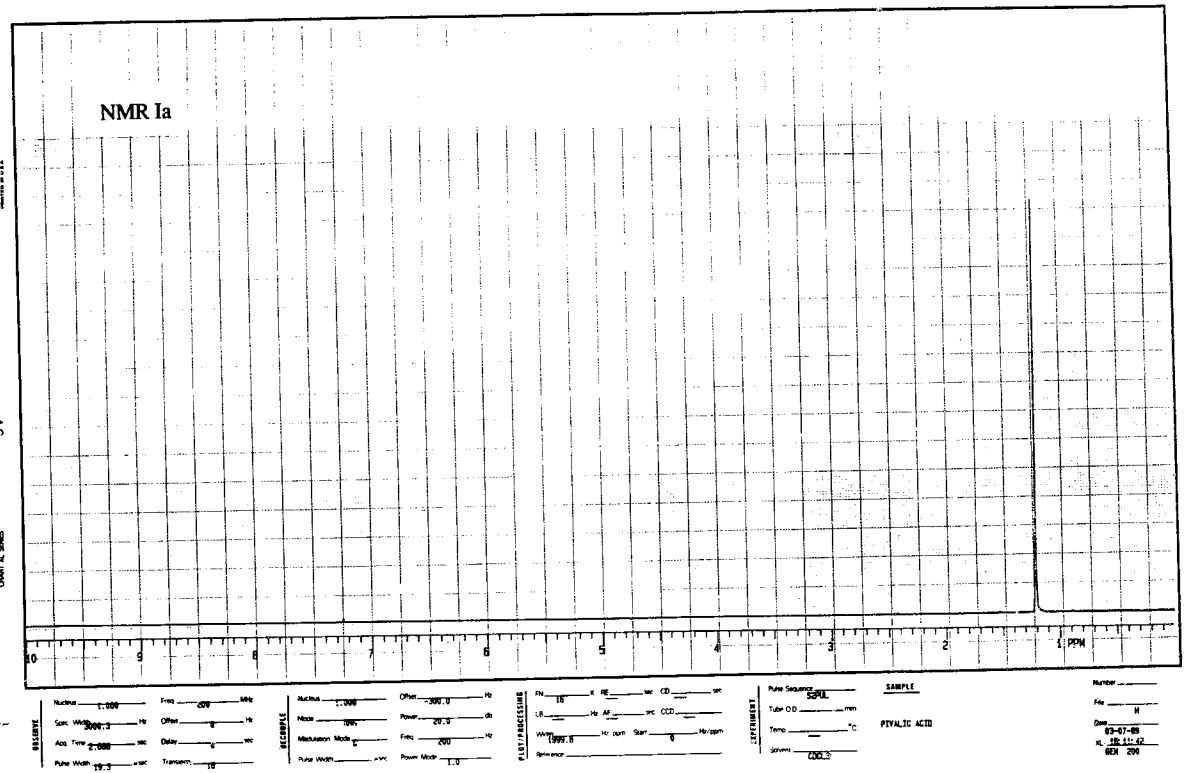
Suggestions for future work

The formation of α,α,α',α'-tetramethyladipic acid is a reaction that should be investigated. Especially pertinent is the reactivity of pivalic acid by the free radical mechanism to form the diacid. Certainly the bis-neopentyl glycol α,α,α',α'-tetramethyladipoate reaction merits investigation. There are a variety of factors which should be considered including the temperature and length of reaction as well as the technique of reacting the the diacid with $SOCl_2$ and pyridine and then after removal of the excess $SOCl_2$, reacting directly with the diol.

Third, an attempt to synthesize and characterize the polyester of neopentyl glycol and α,α,α',α'-tetramethyladipoate, which is of course the ultimate goal of this work, should be undertaken.

Appendix I

NMR Spectra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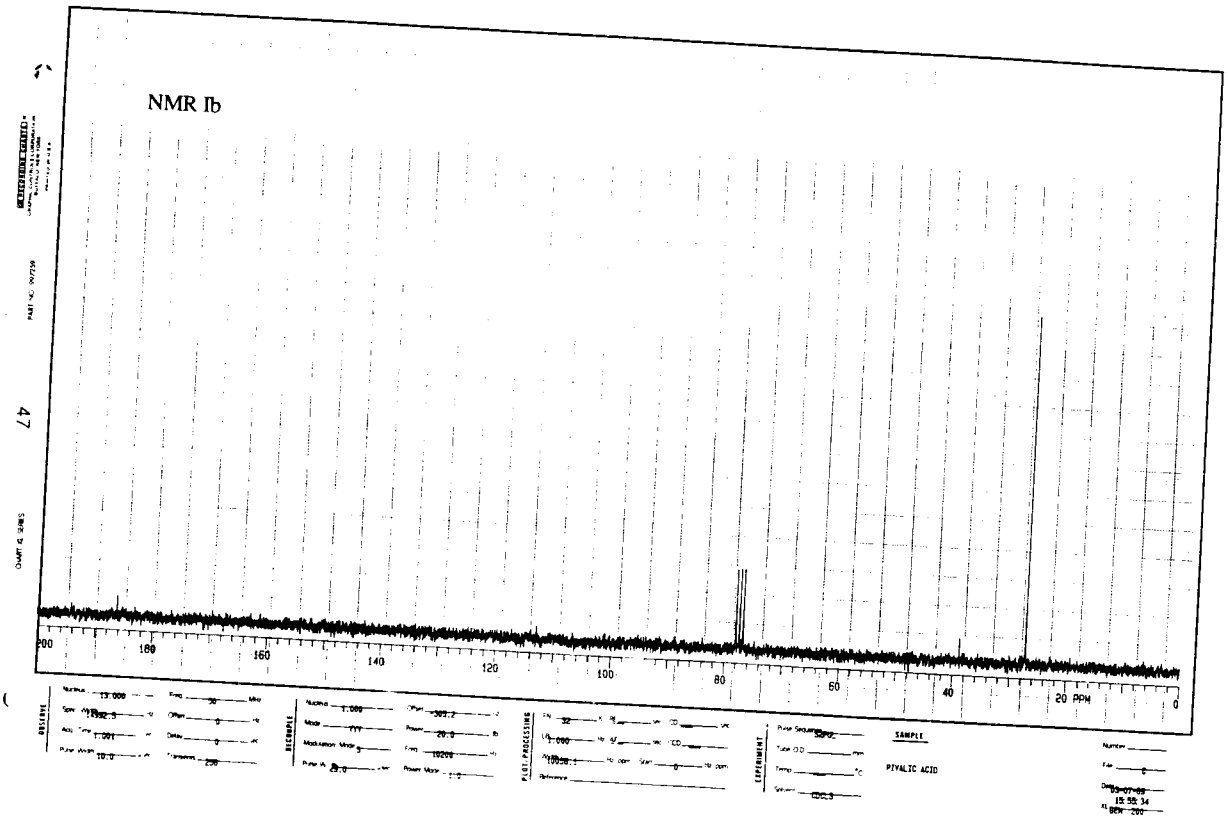
10
9
8
7
6
5
4
3
2
1 PPM
CHART XL SERIES
PART NO 997259
PIVALIC ACID
03-07-09
XL 10:11:42
GEM 200


NMR Ib
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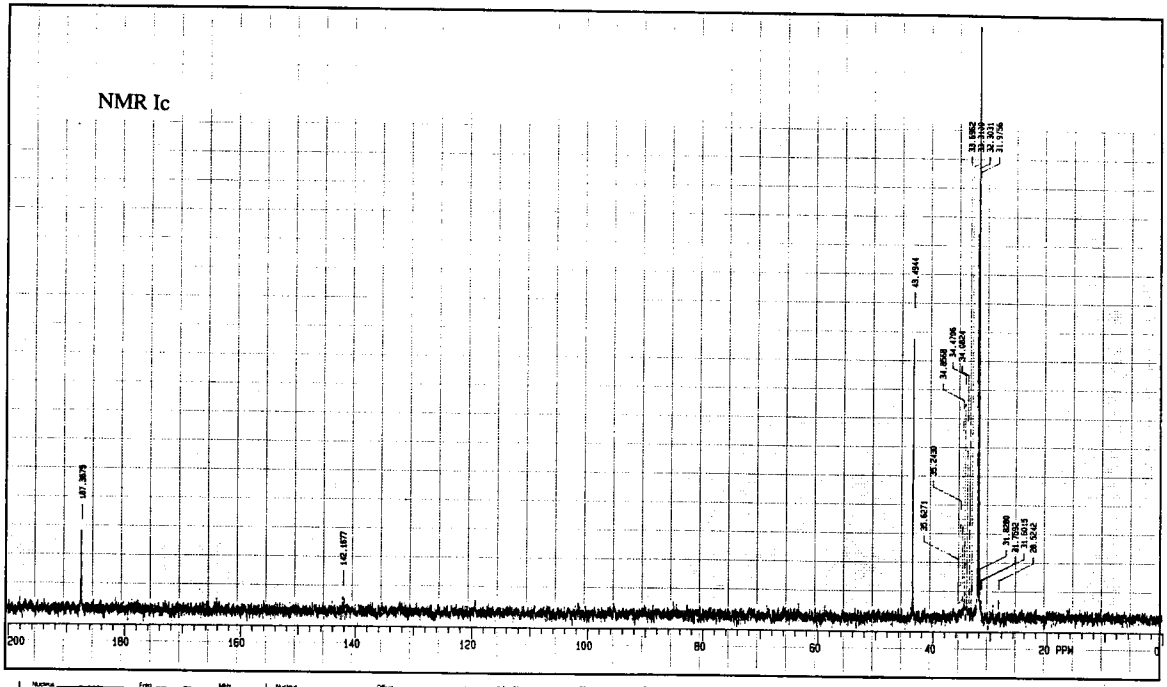
180
160
140
120
100
80
60
40
20 PPM
0
SAMPLE
PIVALIC ACID

NMR Ic



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Acq. Time sec
Pulse Width sec
Freq MHz
Offset Hz
Delay sec
Transmit

DECOUPLE
Nucleus
Mode
Modulation Mode
Offset Hz
Power dB
Freq Hz
Power Mode

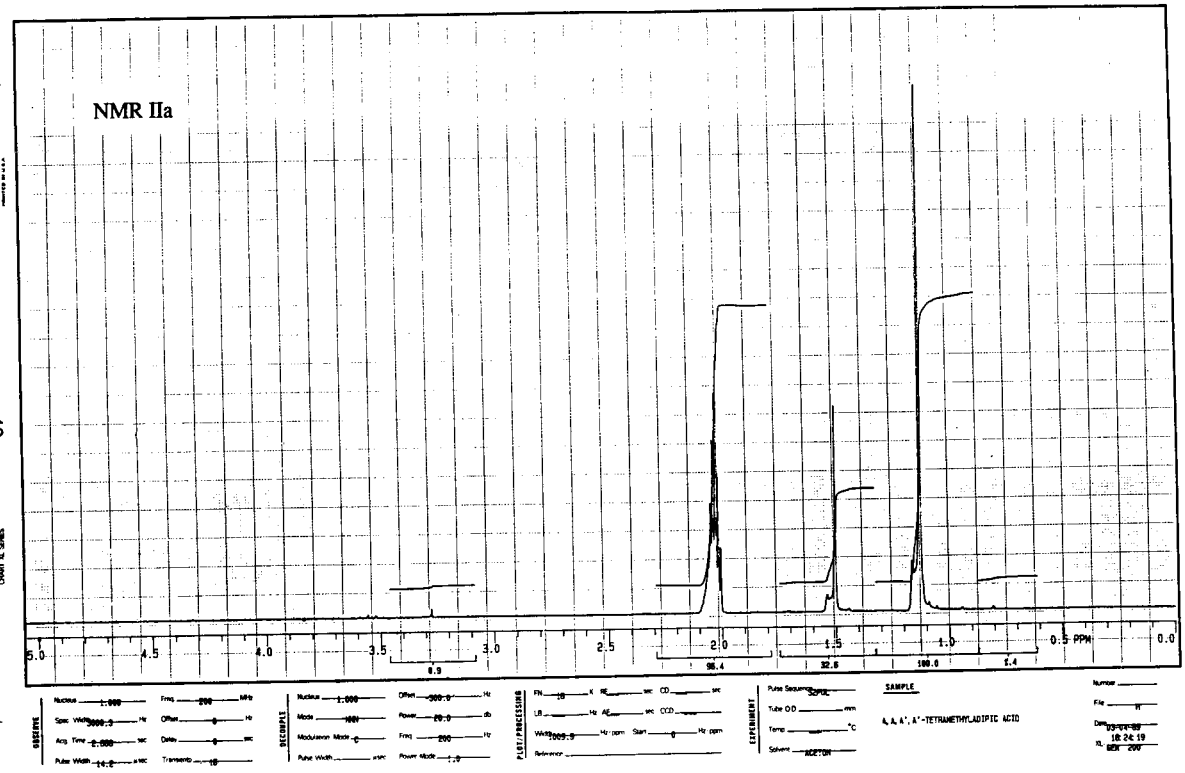
FIRST PROCESSING
FN K RE sec CD sec
LB Hz AF sec CCD
Wi-Ph Hz ppm Vert Hz ppm
Reference

EXPERIMENT
Pulse Sequence
Tube O.D. mm
Temp °C
Solvent

SAMPLE

PIVALIC ACID IN DEUTERATED ACETONE

Number
File
Date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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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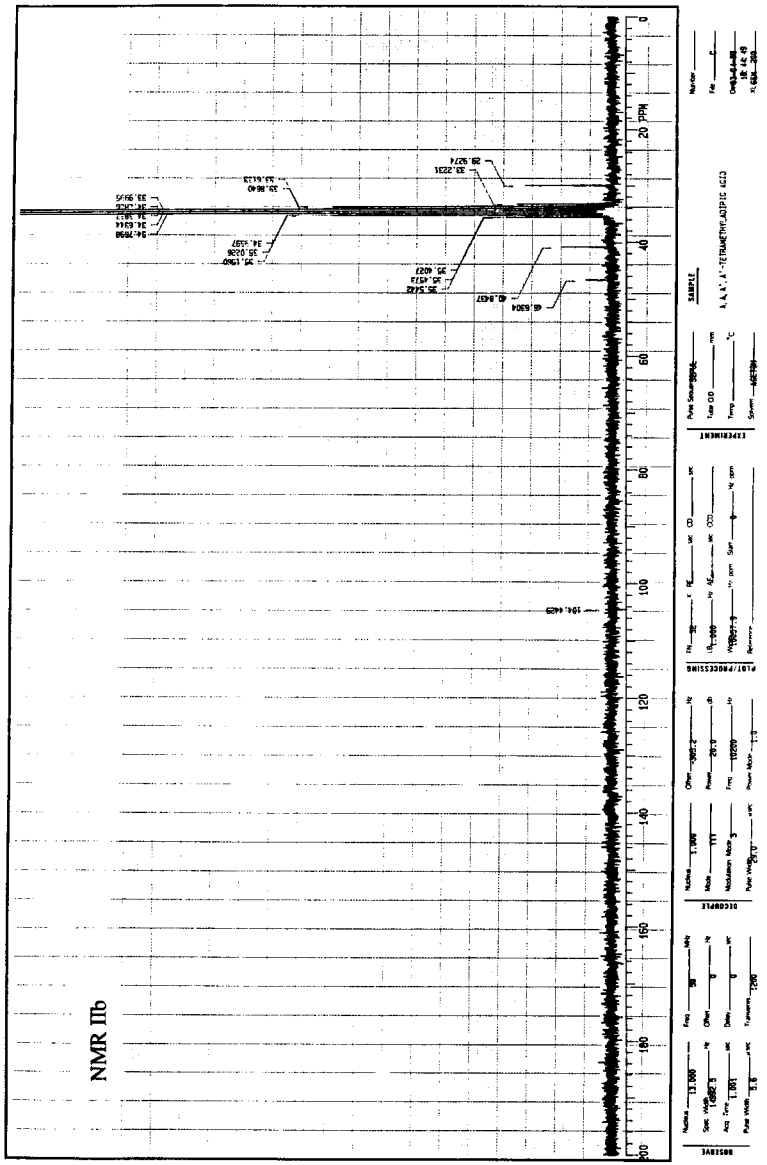
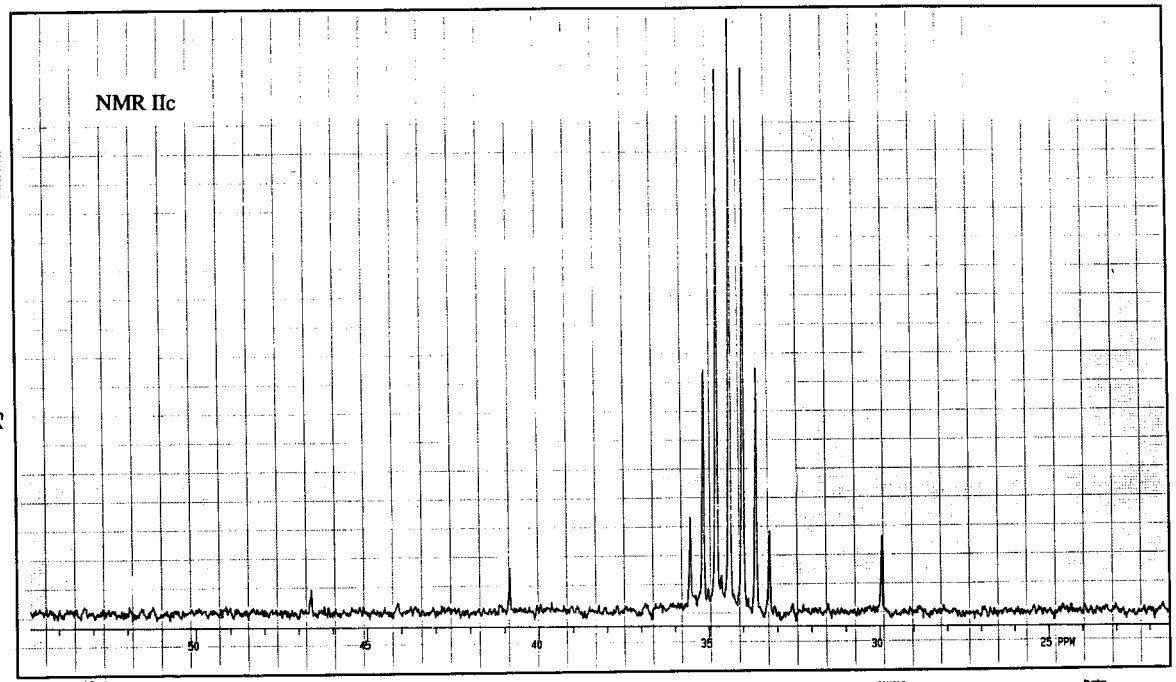
0.0
SAMPLE
4,4,4',4'-TETRAMETHYLADIPIC ACID
ACETON
18 24 19


NMR IIb
CHART XL SERIES
PART NO 997259
50
0
20
40
60
80
100
120
140
160
180
200
PPM
A,A,A',A'-TETRAMETHYLADIPIC ACID
SAMPLE
EXPERIMENT
ACQUISITION
PROCESSING
DISPLAY
PLOT



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DECOUPLE: Nucleus ____; Offset ____ Hz; Mode ____; Power ____ db; Modulation Mode ____; Freq ____ Hz; Pulse Width ____ μsec; Power Mode ____

PLOT/PROCESSING: FN ____ K; RE ____ sec; OD ____ sec; LB ____ Hz; AF ____ sec; OD ____; Width ____ Hz ppm; Start ____ Hz ppm; Reference ____

EXPERIMENT: Pulse Sequence ____; Tube OD ____ mm; Temp ____ °C; Solvent ____

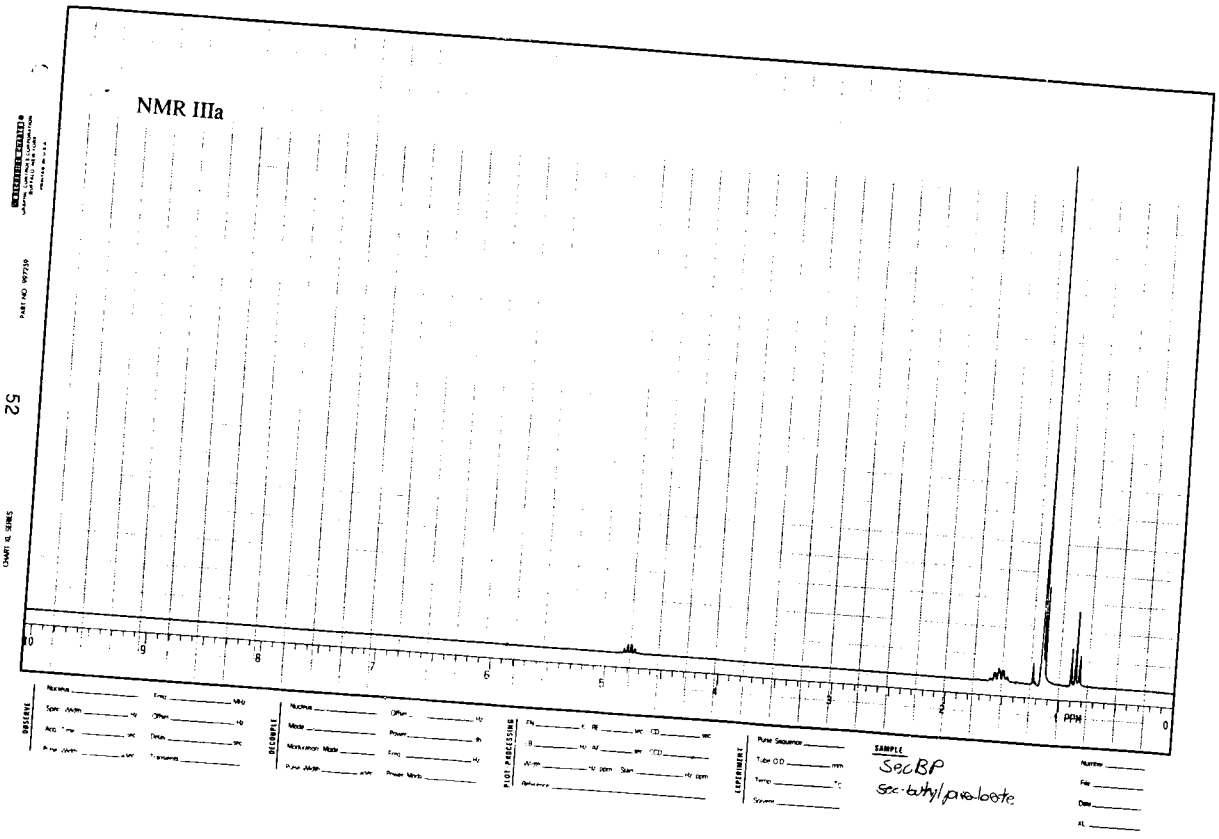
SAMPLE: AA',A',N'-tetramethylsuccinic acid

Number ____; File ____; Date ____; XL ____

PART NO 997259

CHART XL SERIES

51


NMR IIIa
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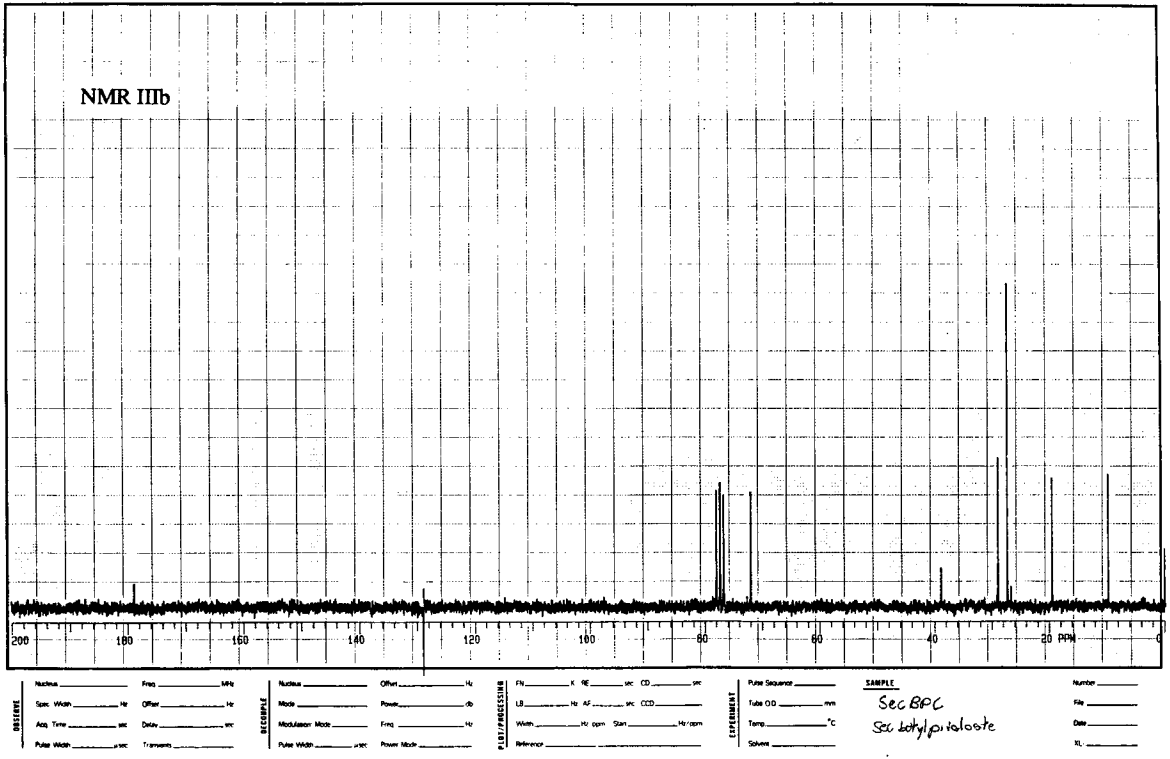
PPM
SecBP
sec-butyl pivaloate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180
160
140
120
100
80
60
40
20 PPM
0
OBSERVE
Nucleus
Freq MHz
Spec Width Hz
Offset Hz
Acq Time sec
Delay sec
Pulse Width µsec
Transients
DECOUPLE
Nucleus
Offset Hz
Mode
Power db
Modulation Mode
Freq Hz
Pulse Width µsec
Power Mode
PLOT/PROCESSING
FN K RE sec CD sec
LB Hz AF sec CCD
Width Hz ppm Start Hz/ppm
Reference
EXPERIMENT
Pulse Sequence
Tube OD mm
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File
Date
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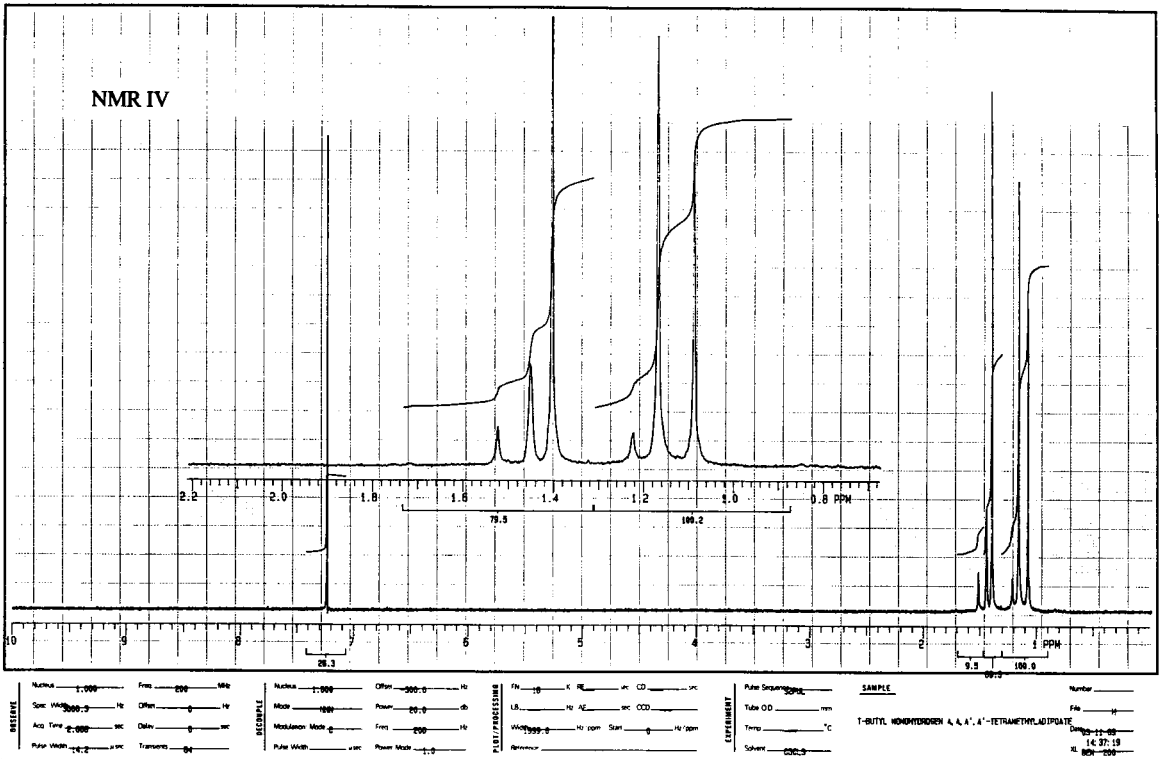
PART NO 997259
CHART XL SERIES
53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1.8
1.6
1.4
1.2
1.0
0.8 PPM
79.5
100.2
26.3
9.5
100.0
1 PPM
PART NO 997259
CHART XL SERIES
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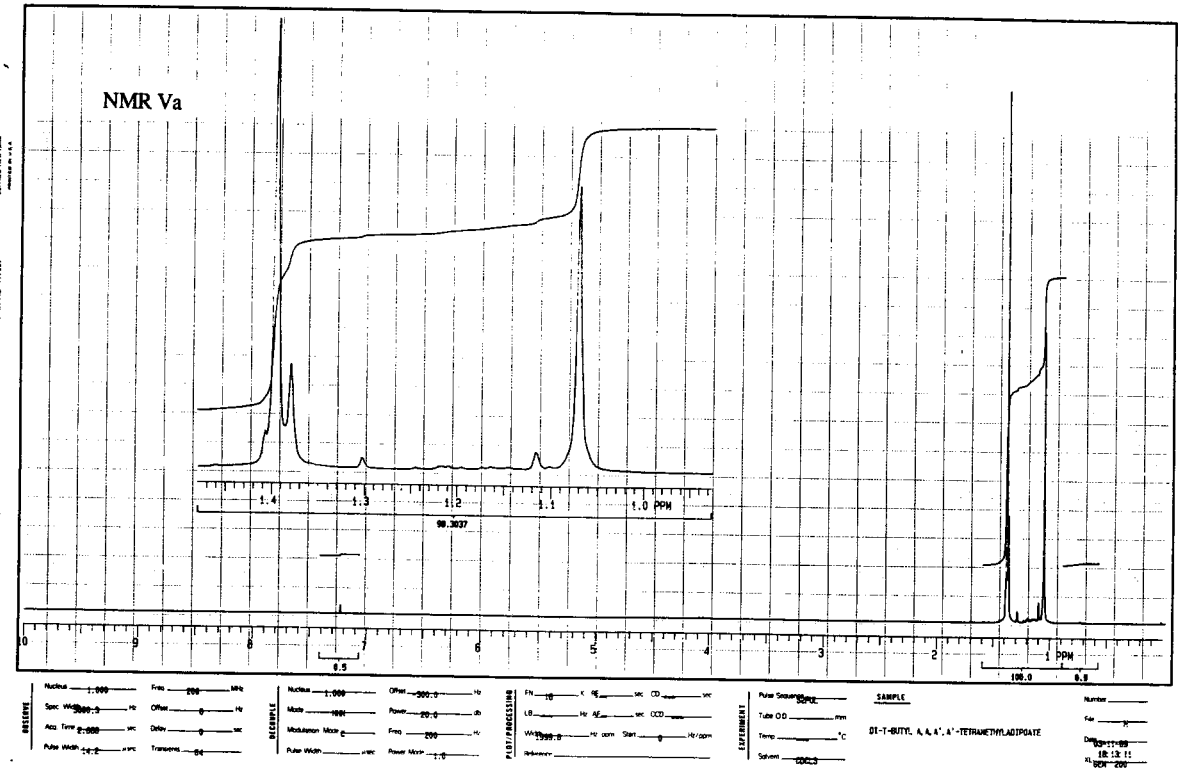
NMR Va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9
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100.0
0.9
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DECOUPLE
PLOT/PROCESSING
EXPERIMENT
SAMPLE
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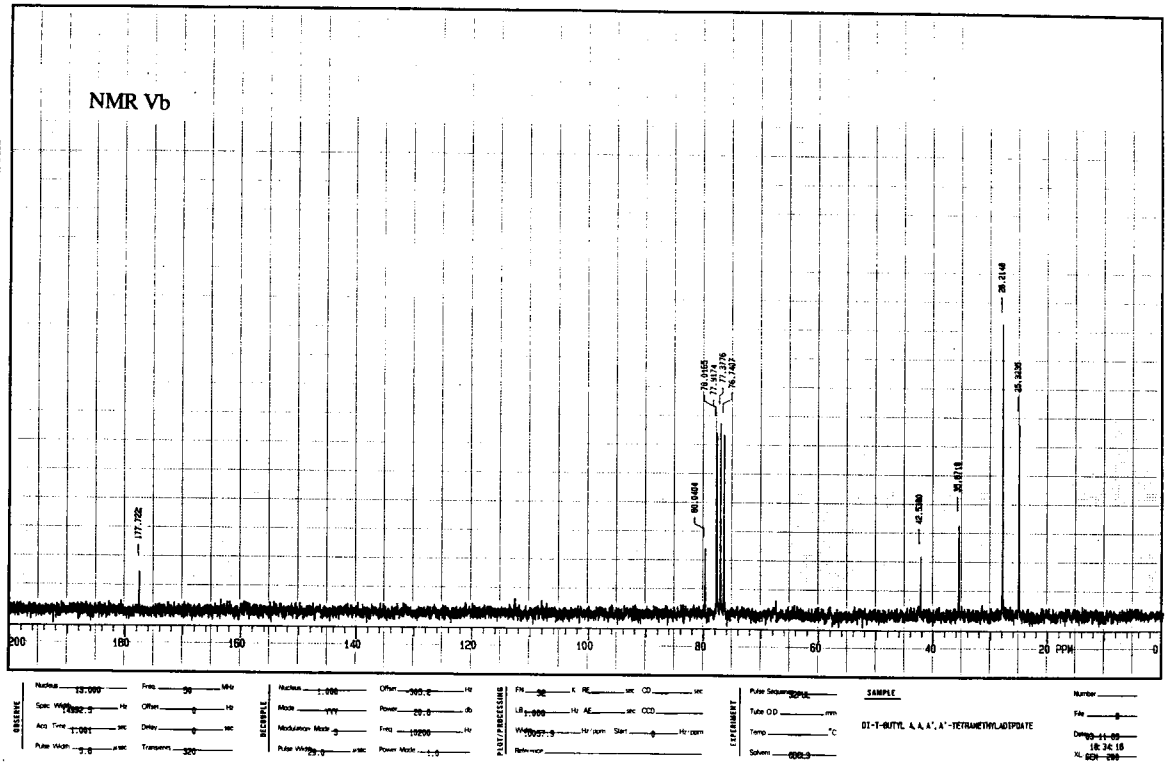
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200
180
160
140
120
100
80
60
40
20
PPM
0
OBSERVE
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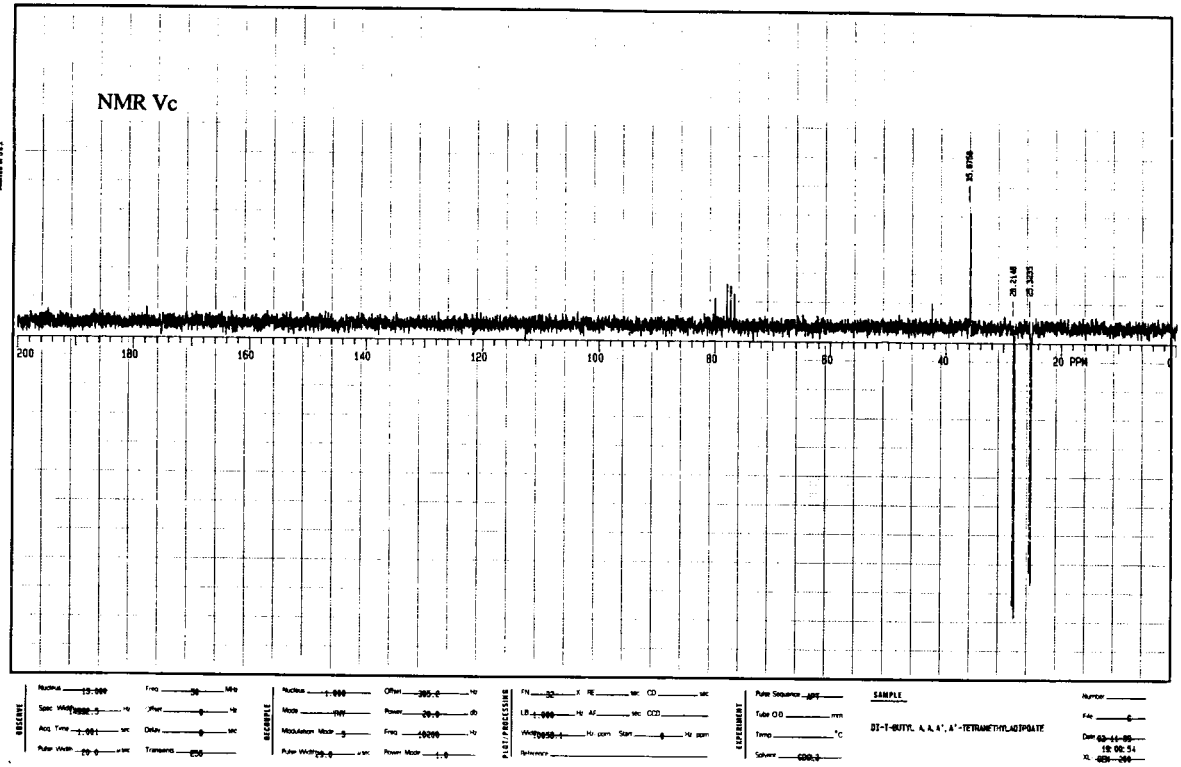
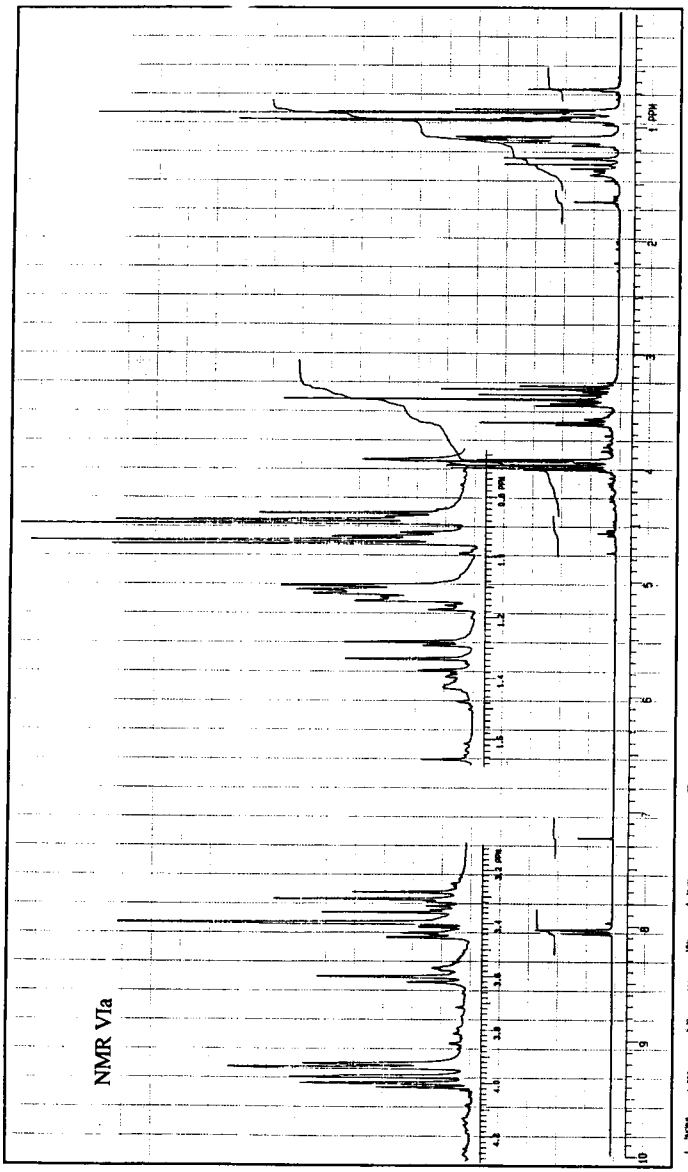
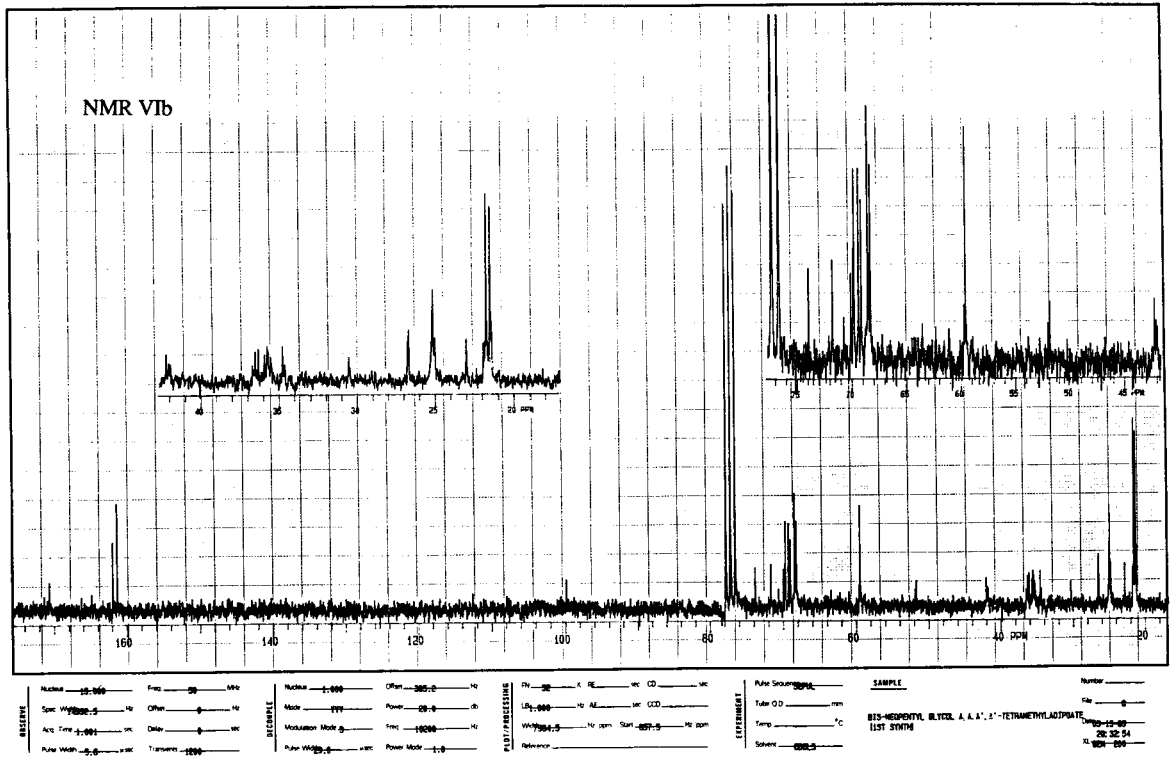
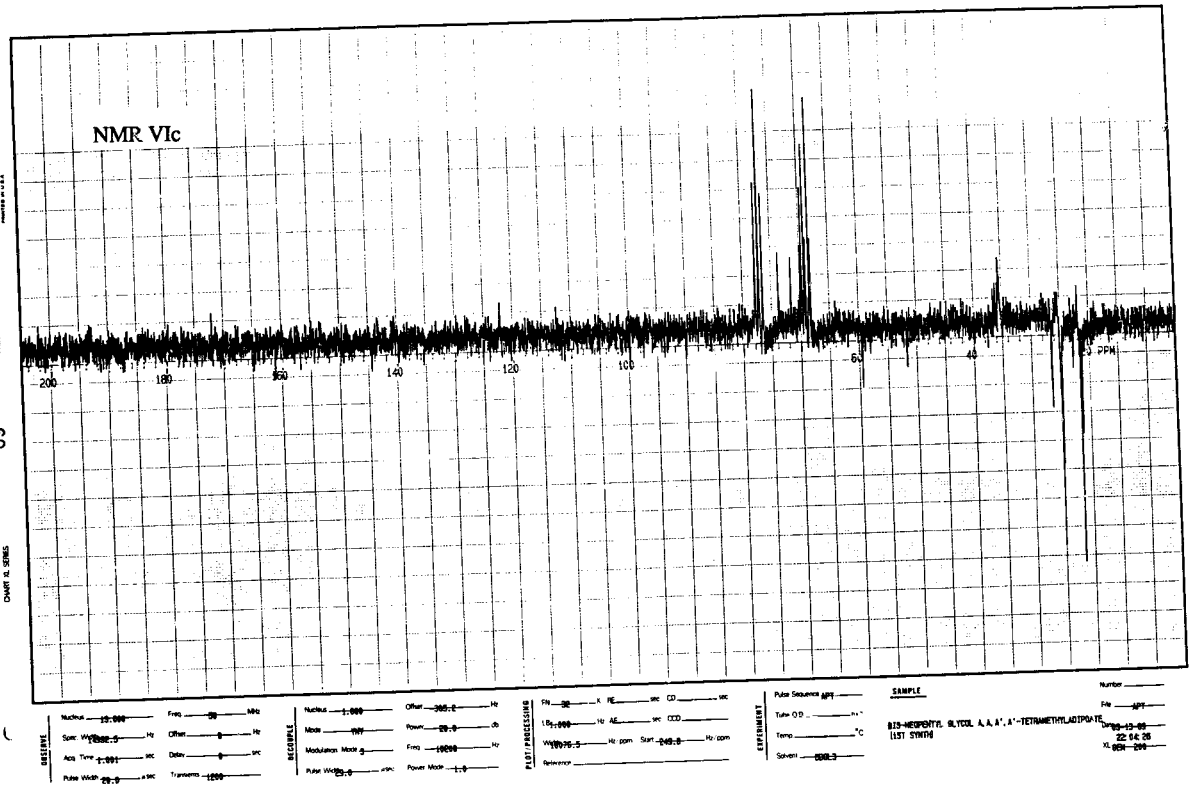
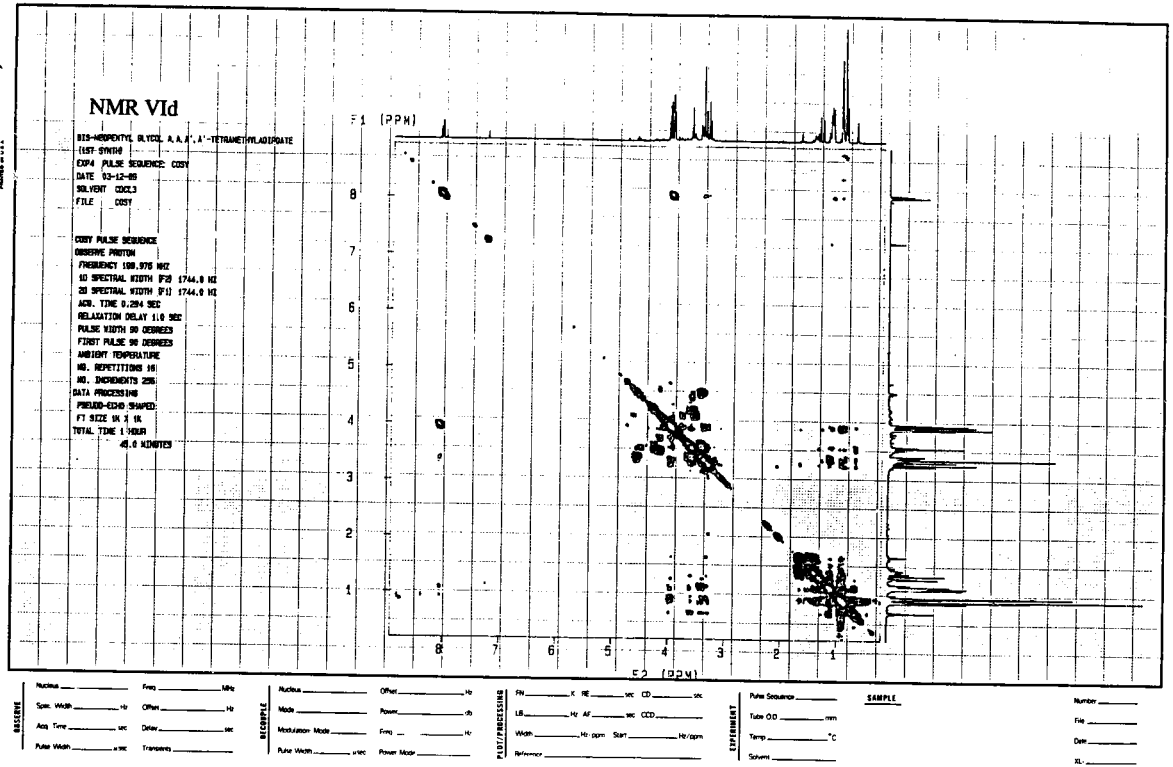
Freq 50 MHz
Spec Width 12992.5 Hz
Offset 0 Hz
Acq Time 1.001 sec
Delay 0 sec
Pulse Width 9.0 usec
Transmit 320
DECOUPLE
Nucleus 1.000
Offset 500.0 Hz
Mode YYY
Power 20.0 db
Modulation Mode 0
Freq 10200 Hz
Pulse Width 29.0 usec
Power Mode 1.0
PLOT/PROCESSING
FN 32
LB 1.000 Hz
Width 12987.5 Hz/cm
Reference
EXPERIMENT
Pulse Sequence SGPUL
Tube OD mm
Temp °C
Solvent CDCl3
SAMPLE
DI-T-BUTYL A,A,A',A'-TETRAMETHYLADIPDATE
Number
File 0
Date 93-11-09
Time 10:34:16
XL 601 200

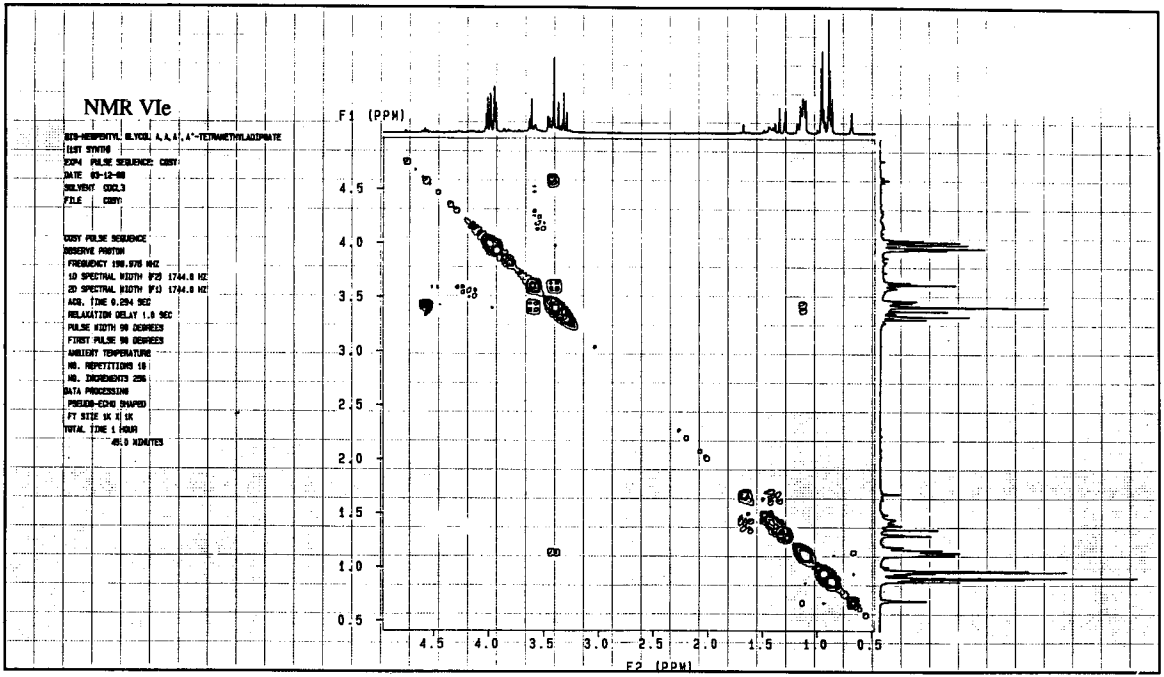

NMR Vc
35.6798
29.3148
25.3225
200
180
160
140
120
100
80
60
40
20 PPM
SAMPLE
DI-T-BUTYL A,A,A',A'-TETRAMETHYLADIPOATE


NMR VIa


NMR VIb
CHART XL SERIES
PART NO 997259
160
140
120
100
80
60
40 PPM
20
SAMPLE
BIS-NEOPENTYL GLYCOL 4,4,4',4'-TETRAMETHYLADIPOATE
1ST SYNTH


NMR VIc
200
180
160
140
120
100
80
60
40
PPM
PART NO. 997259
CHART SL SERIES
09
ACQUISITION
Nucleus 13.000
Spec Width 12082.5 Hz
Acq Time 1.001 sec
Pulse Width 29.0 usec
Freq 50 MHz
Offset 0 Hz
Delay 0 sec
Transients 1200
RECAMPLE
Nucleus 1.000
Mode NNY
Modulation Mode 0
Pulse Width 25.0 usec
Offset 305.2 Hz
Power 29.0 db
Freq 19998 Hz
Power Mode 1.0
PLOT/PROCESSING
FN 32 K PE sec CD sec
LB 1.000 Hz AE sec CCD
Width 10076.5 Hz ppm Start -249.8 Hz ppm
Reference
EXPERIMENT
Pulse Sequence APT
Tube OD in
Temp °C
Solvent CDCl3
SAMPLE
BIS-HEXDECYL GLYCOL A,A,A',A'-TETRAMETHYLADIPDATE
LIST SYNTH
Number
File APT
Date 93-12-08
22:04:26
XL BEH 200


NMR VId
BIS-NEOPENTYL GLYCOL A,A,A',A'-TETRAMETHYLADIPOATE
1ST SYNTH#
EXP4 PULSE SEQUENCE: COSY
DATE 93-12-08
SOLVENT CDCL3
FILE COSY
COSY PULSE SEQUENCE
OBSERVE PROTON
FREQUENCY 199.975 MHZ
1D SPECTRAL WIDTH [F2] 1744.8 HZ
2D SPECTRAL WIDTH [F1] 1744.8 HZ
ACQ. TIME 0.294 SEC
RELAXATION DELAY 1.0 SEC
PULSE WIDTH 90 DEGREES
FIRST PULSE 90 DEGREES
AMBIENT TEMPERATURE
NO. REPETITIONS 16
NO. INCREMENTS 256
DATA PROCESSING
PSEUDO-ECHO SHAPED
FT SIZE 1K X 1K
TOTAL TIME 1 HOUR
45.0 MINUTES
F1 (PPM)
F2 (PPM)
8
7
6
5
4
3
2
1



OBSERVE: Nucleus ____ Freq ____ MHz; Spec. Width ____ Hz; Offset ____ Hz; Acq. Time ____ sec; Delay ____ sec; Pulse Width ____ μsec; Transients ____

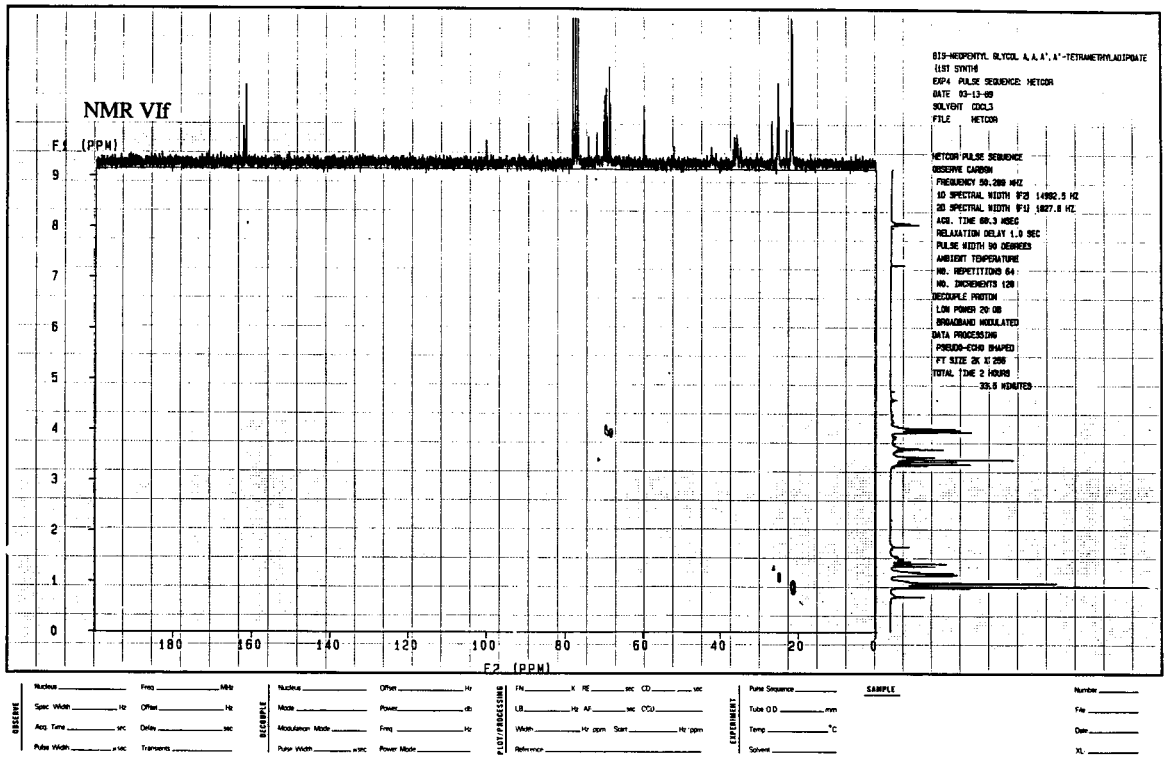
DECOUPLE: Nucleus ____ Offset ____ Hz; Mode ____ Power ____ db; Modulation Mode ____ Freq ____ Hz; Pulse Width ____ μsec; Power Mode ____

PLOT/PROCESSING: PH ____ K RE ____ sec CO ____ sec; LB ____ Hz AF ____ sec CCO ____; Width ____ Hz/ppm Start ____ Hz/ppm; Reference ____

EXPERIMENT: Pulse Sequence ____; Tube O.D. ____ mm; Temp ____ °C; Solvent ____

SAMPLE

Name ____; File ____; Date ____; XL ____



OBSERVE: Nucleus ____ Freq ____ MHz; Spec Width ____ Hz; Offset ____ Hz; Acq. Time ____ sec; Delay ____ sec; Pulse Width ____ μsec; Transients ____

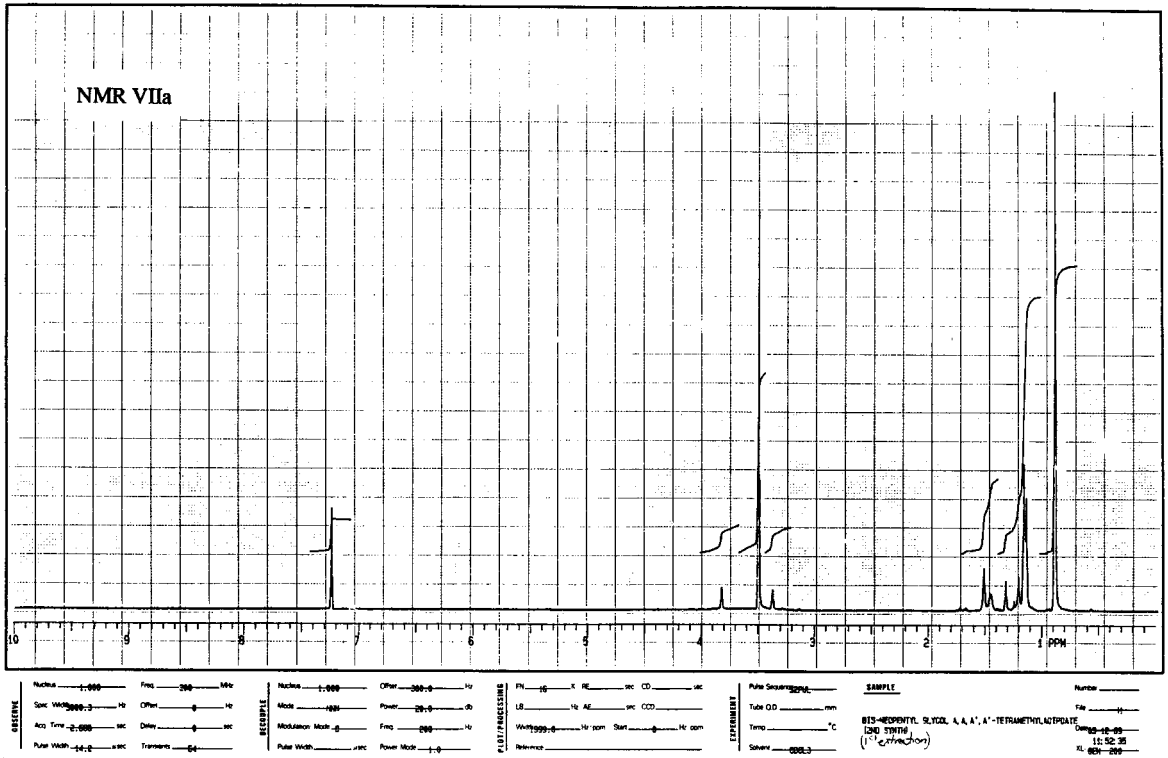
DECOUPLE: Nucleus ____ Offset ____ Hz; Mode ____ Power ____ db; Modulation Mode ____ Freq ____ Hz; Pulse Width ____ μsec; Power Mode ____

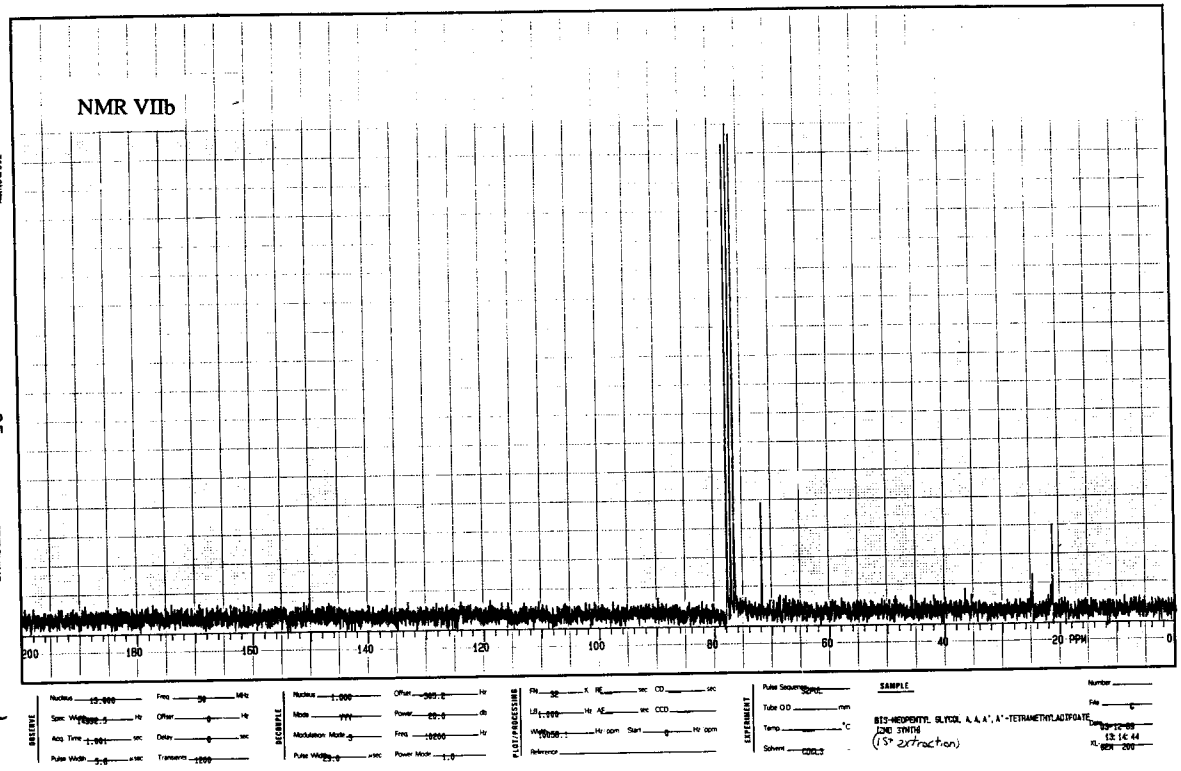
PLOT/PROCESSING: FN ____ K; RE ____ sec; CD ____ sec; LB ____ Hz; AF ____ sec; CCU ____; Width ____ Hz ppm; Start ____ Hz ppm; Reference ____

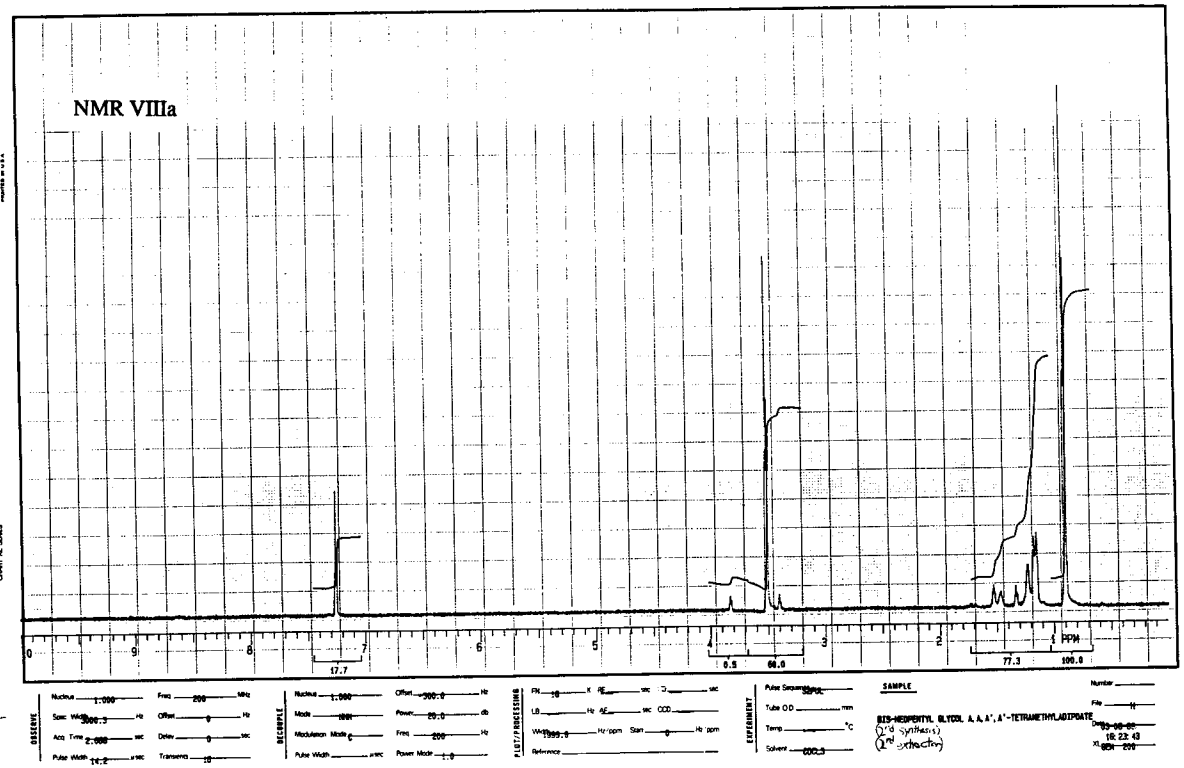
EXPERIMENT: Pulse Sequence ____; Tube O.D. ____ mm; Temp ____ °C; Solvent ____

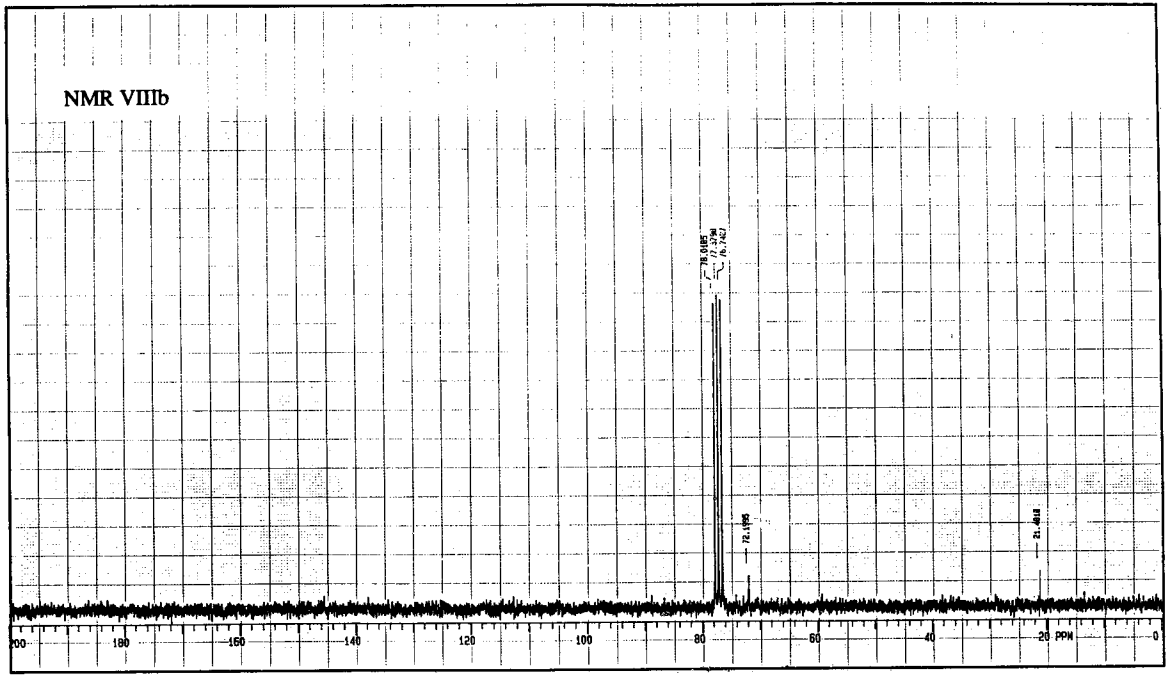
SAMPLE

Number ____; File ____; Date ____; XL ____


NMR VIIa
CHART XL SERIES
64
PART NO 997259
10
9
8
7
6
5
4
3
2
1 PPM
OBSERVE
Nucleus 1.000
Spec Width 5000.3 Hz
Acq Time 2.000 sec
Pulse Width 14.0 usec
Freq 200 MHz
Offset 0 Hz
Delay 0 sec
Transients 64
DECOUPLE
Nucleus 1.000
Mode 1H
Modulation Mode 0
Pulse Width usec
Offset 300.0 Hz
Power 29.0 db
Freq 200 Hz
Power Mode 1.0
PLOT/PROCESSING
FN 16 X RE sec CD sec
LB Hz AB sec CCD
Width 1999.6 Hz ppm Start 0 Hz ppm
Reference
EXPERIMENT
Pulse Sequence S2PUL
Tube O.D. mm
Temp °C
Solvent CDCL3
SAMPLE
BIS-NEOPENTYL GLYCOL 4,4,4',4'-TETRAMETHYLAZEPDATE
12MD SYNTH
(1st extraction)
Number
File 11
Date 89-10-09
11:52:35
XL 6EM-200


NMR VIIb
GE/NICOLET INSTRUMENTS
PART NO 997259
CHART XL SERIES
200
180
160
140
120
100
80
60
40
20 PPM
0
OBSERVE
Nucleus 13.000
Spec Width 14286.5 Hz
Acq. Time 1.001 sec
Pulse Width 5.0 usec
Freq 50 MHz
Offset 0 Hz
Delay 0 sec
Transients 1000
DECOUPLE
Nucleus 1.000
Mode YYY
Modulation Mode 0
Pulse Width 25.0 usec
Offset 385.8 Hz
Power 20.0 db
Freq 10200 Hz
Power Mode 1.0
PLOT/PROCESSING
FN 32 X PE sec CD sec
LB 1.000 Hz AE sec CCD sec
Width 10058.1 Hz ppm Start 0 Hz ppm
Reference
EXPERIMENT
Pulse Sequence SGNOE
Tube OD mm
Temp °C
Solvent CDCL3
SAMPLE
BIS-HEXAMETH. GLYCOL A, A, A', A'-TETRAMETHYLLACTIDATE
IDKI SYNTH
(1st extraction)
Number
File C
Date 93-10-08
13:14:44
XL GEN 200


NMR VIIIa
PART NO. 977259
CHART RL SERIES
99
0
9
8
7
6
5
4
3
2
1 PPM
17.7
0.5
60.0
77.3
100.0
OBSERVE
DECOUPLE
FLT/PROCESSING
EXPERIMENT
SAMPLE
BIS-NEOPENTYL GLYCOL A, A, A', A'-TETRAMETHYLADIPDATE
(2nd synthesis)
(2nd extraction)



PART NO. 997539

CHART 'A' SERIES

67

OBSERVE Nucleus 13.000 Freq 50 MHz; Spec. Width 2882.9 Hz Offset 0 Hz; Acq. Time 1.091 sec Delay 0 sec; Pulse Width 9.0 µsec Transmit 1200

DECOUPLE Nucleus 1.000 Offset -300.2 Hz; Mode YYY Power 20.0 dh; Modulation Mode 0 Freq 10200 Hz; Pulse Width 25.0 µsec Power Mode 1.0

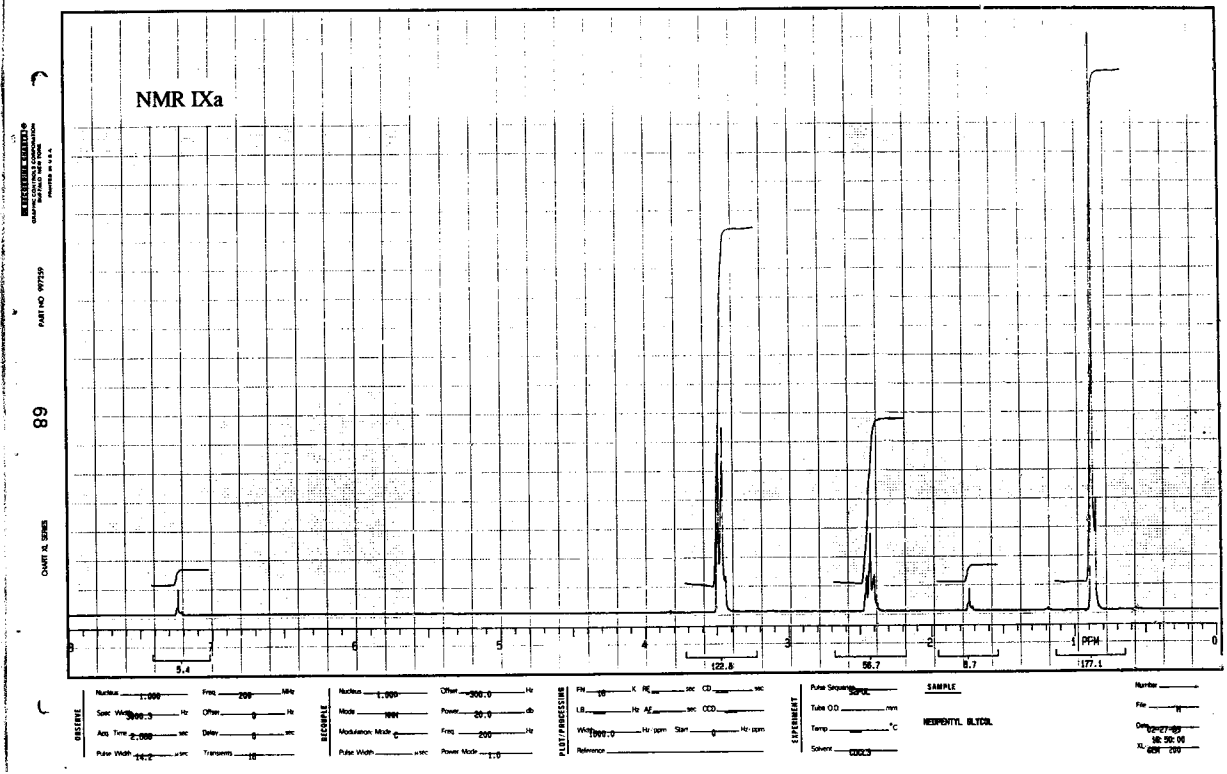
PLOT/PROCESSING FN 32 K RE sec CD sec; LB 1.000 Hz SE sec CCD; Width 10027.9 Hz/ppm Start 0 Hz/ppm; Reference

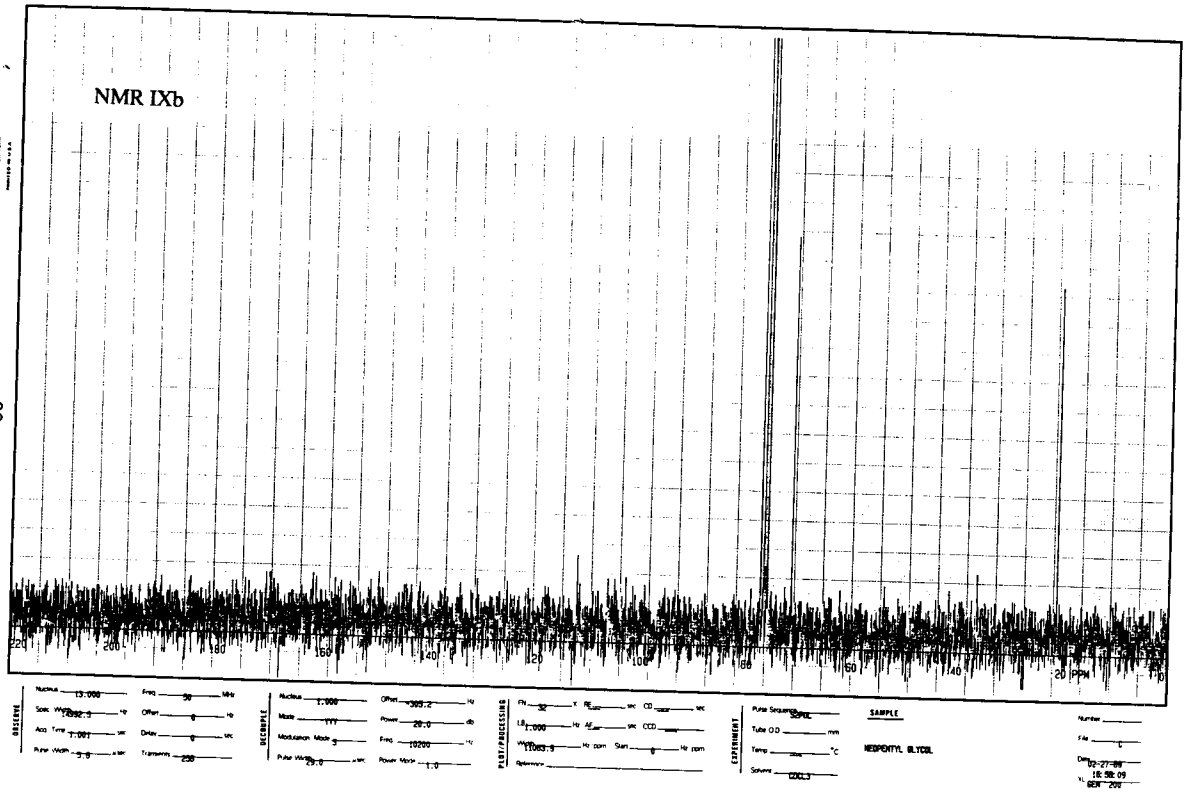
EXPERIMENT Pulse Sequence SGPUL; Tube O.D. mm; Temp °C; Solvent CDCl3

SAMPLE

BIS-NEOPENTYL GLYCOL 4,4,4',4'-TETRANETHYLADIPATE
(2nd Synth)
(2nd extraction)

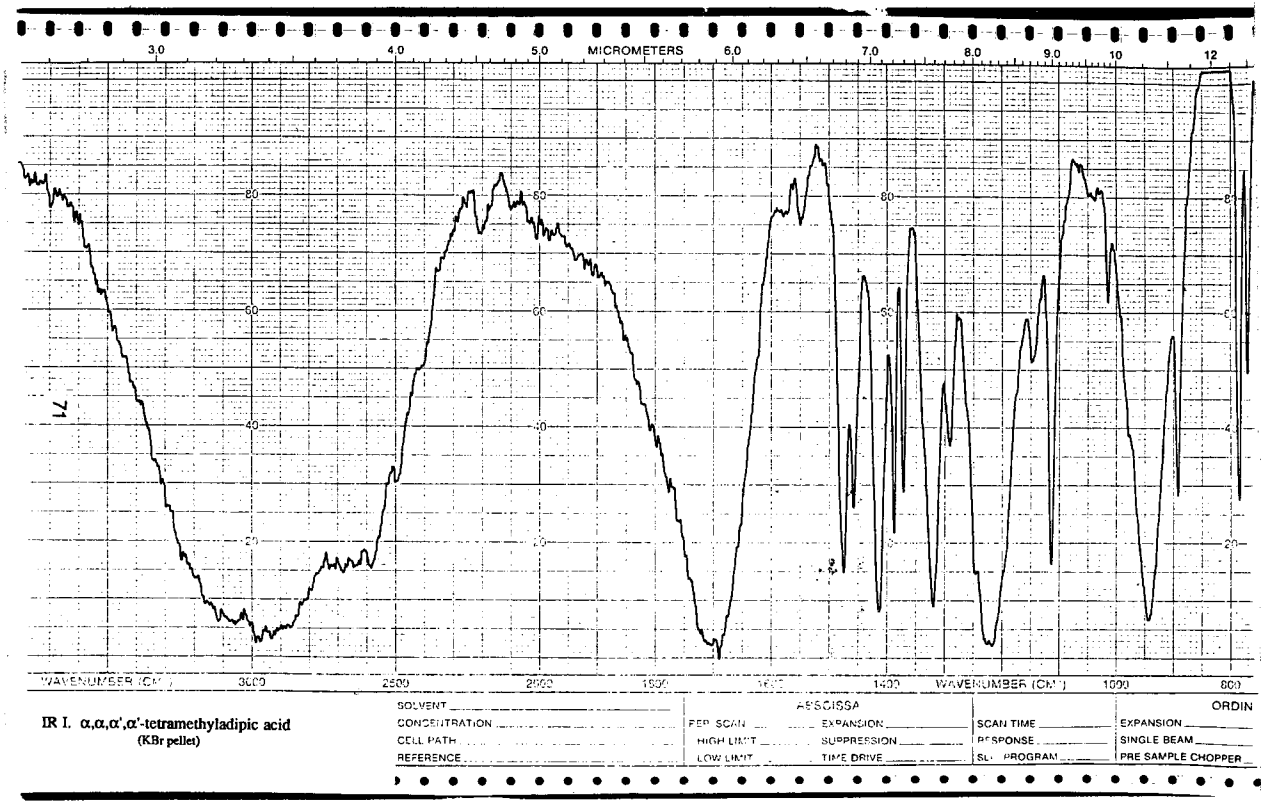
Number; File 0; Date 05-05-95 14:00:00; XGEN 200


NMR IXa
CHART 41 SERIES
89
PART NO 997259
5.4
122.8
56.7
8.7
177.1
PPM
SAMPLE
NEOPENTYL ALCOL
OBSERVE
DECOUPLE
PULSE/PROCESSING
EXPERIMENT

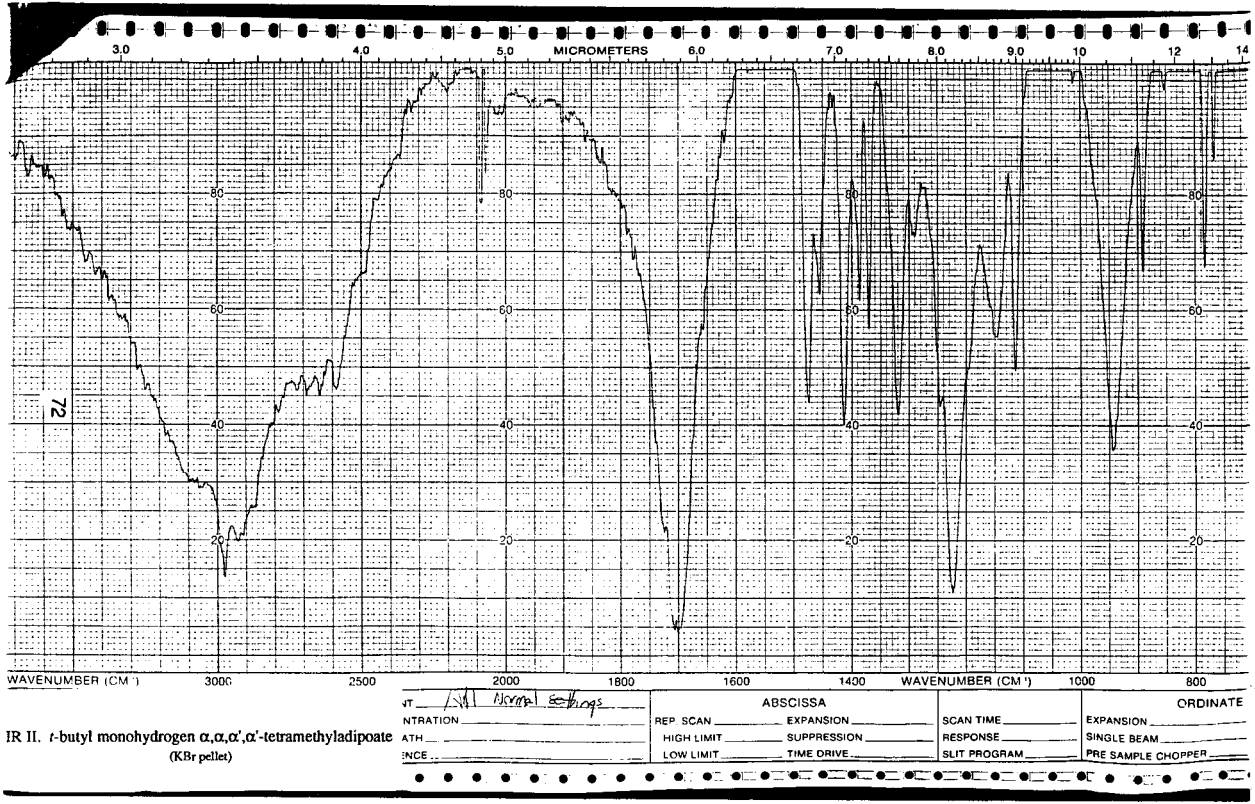

NMR IXb
69
CHART XL SERIES
PART NO 997239
200
180
160
140
120
100
80
60
40
20
PPM
OBSERVE
DECOUPLE
PULSE SEQUENCE
SAMPLE
NEOPENTYL GLYCOL
02-27-09
16:58:09

Appendix II

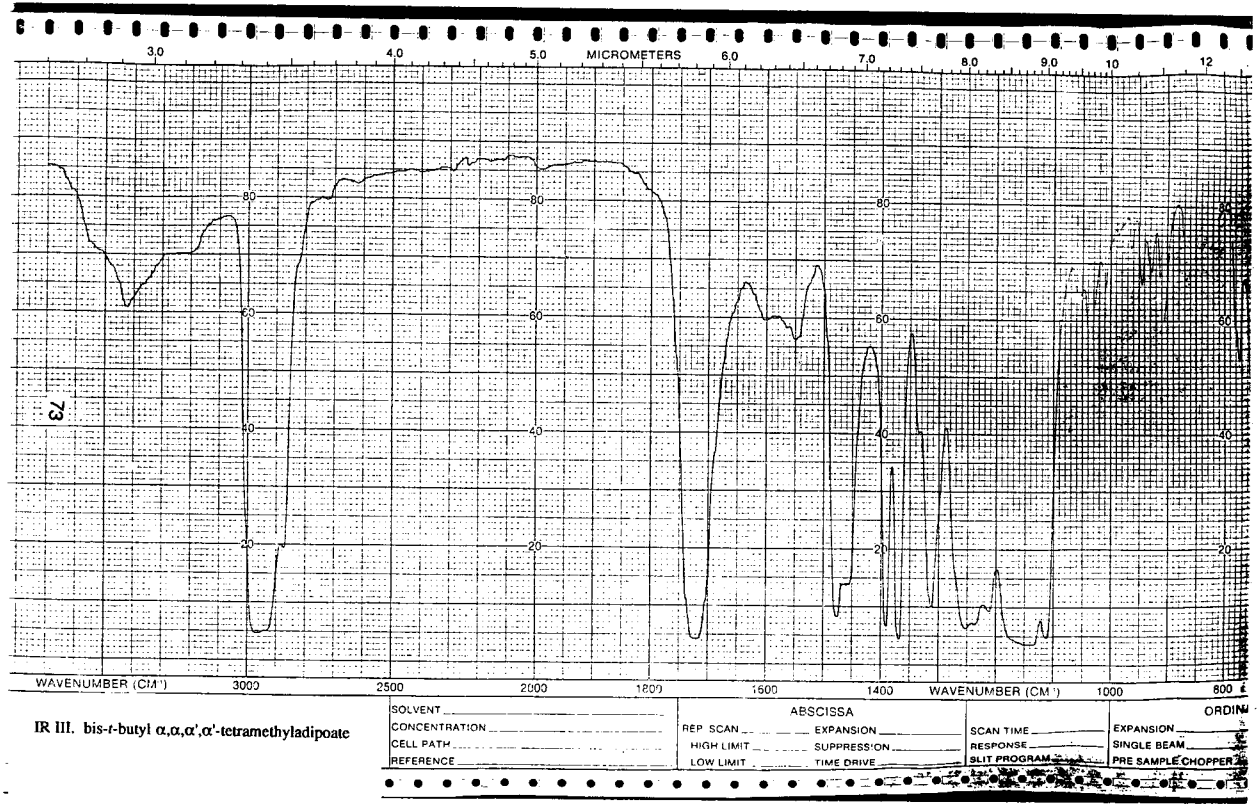
Infrared Spectra



IR I. α,α,α',α'-tetramethyladipic acid
(KBr pellet)

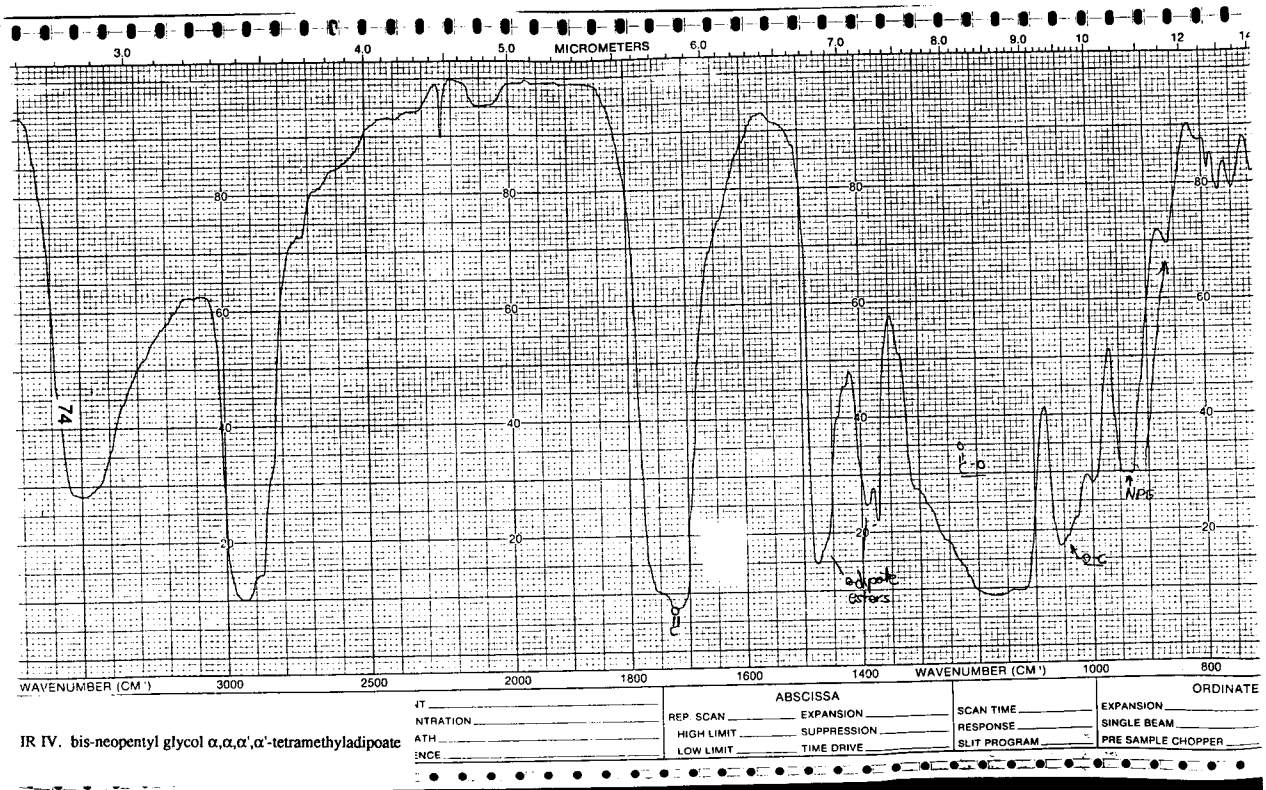


IR II. *t*-butyl monohydrogen α,α,α',α'-tetramethyladipoate
(KBr pellet)

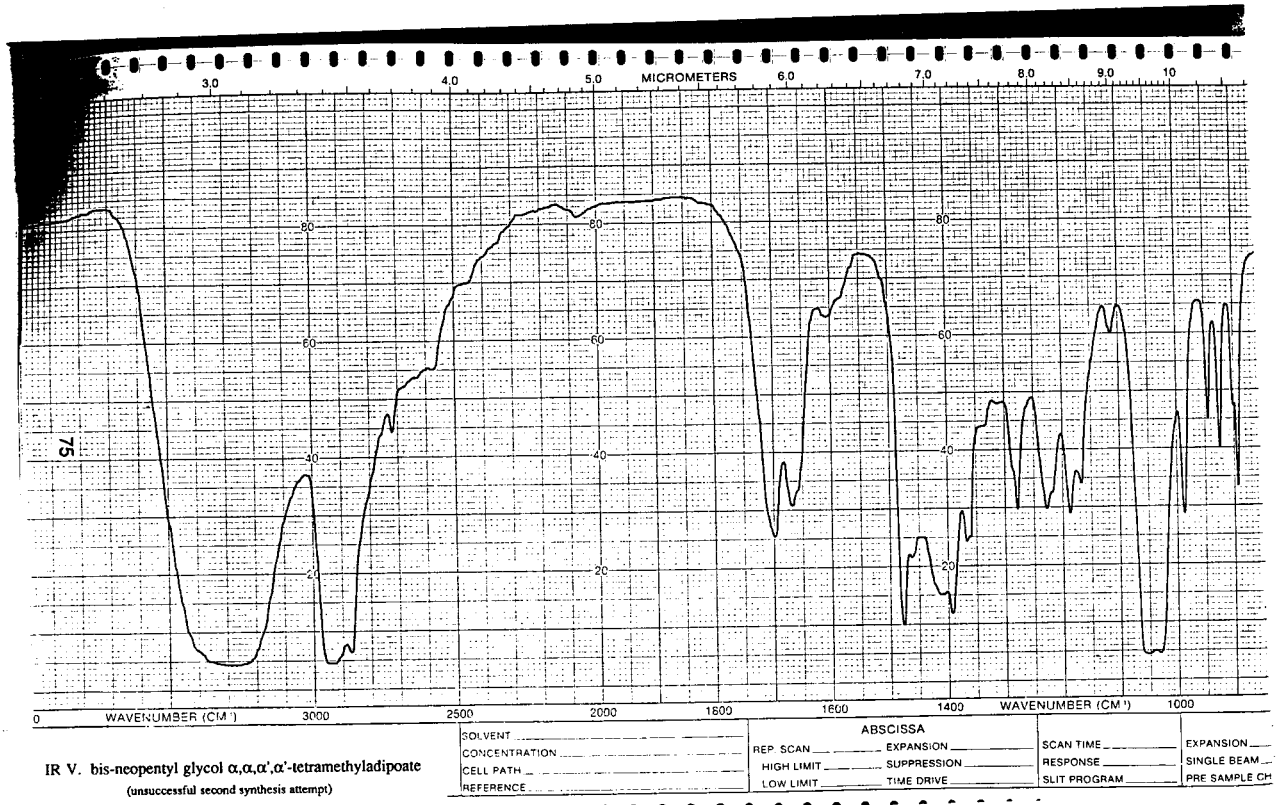


73

IR III. bis-*t*-butyl α,α,α',α'-tetramethyladipoate



IR IV. bis-neopentyl glycol α,α,α',α'-tetramethyladipoate



IR V. bis-neopentyl glycol α,α,α',α'-tetramethyladipoate

(unsuccessful second synthesis attempt)

SOLVENT	ABSCISSA		
CONCENTRATION	REP. SCAN	EXPANSION	SCAN TIME / EXPANSION
CELL PATH	HIGH LIMIT	SUPPRESSION	RESPONSE / SINGLE BEAM
REFERENCE	LOW LIMIT	TIME DRIVE	SLIT PROGRAM / PRE SAMPLE CH

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