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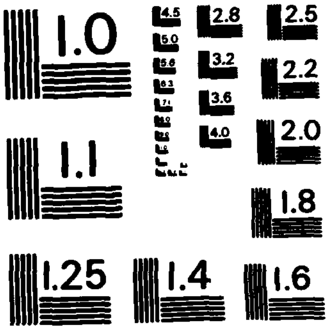

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SYNTHESIS OF SYNTHETIC HYDROCARBONS VIA ALPHA OLEFINS

Gary L. Driscoll
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May 1985

Final Report for Period 17 August 1981 - 31 December 1984

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MATERIALS LABORATORY
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Thermal and oxidative stability of commercially available decene oligomer is compared to oligomer prepared by anionic catalysis. The latter oligomers show somewhat improved stabilities as well as more well-defined isomeric hydrocarbon species. Thermal stressing of oligomers at 350°C in an atmosphere of hydrogen and, alternatively, deuterium, suggest that thermal decomposition is a true bulk property. Normal alkanes were observed as decomposition products, while only small amounts of deuterium were found in the decomposition products, suggesting that radical recombination is a predominate mechanism. NMR analysis of oligomer prepared from 1 decene-2-^{13}C with boron trifluoride catalyst suggests that oligomerization involves secondary carbonium ions resulting from a rapid isomerization of the alpha olefin.

Anionic addition (telomerization) of ethylene to mesitylene and meta xylene yields straight chain alkyl, aromatic oils in which the chain length, structure and point of

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attachment to the aromatic ring can be controlled. These oils exhibited characteristic poor oxidation stability, however, hydrogenation of the aromatic ring in the m-xylene telomer produced a marked improvement in oxidation stability producing an oil equivalent to polydecene.

FOREWORD

This report was prepared by the Applied Research and Development Department (formerly Sun Tech, Inc.) of Sun Refining and Marketing Company, under the auspices of United States Air Force contract F33615-81-C-5058. This program was administered by the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Mrs. Lois Gschwender was Project Engineer.

This final technical report covers work conducted from 17 August 1981 through 17 December 1984.

Dr. G. L. Driscoll was the Principal Investigator for this program, and he, in cooperation with Dr. S. J. G. Linkletter, produced a major portion of the technical data contained herein.

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SECTION I

INTRODUCTION

Alpha olefins have been used for some time as a starting point to produce oligomers in the C_{20}-C_{40+} range. As lubricants, these materials exhibit unique properties in some respects, while in others, are demonstratively poorer than lubricants derived from mineral oils. Polydecenes made with cationic catalyst systems, polyoctenes made with anionic systems and certain alkyl aromatics are examples of such materials which are now either in commercial production or have been produced semi-commercially.

Most catalyst systems do not produce single isomeric structures, but rather somewhat complex mixtures which become increasingly more complex as the number of monomer units in the compound increases. Indeed, subtle variances in isomeric composition of polymer systems can result in distinguishable property differences in products produced by one manufacturer or process, even though the starting material and basic processing appear identical. For example, polyethylene or polypropylene from one source may be superior in one or more characteristics such as thermal/oxidative stability or response to additives than apparently identical polymer from another source.

With this premise in mind, the present program was undertaken with the objective of relating isomeric structure of oligomers to lubricant properties.

This report is presented in major sections, plus appendices, which detail the results of this investigation toward the major objectives.

The first two sections deal with decene oligomers from the standpoint, in Section I, of comparing properties of commercially available oligomer produced with acidic catalysts to properties of a decene oligomer produced by anionic catalysis. The results show that the oligomer produced by anionic means is superior in thermal and oxidative behavior.

Section II contains the results of structural analysis by NMR of an oligomer produced cationically from 1-decene-2-^{13}C. This work provides new insights into the mechanism of polymerization and the structure of this important class of synthetic lubricant produced commercially.

As discussed in Section III, synthetic methods are available to control the structure of alkyl aromatic compounds which affect the side chain structure as well as the point of attachment to the alkyl group. Through the use of these synthetic techniques, alkyl aromatic compounds and their hydrogenated derivatives can be produced which show improved thermal and oxidative properties.

Properties of ethylene/propylene copolymer oils are discussed in Section IV. Although not commercially available, these oils could be an important class of synthetic lubricant exhibiting somewhat unique properties. The major drawback to their production is the lack of a method to control polymerization in the molecular weight range needed for lubricants. Currently oils of this class are produced by hydrocracking low molecular weight polymers.

Certain fluid characterization data was provided by Materials Laboratory, WPAFB, including kinematic viscosity, per ASTM D 445, thermal stability, per modified micro MIL-H-27601 method, acid number, per ASTM D 664, thermal gravimetric analysis and micro oxidation corrosion, per Materials Laboratory method.

SECTION II

ALPHA OLEFIN OLIGOMERS

Decene oligomers have emerged as a rather unique class of synthetic hydrocarbon lubricant. These fluids are distinguished from their petroleum-derived counterparts by excellent low temperature properties, improved thermal and oxidation stability, and significantly improved viscosity index.

Decene oligomers are currently available from a number of sources, and are produced by oligomerization of decene-1 by means of a cationic catalyst; usually boron trifluoride plus a promoter. As a representative example of this type of fluid, a Gulf 2 Cst fluid containing 97.8% C_{20} oligomer, and a Gulf 4 Cst fluid containing C_{30} and C_{40} oligomers were chosen for further study. The latter fluid was distilled to a purity of 99.7% C_{30}.

The Gulf synthetic fluids were compared to similar carbon number oligomer fluids synthesized through the use of anionic (Ziegler) catalyst systems. These systems are purported to give less complex mixtures of isomers and offer the prospect of relating lubricant properties to chemical structure.

The comparative property data for the two types of polydecene fluids are tabulated in Table I. The data show real, if not significant, improvement in thermal and corrosion oxidation stability of the oligomers prepared with anionic catalyst systems compared to the conventional cationic oligomers. With respect to viscosity properties, the anionic materials exhibit slightly higher viscosity indices and comparable viscosities at 100°F. The formation of solids (i.e. increased pour

TABLE 1

COMPARISON OF CATIONIC AND ZIEGLER POLYDECENES*

TEST	C_{20}		C_{30}	
Property	Ziegler	Cationic	Ziegler	Cationic
THERMAL STABILITY**				
$\Delta KV_{100°F}$ (%)	-12.95	-40.0	-44.5	-64.7
New GC Peaks (%)	4.9	23.6	27.5	36.7
MICRO CORROSION OXIDATION***				
Δ $KV_{100°F}$ (%)	11.2	32.6	37.8	40.8
Δ Acid Number	3.8	12.3	16.6	12.9
Weight Loss (%)	0.00	0.55	0.04	0.10
VISCOSITY				
$KV_{210°F}$	1.99	1.63	3.57	3.65
$KV_{100°F}$	5.87	5.15	15.29	16.34
$KV_{-40°F}$	Solid	267	2000	2000
$KV_{-65°F}$	Solid	1661	Solid	11120
VTF-VI	143	--	128	119

* Fully hydrogenated.

** 700°F, 6 hours, N_2 atmosphere, duplicates

*** Fluid formulated with 1% E702, a bis-hindered phenol antioxidant, 375°F, 24 hours, reflux, 5 l/hr. air, 20 ml fluid, metal catalysts present.

points) exhibited by the anionic fluids is probably a result of highly linear chain segments in the oligomer which are capable of crystallization at the lower temperatures.

Thermal stability data for the anionic C_{20} oligomer cut are consistent with values obtained by Cupples, etal[1] for synthetic 9-methylnonadecane. A capilliary gas chromatogram shows that Gulf C_{20} contains, at least, twenty different significant components (see Figure 1). Onopchenko, etal[2] recently published similar chromatograms. Such a mixture is consistent with the good low temperature properties. Quantification of the isomers in the C_{20} samples was done by capillary gas chromatography. The separation was done on a 12-meter OV101 column with a flame ionization detector. The temperature program was 80°C to 270°C at 10°C/min. These conditions resolved the least rearranged materials from the rest, but did little for the more highly scrambled structures.

Prior work[3] on the C_{20} oligomer from anionic systems tentatively identified the major components as n-eicosane (59%) and 9-methylnonadecane (19%). Analysis of the anionic C_{20} oligomer by mass spectrometry confirmed the presence of 56% n-eicosane, 22% 9-methylnonadecane and 2% n-docosane in good agreement with previous work. The presence of n-docosone is a result of a C_{12} olefinic impurity in the starting material.

By contrast, the Gulf C_{20} oligomer was found to contain 3% 9-methylnonadecane and no n-eicosane.

The remaining 97% Gulf C_{20} oligomer, as well as the remaining 22% of anionic C_{20} oligomer, elutes from a capillary gas chromatogram (GC)

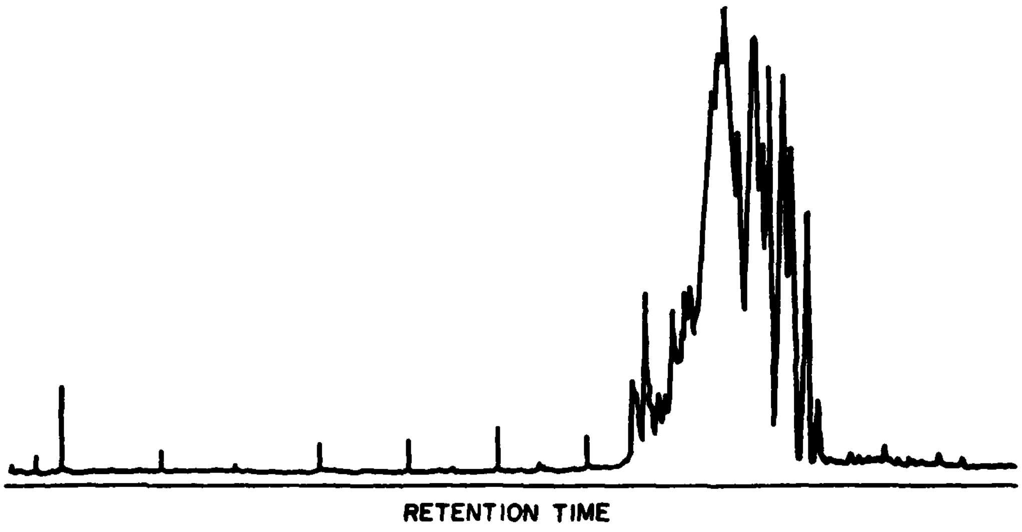


FIGURE 1 : CAPILLARY GAS CHROMATOGRAM GULF C_{20} OLIGOMER

as a broad and incompletely resolved envelope showing no discernable peaks.

A graphic comparison of the unresolved envelope amounting to 97% of the Gulf C_{20} oligomer and 22% of the anionic C_{20} oligomer is possible if the sum of the peaks in the anionic C_{20} oligomer are normalized to the sum of all the peaks over 1% in the cationic C_{20} oligomer. This is shown in Figure 2. It can be seen that the two materials have many peaks in common, with the anionic C_{20} oligomer having relatively more of the materials at lower retention times in this region than the Gulf C_{20} oligomer.

Mass spectroscopy has done little to help in the identification of the materials in this region of the GC scan. In the anionic C_{20} oligomer, where the peaks are better resolved, the amount of material per peak is too low for good data to be obtained. Under electron impact conditions, fragmentation of the materials is too high for a good interpretation to be possible, while the chemical ionization method provides a parent ion and little or no fragmentation. Poor resolution of the peaks in the cationic C_{20} oligomer makes the analysis even more difficult. There is more observable fragmentation in the electron impact spectra, however, the impurity of each peak sampled tends to make all the fragmentation patterns look alike.

The C-13 NMR of anionic C_{20} oligomer displays the typical shifts of n-eicosane and 9-methylnonadecane, and no others. This is not surprising, as any other structure would probably have, on the average, one

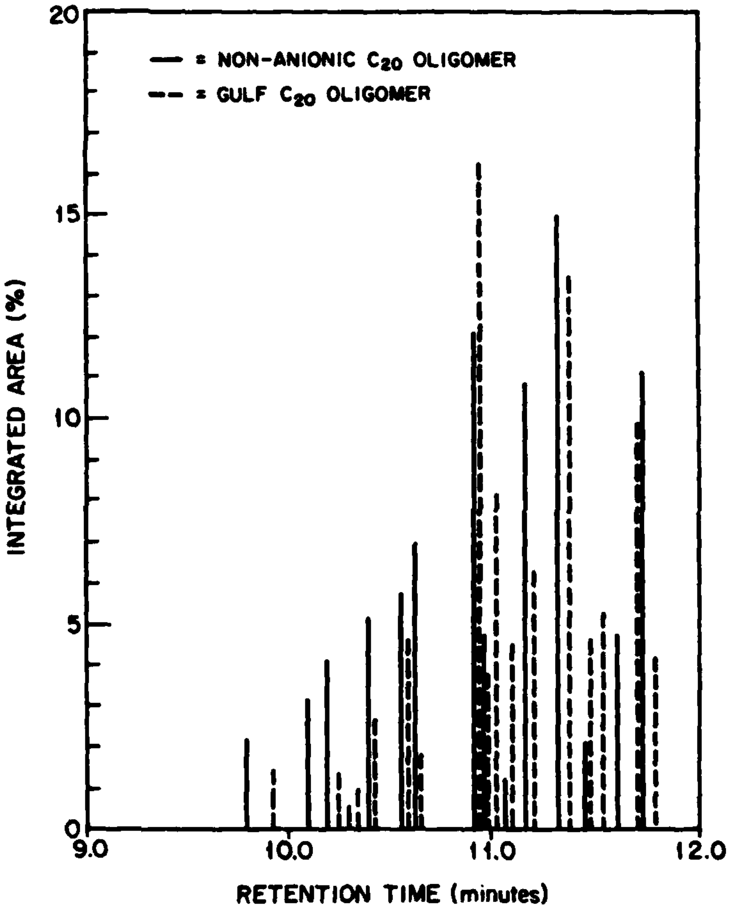


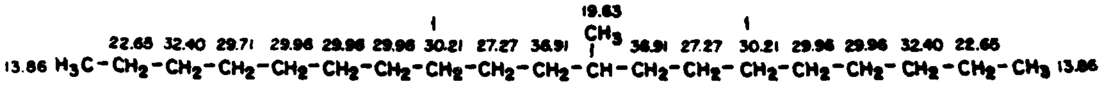
FIGURE 2: COMPARISON OF CATIONIC AND ANIONIC C_{20} OLIGOMER PEAKS BY GAS CHROMATOGRAPHY

unique carbon. One carbon out of 20 carbons per molecule, times 20% of the sample, comes down to 1% of the total signal. This is a maximum number in that it assumes that all of the unidentified 20% of the sample has the same unique shift. The likelihood of observing unique signals from any of the minor components in the anionic C_{20} oligomer sample is nil. One must turn to the cationic C_{20} oligomer for characterization of these isomers.

The broad distribution of products in the cationic C_{20} oligomer, while prohibiting the exact identification of any one product by NMR, increases the chance of observing unique shifts for the more common structural features in this mixture of isomers. As indicated by gas chromatographic analysis, there is no n-eicosane and insufficient 9-methylnonadecane to produce NMR signals from these species. Therefore, any shifts observed must be due to other types of structures. What follows is a deductive analysis of these data based on a comparison of shifts calculated for structures which might reasonably be expected with the actual observed shifts.

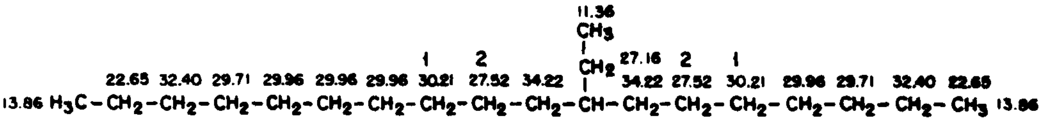
The first set of products predicted by a cationic mechanism consist of attack of a decene cation on an unisomerized 1-decene. The decene cation may be considered to have the option of isomerizing to give a cation on any carbon along the 10-carbon chain. Attack on a 1-decene will then produce any one of the four structures A-D shown in Figure 3. Noted beside each carbon in the structures is the calculated C-13 NMR shift in ppm, as calculated by the parameter method of Surprenant and

STRUCTURE A



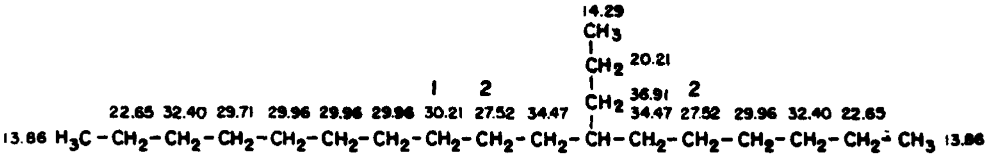
$$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

STRUCTURE B



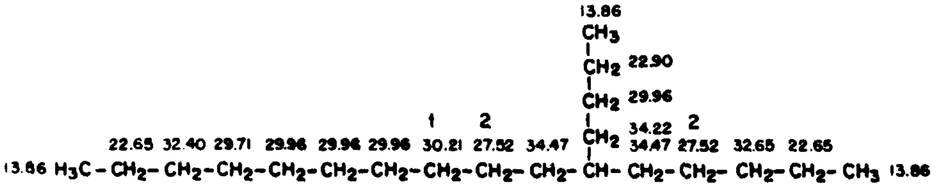
$$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{\overset{|}{\overset{\displaystyle CH_2}{|}}}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

STRUCTURE C



$$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{\overset{\displaystyle CH_2}{|}}}}}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

STRUCTURE D



$$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{\overset{\displaystyle CH_2}{|}}}}}}}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_3$$

FIGURE 3 CATIONIC DECENE DIMER STRUCTURES RESULTING FROM ATTACK OF SECONDARY CARBONIUM ION ON PRIMARY CARBON

TABLE 2

OBSERVED AND CALCULATED NMR SIGNALS FOR CATIONIC C_{20} OLIGOMER

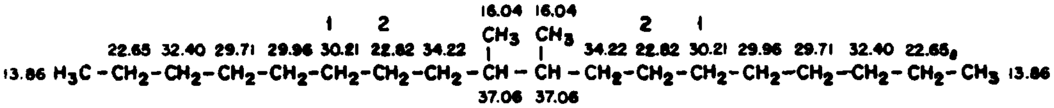
Shift (ppm)		Assignment
Observed	Calculated	
14.2	13.86	Eicosane-type methyl (#1)
22.9	22.65	Eicosane #2 carbon
28.1	27.52	Carbon 2 in Structures B-H
29.6	29.71	Eicosane #4 carbon
30.0	29.96	Eicosane #5 carbon
30.3	30.21	Carbon 1 in Structures A-H
32.2	32.40	Eicosane #3 carbon

Reilley[4]. The seven most intense signals in the cationic C_{20} oligomer NMR consist of one methyl signal and six methylene signals. These are listed in Table 2. The methyl signal and four of the methylene signals are identical with those of the chain ends in n-eicosane and 9-methylnonadecane. These five signals are also predicted for all four of the structures in Figure 3. Of the remaining two intense methylene signals, one possesses a shift identical with the 9-methylnonadecane shift for the carbon separated from the methyne by two other methylene carbons. This is carbon 1 in Figure 3. The remaining signal at 28.1 ppm, is attributable to the signal from the methylene separated from the methyne by one methylene with the side chain consisting of two or more carbons (carbon 2 in Figure 3). These data are not inconsistent with the structures predicted by the traditional cationic mechanism.

Skeletal rearrangement of carbonium ions during oligomerization was proposed by Shubkin, etal[5] to explain the methyl/molecule ratio which they observed in proton NMR. The skeletal rearrangement would produce the four structures E-H shown in Figure 4. These structures would be expected to produce the same seven most intense C-13 NMR peaks as structures A-D, and cannot be ruled out on that basis alone. In order to attempt to confirm or deny the existence of structures E-H, two approaches were taken.

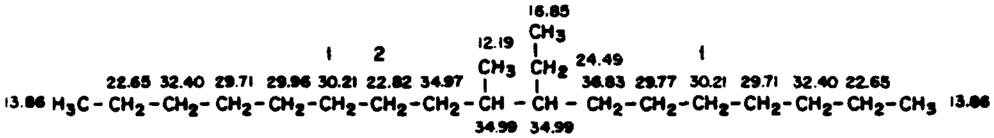
The first approach was to measure the methyl/molecule ratio for all the decene oligomer samples by proton NMR. The results are given in Table 3, along with the literature values and/or calculated values. While these values are in good agreement with published or expected values, some caution should be exercised in their interpretation. Vary-

STRUCTURE E



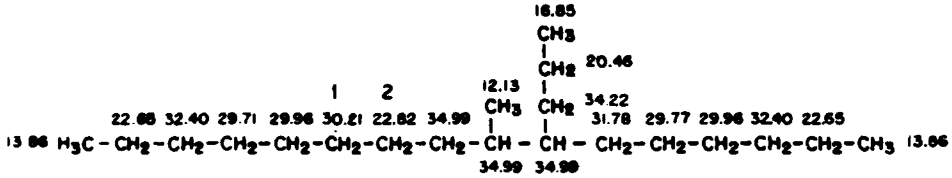
$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

STRUCTURE F



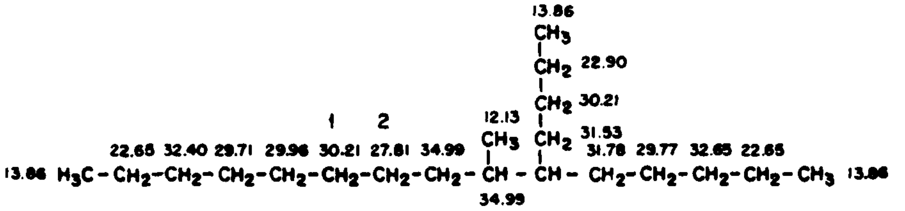
$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{\overset{CH_2}{\overset{|}{CH}}}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

STRUCTURE G



$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{\overset{CH_2}{\overset{|}{\overset{CH_2}{\overset{|}{CH}}}}}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

STRUCTURE H



$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{\overset{CH_2}{\overset{|}{\overset{CH_2}{\overset{|}{\overset{CH_2}{\overset{|}{CH}}}}}}}}-CH_2-CH_2-CH_2-CH_2-CH_3$

FIGURE 4 : CATIONIC DECENE DIMER STRUCTURES RESULTING FROM ATTACK OF SECONDARY CARBONIUM ION ON SECONDARY CARBON

TABLE 3

METHYL GROUPS PER MOLECULE FOR CATIONIC AND ANIONIC OLIGOMERS

Material	Methyl/Molecule	
	Measured	Reference (source)
Gulf C_{20}	3.9	3.8 (4)
Gulf C_{30}	4.4	4.6 (4)
Sun C_{20}	2.6	2.6 (*)
Sun C_{30}	3.4	3.6 (*)

(*) Calculated value based on the assumed identity of the two major components, plus the assumption that the remaining material is identical in nature with the Gulf materials as measured.

ing the choice of integration limits can change the calculated methyl/molecule by as much as 0.3. When these data are used to determine the percent content in a mixture of two materials containing, respectively, n methyls/molecule and (n+1) methyls/molecule, a difference of 0.1 methyl/molecule translates into a 10% difference in composition. The approach to the problem of integration limits was to set the methyne/methylene limit at an arbitrary point which gave the most realistic methyl/methyne ratio. The validity of the quantification is probably no better than ±10%, but the presence of the more highly branched materials is confirmed. With the cationic C_{20} oligomer, 90% ± 10% of the material has 4 methyls/molecule, as opposed to the classical 3 methyls/molecule.

A second approach involved a comparison of the observed C_{13} NMR peaks to those predicted on the basis of structures A-D and E-H as shown in Figures 3 and 4. Table 4 represents a tabulation of calculated chemical shifts for structures A-H, together with the absolute distance (given in ppm) to the nearest observed peak under conditions that no observed peak be assigned to two different calculated values. Structures A-D would result from attack of a secondary carbonium ion on primary carbon whereas structures E-H would result from attack of a secondary carbonium ion on secondary carbon. From the data in table 4, it is evident that a greater number of the calculated peaks for structures E-H can be assigned to observed peaks than can be assigned on the basis of structures A-D. This comparison suggests that the C_{13} NMR spectrum of

TABLE 4

CALCULATED NMR SHIFTS AND OBSERVED VARIATIONS FOR CARBONIUM ION INTERMEDIATES

	A		B		C		D	
	Calc. Shift,ppm	Observ. Δ ppm	Calc. Shift,ppm	Observ. Δ ppm	Calc. Shift,ppm	Observ. Δ ppm	Calc. Shift,ppm	Observ. Δ ppm
1°	19.63	5.03	11.36	1.04	14.29	0.01	--	--
2°	27.27 36.91	0.37 1.91	27.16 34.22	0.17 0.32	20.21 34.47 36.91	2.59 0.53 1.91	22.90 34.22 34.47	0.50 0.32 0.53
3°	32.52	1.88	39.12	1.32	37.02	0.32	37.02	0.32
	E		F		G		H	
1°	16.64	0.25	11.85 17.13	0.55 1.53	14.35 17.13	0.05 1.53	17.13	1.53
2°	34.22	0.32	24.47 27.77 31.53 34.47	1.53 0.53 0.93 0.23	20.46 27.77 32.78 34.22 34.77	2.34 0.53 0.28 0.32 0.53	22.90 27.77 31.53 31.78 34.77	0.50 0.53 0.93 0.28 0.53
3°	37.06	0.32	34.99 43.66	0.59 1.29	34.99 41.59	0.59 0.81	34.99 41.59	0.59 0.81

cationic C_{20} oligomer more resembles structures E-H than A-D and that oligomerization is occurring through attack of secondary carbonium ions on secondary carbon. This observation would also be consonant with the number of methyl groups observed per molecule.

Resolution of the trimer fraction by gas chromatography was less successful than for the dimer fraction. None-the-less, the anionic C_{30} oligomer was determined to contain 52 percent of 11-octyl-docosane and 22 percent 9-methyl-11-octyl heneicosane, with the remaining 26 percent of material being unresolved. The Gulf C_{30} oligomer contained 21 percent of material analyzing as 9-methyl-11-octyl heneicosane. Mass spectral data confirmed the molecular weight, but provided no structural information.

One approach to a thermally more stable polydecene oil would involve subjecting ordinary polydecene to high temperatures for a limited time. If the thermal instabilities are present in a small proportion of the molecules, these weak links would be removed from the system. On the other hand, if stability is intrinsic to the structure of most of the molecules, "thermal pre-stressing" will not improve stability. It is, of course, necessary to distill out the resulting fragments to restore the original viscosity and volatility characteristics before testing.

In addition, it might be possible to learn much about the nature of the weak points in the original molecules if fragments can be isolated and analyzed without further rearrangement. The approach taken was to conduct "pre-stressing" under several atmospheres of hydrogen (or, alternatively, deuterium) at 350°C for a length of time (3-4 hours) required to decompose about 30% of the original polydecene oil.

TABLE 5

EFFECT OF "THERMAL PRE-STRESSING"
POLYDECENE THERMAL STABILITY

	Original Gulf 4 cSt Oil	851182 After 350°C Treatment
KV_{100} Before	16.34	17.52
ΔKV_{100} % After Test	-64.7	-61.7

The data in Table 5 show that the treatment had no measurable effect on thermal stability after 30% of the sample has decomposed. This would suggest that the thermal stability is a true bulk property of the polydecene oil.

Examination of the products from this cracking process, however, indicated some extremely interesting results. Figure 5 shows a gas chromatogram obtained for one of these runs (time extended somewhat to increase cracking yields). The chromatogram should be compared to the starting material shown in Figure 6. The cracked product is characterized by a regular series observable at each carbon number from 5 to 20. Comparison at 4 points (octane, decane, tetradecane, eiosane) with authentic materials indicates that the retention times are a match for the corresponding n-alkanes. This identification is supported by GC/MS data and by ^{13}C NMR on the distillate. (^{13}C NMR must be used cautiously, since, contrary to proton NMR, responses frequently are not quantitatively related to the ratios of types of carbons present.)

It should also be noted that GC/MS revealed only a small amount of deuterium incorporation (typically <10%) and no double deuterium incorporation as would occur by hydrogenation of an olefin. This suggests that radical recombination was the primary fate of radicals produced by thermal stressing.

Since there is no reasonable cationic mechanism for forming normal C_{20} chains in the oil (and good evidence from low temperature properties that they are absent), it is apparent that these must result from the radical recombination process. This information is a strong indicator of the environment around the site of thermal bond breakage. Despite care to avoid any unwarranted conclusions and best efforts at unequivocal analysis, the unusual nature of this decomposition requires further study. Although the effect of olefinic unsaturation is well known with respect to oxidation stability (olefins are readily oxidized, frequently forming autocatalytic systems) no corresponding data seem to exist with respect to thermal stability. Accordingly, a sample of decene oligomer was prepared (Boron trifluoride catalysis) in the laboratory. Part of this material was hydrogenated to less than 0.5% residual olefinic unsaturation by iodine number to provide a sample identical in origin to the unsaturated material. Viscosities and the results of the 700°F thermal stability test are tabulated in Table 6. Except for the poor oxidation stability, as shown in Table 7, there was no substantial difference in thermal stability between the saturated and unsaturated polydecene samples.

TABLE 6

EFFECT OF OLEFINIC UNSATURATION IN DECENE OLIGOMER

	Before H_2	After H_2*
	851188	851188
$KV_{210°F}$	2.78	2.92
$KV_{100°F}$	11.7	12.7
$KV_{-40°F}$	1200	1400
$KV_{-65°F}$	5900	7900

700°F Thermal Stability Test

(6 hr., N_2 atmosphere)

ΔKV_{40C} %	-64.0	-64.2
New GC Peaks %	53.7	41.4

*Less than 0.5% residual unsaturation by iodine numbers.

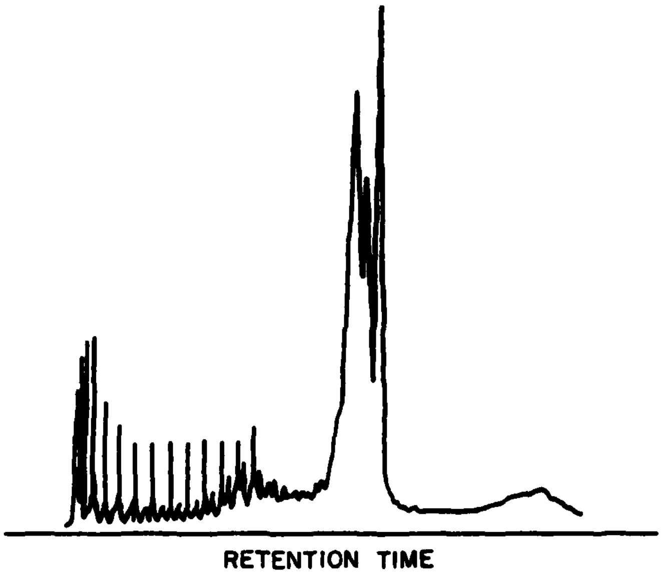


FIGURE 5: GAS CHROMATOGRAM OF THERMALLY STRESSED GULF 4 cSt OLIGOMER

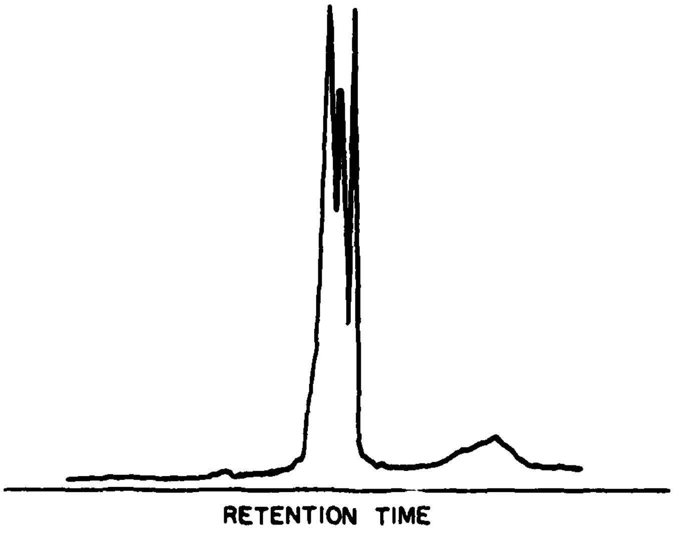


FIGURE 6 GAS CHROMATOGRAM OF GULF 4 cSt OLIGOMER BEFORE THERMAL STRESS

TABLE 7

CORROSION OXIDATION STABILITY OF SATURATED AND UNSATURATED DECENE OLIGOMER

(347°F Oxidation Test)

Property	Saturated* Oligomer	Unsaturated* Oligomer
Kinematic Vis. @ 100°F	12.7	11.7
Viscosity Change, %	1.7	250
Acid Number, mgKOH/g	0.12	0.12
Acid Number Change, mgKOH/g	0.00	23.3
Change in Weight Metals, mg/cm^2		
350 steel	-0.04	+0.10
440 steel	+0.02	+0.04
Cu	-0.02	-0.50
Ag	0.00	+0.02
Ti	+0.04	+0.04

*Fluid formulated 1.0% E702 with a bis-hindered phenol antioxidant , 5 l/hr. air, reflux,24 hours, 20 ml fluid, metal catalysts present

SECTION III

STRUCTURAL ANALYSIS OF 1-DECENE-2-^{13}C OLIGOMER BY NMR TECHNIQUES

As is apparent from the discussion in the preceding section, the question of the relative importance of competing carbonium ion (skeletal) rearrangements during the oligomerization of decene-1 proved to be particularly vexing. This is in part due to limitations of proton and carbon-13 NMR analytical methods for elucidating structures of the products and the mechanistic detail of their formation.

The primary objective of the work to be discussed in this section was to further expand the NMR analytical capability with the aid of specifically labeled Carbon-13 and deuterium substrates. Accordingly, decene-1 specifically labeled with Carbon-13 in the 2 position was synthesized for this program by Dr. A. Marchand at North Texas State University. Details of the synthetic process and final purification of the Carbon-13 labeled decene are provided in Appendix B.

Characterization of the labeled decene was accomplished by means of C-13 NMR as shown in Figure 7. Further analysis of the fine structure as shown in Figure 8 permits assignment of the adsorption to specific carbon atoms. The assignment of C_6 and C_7 are tentative, as they could be reversed with respect to each other.

The resultant labeled decene-1 was diluted (3:1) with unlabeled decene-1 and subjected to oligomerization with boron trifluoride catalyst. The oligomers thus obtained were saturated catalytically

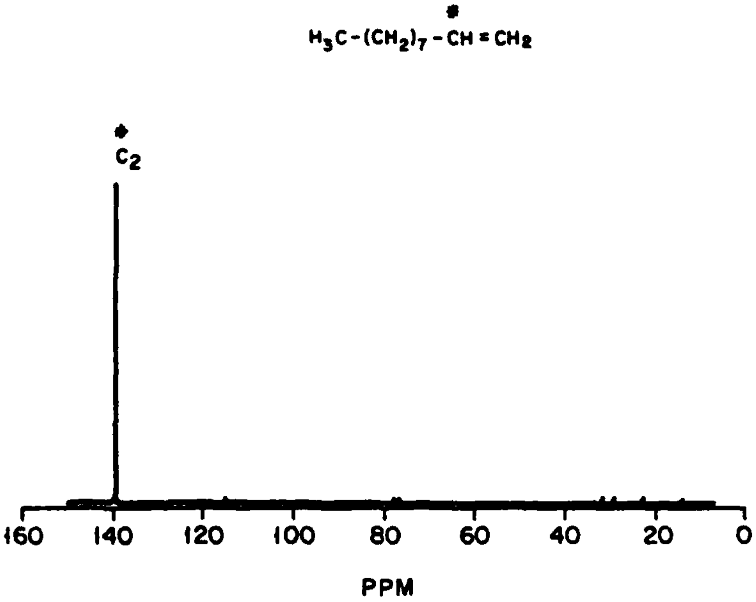


FIGURE 7: C-13 NMR SPECTRUM - 1-DECENE-2-^{13}C

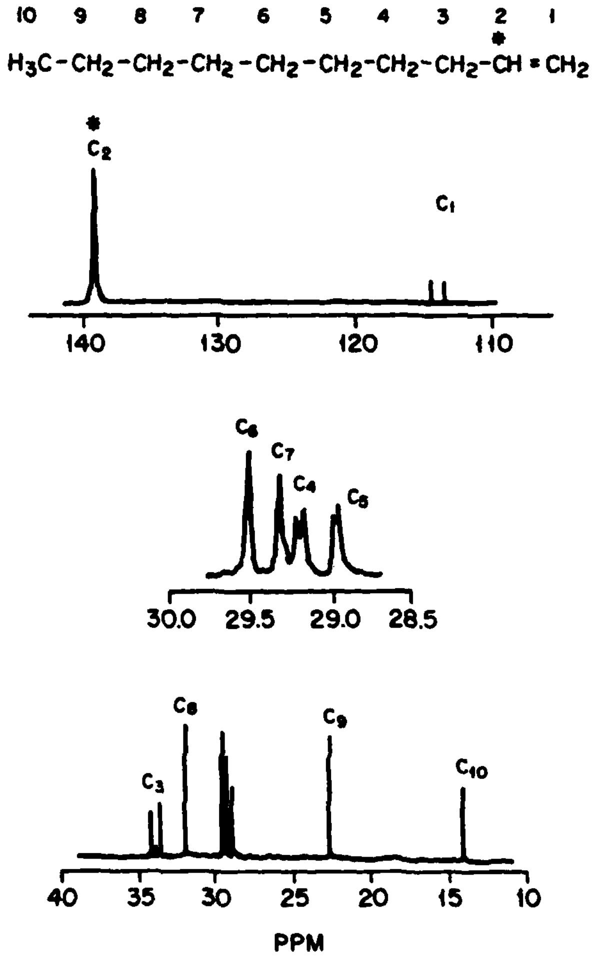


FIGURE 8 : EXPANDED C-13 NMR SPECTRUM 1-DECENE-2-^{13}C WITH ASSIGNED CARBONS

with hydrogen and deuterium to provide samples necessary for further Carbon-13 NMR analysis.

Figure 9 is the C-13 NMR spectrum of the hydrogenated C-13 labeled decene oligomer, while Figure 10 is an expansion of the spectrum in the 10-50 ppm range. The spectrum appears to be very complex, probably due to the dilution with unlabeled decene-1 and the nature of the product obtained. Under these circumstances, attention is focused only on the strongest absorptions as the weaker ones may not have come from labeled carbons. It appears that the four most intense peaks are: 14.1, 22.8, 29.9 and 32.1 ppm.

Significant conclusions can be drawn from a comparison of the peaks at 14.1, 22.8 and 32.1 ppm with the same absorptions in the unlabeled oligomer.

Reference is made to Figure 11, which is the gated-decoupled C-13 NMR spectrum of the reference Gulf decene oligomer. Figure 12 is the expansion of this spectrum in the 10-50 ppm range. In this spectrum, the three peak intensities at 14.1, 22.8 and 32.1 ppm are approximately equal, which is characteristic of a terminal methyl group and two methylene groups in a straight chain configuration, viz.: CH_3-CH_2-CH_2-. This grouping was further confirmed by determination of the number of protons attached directly to carbon by means of the Attached Proton Test (APT) using a J-modulated spin-echo technique (Figure 13).

Again with reference to Figure 10, the peaks at 14.1 and 32.1 ppm are observed to be of equal intensity, but the peak at 22.8 is slightly more than twice the intensity of both of them. This enrichment (increase in

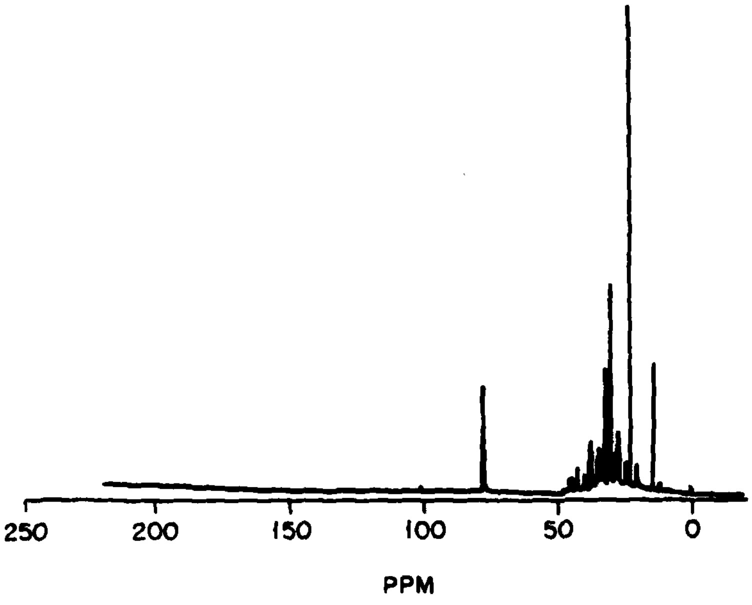


FIGURE 9 : C-13 NMR SPECTRUM - HYDROGENATED, C-13 LABELED DECENE OLIGOMER

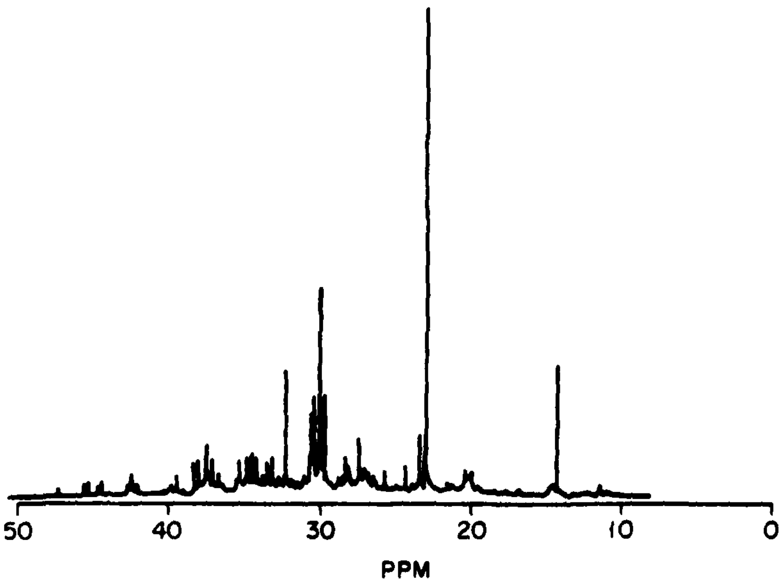


FIGURE 10 : C-13 NMR SPECTRUM - HYDROGENATED, C-13 LABELED OLIGOMER EXPANDED IN THE 10-50 ppm RANGE

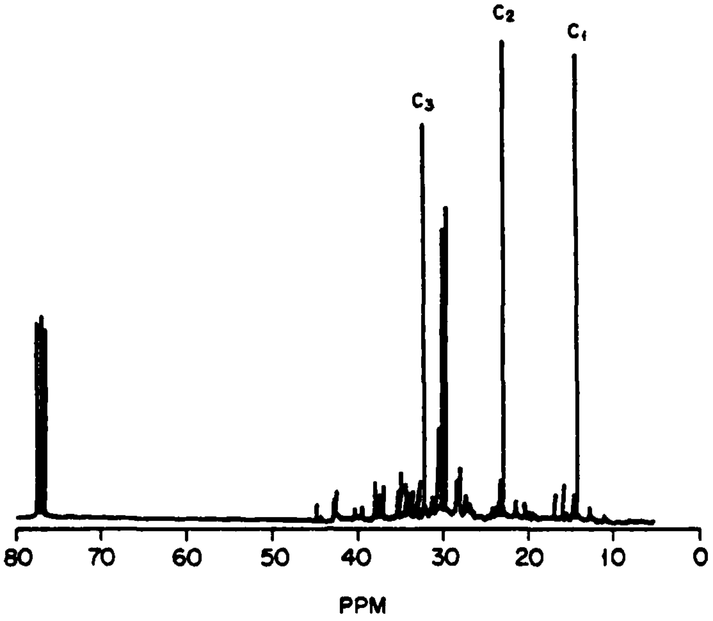


FIGURE 11 : C-13 NMR SPECTRUM - UNLABELED GULF REFERENCE OLIGOMER

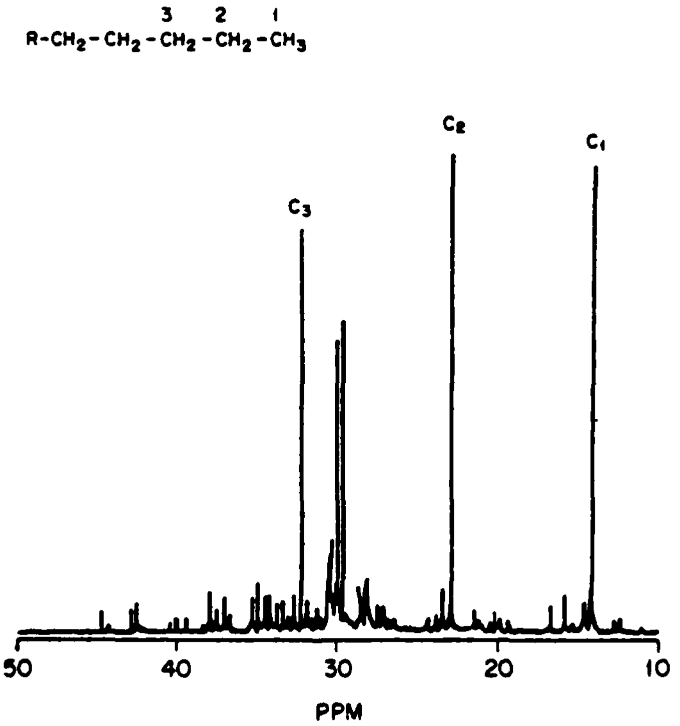


FIGURE 12 : C-13 NMR SPECTRUM - UNLABELED GULF REFERENCE OLIGOMER EXPANDED IN THE 10-50ppm RANGE

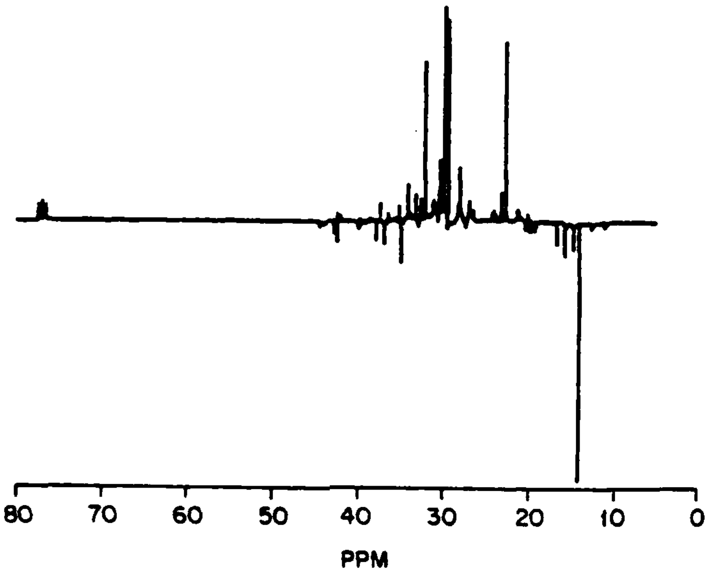


FIGURE 13: C-13 NMR SPECTRUM – UNLABELED GULF REFERENCE OLIGOMER J-MODULATED APT (Attach Proton Test)

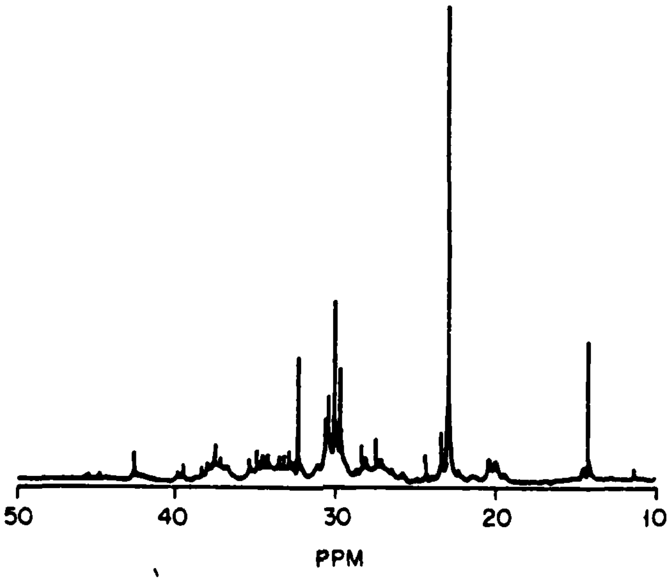


FIGURE 14: C-13 NMR SPECTRUM – LABELED OLIGOMER NORMALIZED TO UNLABELED GULF OLIGOMER

3 peak intensity) is due to the presence of labeled C-13 at the C_2 position, assuming that the probability of the label (C_2 of decene-1) being scrambled to the C_1 or C_3 position is very small, and that peaks at 14.1 and 32.1 are due to unlabeled carbon at C_1 and C_3. This seems to be a reasonable assumption because it is highly unlikely that interchange at C_1 and C_3 would occur and not be accompanied by extensive skeletal rearrangement ie chain branching.

The peak at 29.9 ppm (Figure 11) is suggestive of a methylene group in a straight chain of more than three carbon atoms as follows:

CH_3	-	CH_2	-	CH_2	-	CH_2	-	CH_2
14.1 ppm		22.8 ppm		32.1 ppm		29.9 ppm		29.9 ppm

On this basis, it seems reasonable to conclude that straight chain groupings of greater than three carbon atoms; possibly up to five carbons, are present in the oligomer. This would also be consistent with the presence of straight chain hydrocarbons identified in the products of thermal decomposition of the decene oligomer as discussed in Section I.

Enhancement of the peak at 29.9 ppm is more readily observed by comparing the spectrum shown in Figure 10 with that shown in Figure 14. The latter spectrum was obtained by normalizing the signal at 14.1 ppm of the unlabeled decene oligomer to the intensity of the corresponding signal of the C-13 labeled oligomer. In this way, the enrichment due to labeled carbons is more dramatically shown both for the peaks at 22.8 ppm and 29.9 ppm.

Accompanying the enhancement observed at 29.9 ppm is the appearance of a new peak at 29.5 ppm that is not present in the unlabeled reference oligomer. The structural implications due to these phenomenon are not readily apparent from the spectral data provided by this work.

Extensive line broadening was observed through the entire spectrum as shown in Figures 15 and 16 for the deuterated Carbon-13 labeled oligomers. This is taken as substantial evidence that unsaturation was present at various carbon atoms in the oligomer prior to deuteration.

The spectral evidence presented above leads to the conclusion that the decene oligomer contains methyl terminated straight chain segments of, at least, three and possibly four or five carbons. Based on the enhancement observed at 22.8 ppm, the carbon label is prevalent adjacent to the terminal methyl group in these straight chain segments. This strongly implies that oligomerization did not occur for the most part at the terminal double bond, but rather at an internal site in the molecule. On this basis, double bond isomerization would have occurred at a substantially faster rate than oligomerization. Therefore, the first step of the mechanism is rapid equilibration of the olefin as shown below:

$$H_3C(CH_2)_7{}^*CH = CH_2 \leftrightarrow H_3C(CH_2)_mCH = CH(CH_2)_nCH_3 \leftrightarrow H_2C = CH(CH_2)_6{}^*CH_2CH_3$$

$$n+m=6$$

Oligomer Formation

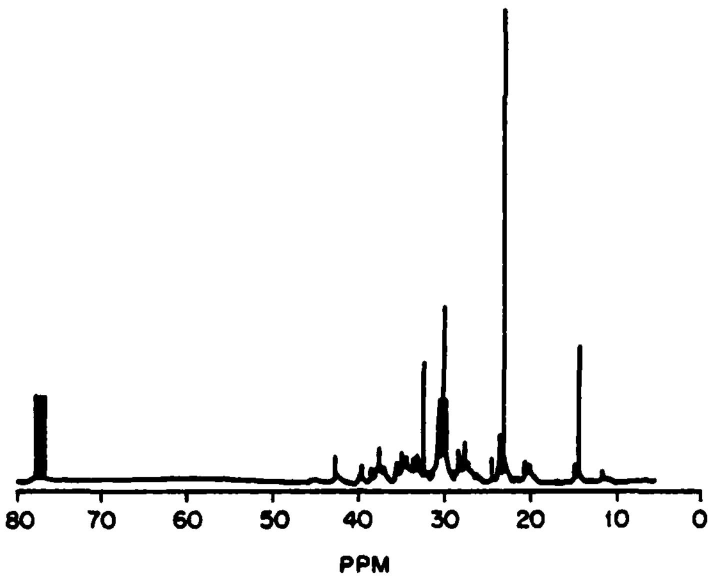


FIGURE 15: C-13 NMR SPECTRUM - DEUTERATED, C-13 LABELED OLIGOMER

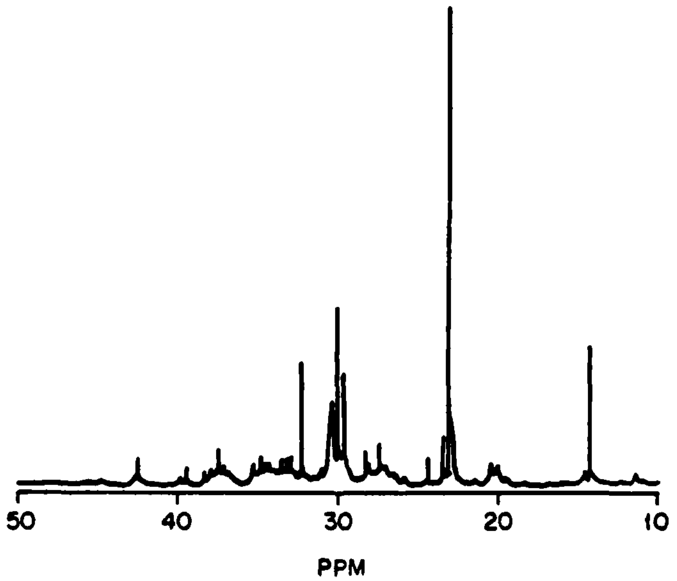
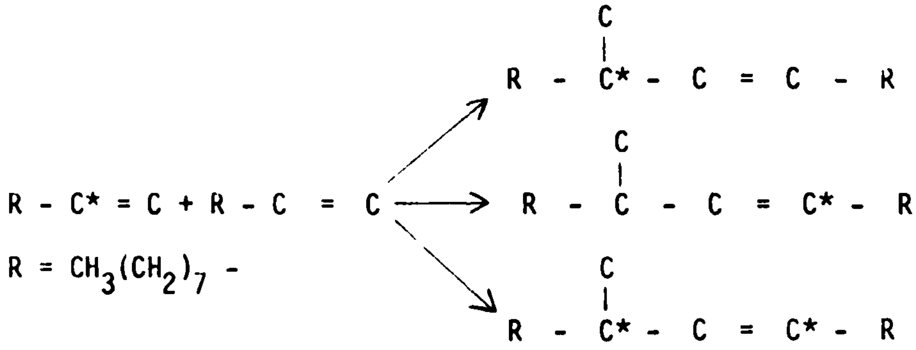


FIGURE 16: C-13 NMR SPECTRUM - DEUTERATED, C-13 LABELED OLIGOMER EXPANDED IN THE 10-50ppm RANGE

The first step toward oligomerization would involve formation of dimer through attachment of a secondary carbonium ion on a primary or secondary olefin. With a linear olefin such as decene, there is probably little thermodynamic preference for the possible internal olefin isomers, and hence, carbonium ion formation would be random along the chain. Attack on a primary olefin would be preferred sterically but not statistically.

The consequence is a random attachment, primarily through secondary carbons leading to a significant number of isomers with straight chain terminals containing the labeled carbon adjacent to the methyl group. This would also account for the presence of a greater number of methyl groups than predicted by attack of a secondary carbonium ion on a primary olefin (classical cationic mechansim). Further, the classical mechanism which ignores olefin isomerization, would require the labeled carbon to be found within the dimer and not near the terminal ends as observed, viz.:



$$R - C^* = C + R - C = C \longrightarrow \begin{cases} R - \overset{\displaystyle C}{\overset{|}{C^*}} - C = C - R \\ R - \overset{\displaystyle C}{\overset{|}{C}} - C = C^* - R \\ R - \overset{\displaystyle C}{\overset{|}{C^*}} - C = C^* - R \end{cases}$$

$R = CH_3(CH_2)_7 -$

*denotes labeled carbon

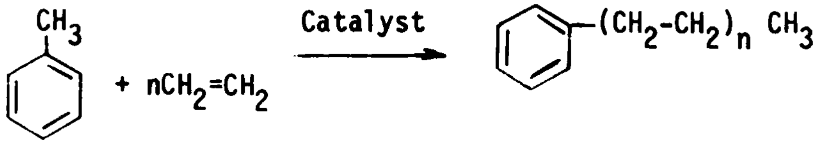
Shubkin etal[5] have proposed rearrangement of a cyclopropenyl carbonium ion intermediate at the dimer stage to explain the presence of additional methyl groups in the oligomer product. Although these labeling studies would not rule out this mechanism, they are not consistent with it particularly with respect to explaining the preponderance of labeled carbons near the straight chain ends.

SECTION IV

ALKYL BENZENE COMPOUNDS

The primary thrust of work in this area was an attempt to ascertain if changes in synthetic techniques might lead to changes in physical properties of alkyl aromatic compounds which would extend their utility as lubricants. As with alpha olefin oligomers (see Section I), significant differences in physical properties are observed for oils prepared by cationic or anionic catalysis. Major property differences might also be expected with alkyl aromatics by taking advantage of anionic chemistry to alter chain length and structure as well as point of attachment of the alkyl moiety.

Anionic reactions[6] of this type, frequently referred to as telomerization reactions, involve addition of ethylene to substituted methyl benzene, e.g., toluene, to produce a linear alkyl side chain. The length of the side chain can be controlled by reaction conditions. Viz:



The advantages of such reactions are: (1) the point of attachment of the alkyl group is through methylene, thus minimizing branching adjacent to the aromatic ring, thus reducing susceptibility to oxidation; (2) the resulting side chain(s) is linear, thus taking advantage of the stability and viscosity properties of a normal paraffin segment; and (3) the number and location of side chains can be controlled by starting with the desired substrate.

Initial telomerization experiments along these lines were carried out with ethylene using mesitylene (1,3,5-trimethyl benzene) as the substrate and butyllithum as catalyst. This reaction produced two fractions in the lubricating oil boiling ranye as shown in Table 8, together with carbon number distribution.

Further analysis of structure was accomplished by capillary gas chromatography. The column used was a 100-meter SE 54, and the detector method was flame ionization. The temperature program was 100°C for 4 minutes, followed by a 2°C/minute rise to 270°C. Complete analysis of the heavier distillation cut took 123 minutes.

Identification of the individual GC components was accomplished by analysis of fragmentation patterns by 70-volt electron impact mass spectroscopy, augmented by chemical ionization mass spectroscopy at the higher (C_{27-31}) molecular weights. For reasons similar to those given in the polydecene analysis section, this method fails at about C_{30}. Fortunately, this still afforded identity of most of the material.

Certain structures are predicted by the mechanism of the telomerization process used to produce this material. This anionic "living polymer"-type process is initiated by the attack of the n-BuLi on benzylic or

TABLE 8

BOILING RANGE AND CARBON NUMBER DISTRIBUTION FOR TELOMER OILS PRODUCED FROM MESITYLENE

	851146-3	851146-4
Boiling Range, °C @ 3 mmHg	135-210	210-240
Carbon Number, %		
15	5.23	--
17	21.58	--
19	26.88	--
21	22.90	1.10
23	15.24	19.31
25	4.08	29.50
27	0.61	22.38
29	--	13.08
31	--	9.18
Unknown	3.43	5.48

nuclear positions in the aromatic telogen. Attack on benzylic positions is more rapid than attack on nuclear positions and, in mesitylene, virtually the only reaction path. Attack on primary benzylic positions results in a normal paraffin chain grown onto the aromatic ring. Attack on secondary benzylic positions results in benzylic-branched chains. Proper manipulation of the reaction conditions can minimize branching by keeping the number of primary potential attack sites high compared to the secondary sites. The first three sets of products resulting from the above mechanism operating on mesitylene are shown in Figure 17. The number of possible isomers grows at each step, until at C_{21}, there are 28 isomers predicted.

Simplification of the analysis is possible if one chooses to leave the benzylic-branched material undifferentiated which makes up the greater number of the predicted structures, but less than 20% of the actual observed material. Benzylic-branched material can easily be identified by the (virtually) complete absence of any of the mesitylene derived peaks around m/e = 120. Rather, a set of peaks around m/e = 105 is seen. This represents a loss of a complete side-chain by breaking of the benzylic bond. This simplification reduces the number of possible structures to be completely elucidated at the C_{21} level to 7, a much more manageable number.

These completely normal-chain materials can be further divided into materials possessing 1, 2, or 3 chains. At every carbon number, there is

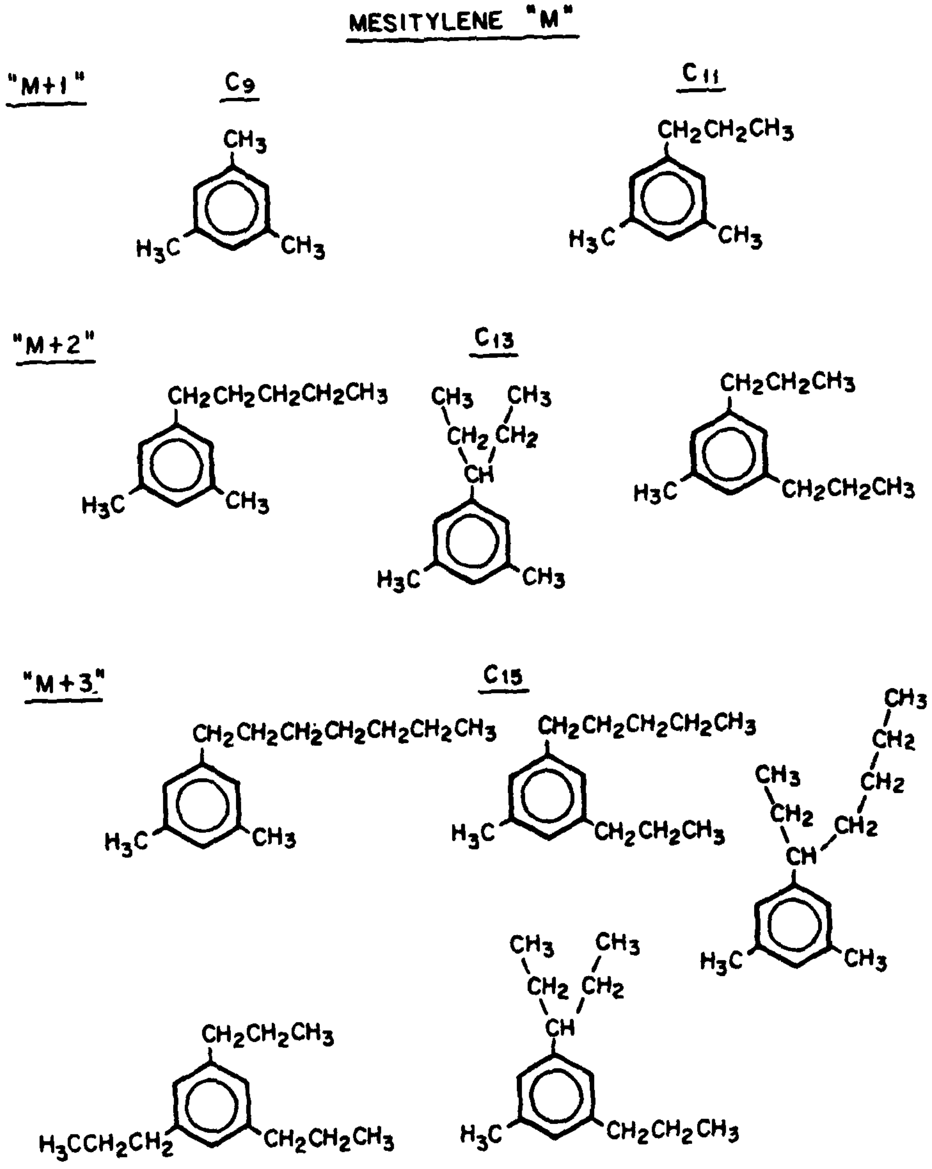


FIGURE 17: TELOMER INTERMEDIATES FROM MESITYLENE

one structure possible which contains 1 chain. This material displays a highly unique peak at m/e = 120. This is traditionally explained as representing the formation of a tropylium cation by skeletal rearrangement[7]. Materials containing 2 or 3 chains display a major peak at m/3 = 119, and a minor peak at m/e = 105, with the m/e = 105 being slightly larger for the material with 3 chains. Further, structural information is found in the peaks intermediate between the parent ion and the mesitylene ion.

Intermediate peaks with m/e values equal to a parent ion for some lighter mesitylene derivative represent the loss of one chain through the tropylium cation mechansim, and by their masses give directly the chain lengths of all chains present which are more than three carbons long. The intermediate peak formed by loss of two carbons from a three-carbon chain does not result in a tropylium cation. This fact is not explained, but is noted in the literature[7].

At higher carbon numbers (i.e., C_{27} and up), chain fragmentation prevents the observation of the parent ion in much the same way as was observed for the polydecenes. Chemical ionization methods produce a parent ion, but little structural information. These considerations, combined with the relatively small amounts of each isomer present at the level of C_{31} and up, limited the analysis. Nevertheless, it was possible to identify all but 3.4% of the material in the C_{15}-C_{27} (851146-3) carbon number fraction, and all but 18.3% of the material in the C_{21}-C_{31} (851146-4) carbon number range (cf Table 8), fairly

TABLE 9

STRUCTURAL ANALYSIS OF MESITYLENE TELOMERS

Structural Component	Sample 851146-3	 851146-4
	%	%
Straight-Chains	87.6	90.1
Benzylic Branched Chains	12.4	9.9
1-Chain	34.9	21.9
2-Chains	59.6	62.5
3-Chains	5.5	15.6

explicitly. An additional 12.8% of C_{21}-C_{31} material could be assigned a minimum carbon number but no structure. Table 9 provides a tabulation of the structural features developed as a result of this analysis.

A comparison of thermal, oxidative and viscosity properties of the aromatic telomer oils, C_{15}-C_{27} and C_{21}-C_{31}, with the Gulf C_{20} oligomer, the anionic C_{20} oligomer, and the ethylene-propylene copolymer oils is provided in Table 10. Somewhat striking is the fact that the aromatic telomer oils exhibit thermal stabilities equivalent to the anionic decene oil, which in turn, is better than the cationic decene oligomer oil. On the other hand, oxidation stability was significantly poorer, while viscosity characteristics were comparable. The relatively high pour points observed (-40°C) appear to be a result of crystallization of relatively long straight chain alkyl groups in the molecule. This seems apparent from the data in Table 9 in which a significant percentage of molecules possess single straight chain groupings.

Telomerization of ethylene onto m-xylene substrate produced an oil of approximately the same molecular weight as the mesitylene oil (851146-3). However, this oil appeared to exhibit somewhat improved oxidation stability. Thermal stability was slightly degraded as shown in Table 11.

Hydrogenation of the aromatic ring in the m-xylene telomer produces a marked improvement in oxidation stability as shown by the data in Table 12.

One might speculate that susceptibility to oxidation in the aromatic telomers is due to the presence of unreacted methyl groups and/or benzylic branching. Hydrogenation of the aromatic ring serves to deactivate these susceptible sites.

TABLE 10

PROPERTIES OF SYNTHETIC OILS

	700°F Thermal Stability KV_{100} %	347°F* Oxidative Stability KV_{100} %	KV_{210}	KV_{100}	KV_{-40}	VTF-VI
Gulf C_{20} Oligomer	-75.3	N/A	--	8.90	--	--
Anionic C_{20} Oligomer	-13.0	+2.3	1.99	5.87	Solid	143
Ethylene/Propylene	-24.6	19.1	2.51	8.73	Solid	127
851146-3 Aromatic Telomer	-10.8	274.4	--	--	--	--
851146-4 Aromatic Telomer	-13.1	139.6	3.56	15.38	Solid	125

* Fluid formulated with 1% E702, a bis-hindered phenol antioxidant, 24 hours, reflux, 5 l/hr. air, 20 ml fluid, metal catalysts present.

TABLE 11

OXIDATION/THERMAL TESTS

Property	Mesitylene Substrate		M-Xylene Substrate
	851146-3	851146-4	851188
Viscosity Change*, Micro Oxidation Test 347°F**	+274	+140	+64
Viscosity Change*, 700°F Thermal Test	-10.8	-13.1	-19.8

* Kinematic Viscosity @ 100°F

**Fluid formulated with 1.0% E702, a bis-hindered phenol antioxidant, 5 l/hr. air, reflux, 24 hours, 20 ml fluid, metal catalysts present

TABLE 12

PROPERTIES OF TELOMER OIL DERIVED FROM m-XYLENE (347°F Oxidation Test*)

Property	m-Xylene Telomer	Hydrogenated m-Xylene Telomer
Kinematic Vis. @ 100°F	6.22	7.86
Viscosity Change, %	+64	+3.8
Acid Number, mgKOH/g	0.07	0.05
Acid Number Change, mg KOH/g	21.7	0
Change in Weight, Metals, mg/cm^2		
350 steel	+0.04	+0.02
440 steel	+0.04	+0.12
Cu	-7.02	+0.06
Ag	-0.02	+0.02
Ti	+0.06	+0.08

*Fluid formulated with 1.0% E702 a bis-hindered phenol antioxidant, 5 l/hr. air, reflux, 24 hours, 20 ml fluid, metal catalysts present

SECTION V

ETHYLENE/PROPYLENE COPOLYMER OILS

Poly α-olefins such as polyoctene and polydecene have been used as synthetic hydrocarbon lubricants because they optimize the Viscosity Index (VI) and pour point relationship. PAO's have high VI's because of their relatively long linear methylene segments, and they possess low pour points because the linear methylene segments are not sufficiently long to furnish the required steric environment leading to crystallinity. An alternative means toward providing a limited sequence of linear methylene groups is a copolymer of ethylene and propylene. Previous work has demonstrated that an ASTM VI of 140 (VTF-VI of 123) and a pour point of -65°F can be obtained with a $C_2=/C_3=$ copolymer containing 46 mole % ethylene (54 mole % $C_3=$). As the mole fraction of ethylene increases, the VI increases and the pour point is raised. A procedure for preparing these $C_2=/C_3=$ copolymer oils has already been described[8]. It was found that $C_2=/C_3=$ copolymer oils had excellent oxidative and thermal stability, actually better than polyoctene and polydecene. The physical and chemical properties of $C_2=/C_3=$ copolymer oils make them of interest as an improvement over PAO's such as commercial polydecene.

While earlier work established the apparent superior thermal stability of ethylene propylene copolymer oils having good VI and pour points, it failed to identify a synthesis which would provide a commercial source of these materials. The present work attempted to identify a catalyst system which would improve the control of methylene sequence length to improve VI, while keeping the pour point below -65°F, and that at the same time would result in a good yield of oil in the KV_{210} 4-8 centistoke range.

In the time budgeted for this work, no progress was made in the identification of an improved catalyst system over diisobutyl-aluminum chloride and diethoxychlorovanadate in the ratio 10 to 1. The molecular weight of the product was controlled with hydrogen, the greater the hydrogen pressure, the lower the average molecular weight and the lower the viscosity. But at the same time, the yield of oil is reduced. Efforts to improve better molecular weight control also failed. The mechanism of the "anionic" polymerization, where hydrogen acts as a chain transfer agent through a catalyst complex, apparently does not allow the statistical distribution of molecular weights to be circumvented. Samples of $C_2=/C_3=$ oils were, therefore, obtained by hydrocracking of an ethylene-propylene copolymer rubber using platinum on aluminum as the hydrocracking catalyst.

The data on the ethylene-propylene copolymer oils (designated EP) are tabulated in Table 13, together with the data on other PAO products. To the extent that thermal data are considered reproducible, we can conclude that there is a distinct advantage for $C_2=/C_3=$ oils in terms of thermal stability over polydecene made with a cationic catalyst, anionic polyoctene and hydrogenated squalene. The thermal stability of the copolymer oils is comparable to that of superrefined mineral oil and hydrocracked petroleum oils. The reproducibility of the oxidative stability data is suspect because of the effect of small amounts of

TABLE 13

PROPERTIES OF PAO SYNTHETIC OILS

Oil	C#	TGA °C @ 10% Loss	KV_{210} (cSt)	KV_{100} (cSt)	KV_{-40} (cSt)	KV_{-65} (cSt)	ASTM-VI	VTF-VI	700°F Thermal Stability	Unformulated 225°F Oxidative Stability		Formulated 375°F Oxidative Stability	
									% KV_{100}	% KV_{100}	Acid#	% KV_{100}	Acid#
Alkylbenzene Avg. 851146-3	19	225	1.82	6.10	605	Solid	--	--	-11	+274	49	--	--
Gulf C_{20}	20	214	1.63	5.15	267	1661	--	--	-40	+ 16	3.6	+ 33	12.3
Sun C_{20}	20	230	1.99	5.87	Solid	Solid	161	143	-13	+ 2	0.4	+ 11	3.8
EP7030205		265	2.51	8.73	Solid	Solid	131	127	-25	+ 19	1.2	--	--
EP7030-225		290	3.43	13.71	Solid	Solid	140	129	-30	--	--	--	--
Alkylbenzene Avg. 851146-4	25	285	3.56	15.38	Solid	Solid	125	118	-13	+140	32	--	--
Gulf C_{30}	30	285	3.65	16.34	2000	11120	119	114	-65	+ 19	4.3	+4.1	12.9
Sun C_{30}	30	292	3.57	15.29	2000	Solid	128	120	-45	+ 10	1.0	+3.8	16.6
Squalane A	30	288	4.17	19.99	24500	60000	123	114	-55	+ 74	2.5	+ 52	25.5
Squalane B	30	280	4.14	20.15	14100	48000	118	111	-57	+ 6	0.1	+ 41	15.7

residual unsaturation that are often difficult to assess. Residual unsaturation can be removed by treating the oil with fuming H_2SO_4. The extent to which color develops in the acid layer is also related to the level of residual unsaturation.

Conclusions

Compelling evidence based on C-13 NMR analysis of decene oligomers produced with acidic catalysts suggests that the dominant mechanism of oligomer formation involves attack of secondary carbonium ions on secondary olefins bonds resulting in a complex mixture of isomers containing straight chains attached through secondary carbons. By contrast, oligomers prepared with anionic catalysts produce significantly less complex isomeric mixtures of which the molecular species n-eicosane and 9-methylnonadecane are confirmed as major components.

Decene oligomers produced by anionic catalysts exhibit superior thermal and oxidative stability compared to oligomers produced by cationic catalysts.

Analysis of the thermal behavior of decene oligomers leads to the conclusion that thermal stability is a true bulk property of the oil and that thermal decomposition occurs through a radical process.

Ethylene-propylene copolymer oils offer the potential for a useful synthetic lubricant exhibiting somewhat unique properties at lower cost, however, a major obstacle is the lack of a method to control polymerization in the molecular weight range needed for lubricants.

Oils produced by telomerization of ethylene on to meta-xylene substrate exhibited thermal stabilities equivalent to decene oils but showed poor oxidation stability which is thought to be due to the presence of unreacted methyl groups. Saturation of the aromatic ring improved oxidation stability.

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APPENDIX A

LITERATURE REVIEW OF SYNTHETIC LUBRICANTS

INTRODUCTION

The initial task under this program involved a thorough review of the literature pertaining to chemical structure and physical properties of synthetic hydrocarbon lubricants. The scope of the literature articles reviewed was limited to saturated alkyl and alkyl aromatic compounds. Pertinent references cited in the bibliography include 12 literature articles and 24 United States Patents drawn from literature searches by topic as follows:

Title	No. References Generated
Ethylene/propylene reactions on Ziegler catalysts	34
Ethylene/propylene reactions on other catalysts	135
Alpha olefin reactions on Ziegler Catalysts	51
Alpha olefin reactions on other catalysts	119
Other olefin reactions on other catalysts	42
Properties of octane/decane trimers/tetramers	21
Other information on octane/decane trimers/tetramers	98
Molecular structure-property relationships of alkanes, olefins, dimers and isomers	7

CORRELATIONS ON MIXED PRODUCTS

Generally, although many synthetic lubricants are produced from a pure starting material initially by oligomerization, the vagaries of the chemical path inevitably lead to rather complex mixtures. A great deal of information on such products is available from the patent literature, and to some extent, from other publications. While these sources do not elucidate structure-property correlations per se, they do indicate areas of interest. Patented lubricants include both homopolymers and copolymers. The patented homopolymers are based on isobutylene, octene or decene. The copolymers include ethylene/propylene, both with and without an additional α-olefin, and mixtures of higher α-olefins centering around decene.

Homopolymers based on 1-decene are most common in the patent literature. Gulf, Mobil and Ethyl all hold patents on cationic polymerization of 1-decene by BF_3-based catalysts. Mobil and Bray hold patents on cationic $AlCl_3$-based catalyst systems; Bray, in addition, has an $AlCl_3$-$TiCl_4$-based system which is probably cationic. Sun holds a patent[1] on polymerization of 1-octene by an aluminum alkyl-$TiCl_4$ catalyst system which is purportedly anionic. This system is also used for polymerizing 1-decene. While the anionic nature of the system is in dispute, the resulting products do differ in nature from those from other cationic systems. There are also some free radical polymerizations of 1-decene mentioned. Mobil compares thermally-initiated with chemically-initiated free radical polymerizations in one of their patents.

Homopolymerization of smaller α-olefins is the subject of a number of Sun patents. Polymerization of isobutylene is accomplished with a variety of $SnCl_4$ or $CoCl_2$-based cationic catalyst systems. 2-methyl-1-butene and 2-methyl-1-pentene are also polymerized by these systems.

Copolymerization of ethylene and propylene is the subject of four patents by Sun by means of a vanadium-based Ziegler-Natta catalyst system. Mobil also holds a patent on a Ziegler-Natta copolymerization of ethylene and propylene. Sun uses hydrogen to control molecular weight and chooses as the optimal composition, a composition which compromises between viscosity index and pour point. Mobil chooses a composition which optimizes viscosity index, but requires dewaxing for an acceptable pour point.

Addition of various other olefins to the ethylene/propylene mixture is the subject of a Mobil patent. The two-step process consists of polymerizing ethylene and propylene with a Ziegler-Natta system, and then incorporating a third olefin with a BF_3-based cationic system.

All of the decene patents claim α-olefins from hexene through dodecene or higher and also mixtures thereof; some of these claims are backed by examples and some are not. Another source of higher olefins for polymerization is wax-cracking. These contain some branched and internal olefins, as well as the linear α-olefins which are used in commercial decene polymerizations.

There is a patent held by Exxon which uses a two-stage thermal process to produce oil from wax. In this patent, the polymerization process is presumably thermally-initiated free radical.

Examination of products by viscosity indices shows general trends. The pattern is not discernible with ASTM-VI as the products vary so much in viscosity, but VTF-VI weeds out this artifact[2] and clearly defines some categories.

An examination of homopolymers shows two trends. One is an increase in VTF-VI with increasing mildness of the catalytic system. For a single monomer, the milder the conditions used to produce them using a particular catalyst type (i.e., cationic, free radical, etc.), the better the VTF-VI. This is true across a wide range of product viscosities, as shown in Table A-1. The second trend is by monomer branching. The more highly branched the monomer, the lower the VTF-VI of the resulting polymer oil. This is in Table A-2. The total data are in Table A-3.

An examination of copolymers confirms the catalyst trend, i.e., for a particular monomer feed, Ziegler-Natta systems give products with similar VTF-VI's which are higher than the VTF-VI's for products of combined Ziegler-Natta plus cationic systems. This is in Table A-4. With copolymers, the variation of VTF-VI with monomer feed follows the rule that the higher the proportion of a more highly branched monomer there is in a mixed feed, the lower the VI. This is in Table A-5. Note the leveling off of VI from hexene through decene. This is further evidence of the equivalency of octene and decene with respect to VI properties. The total data are in Table VI.

Pour point is the next most commonly used indicator of oil quality. Unfortunately, much of the patent data is obtained on unhydrogenated material which has been shown to have a different pour point from hydrogenated material, and the difference is not consistently up or down. What comparable evidence is available indicates that the longer the uninterrupted chains of methylene groups, the higher the pour point.

TABLE A-1

VISCOSITY PROPERTIES OF LIGHT-ENDS STRIPPED OILS OCTENE OR DECENE AS MONOMER*

Catalyst	KV_{210}(cSt)	VTF-VI
$AlCl_3$	18	111
Modified $AlCl_3$, BF_3 or $AlCl_3 + TiCl_4$	4.84-5.83	116-122
Thermally-Initiated Free Radical	7.39	126
Chemically-Initiated Free Radical	9.12	137
Aged Modified $AlCl_3$, $AlBr_3$ or $AlCl_3 + TiCl_4$	5.20-37.72	132-137
$TiCl_4 + Al_2Et_3Cl_3$ + Propylene Oxide	18.2-20.7	151-153

*These monomers are equivalent as far as VI is concerned.

TABLE A-2

VISCOSITY PROPERTIES OF LIGHT-ENDS STRIPPED OILS

$AlCl_3$ AS CATALYST

Monomer	KV_{210} (cSt)	VTF-VI
2-methyl-1-butene	12-18	3-15
Isobutylene	14-31	58-71
Octene or Decene	18	111

TABLE A-3

PROPERTIES OF LIGHT-ENDS STRIPPED PRODUCTS

MONOMER	CATALYST	KV_{210}(cSt)	VTF-VI
2-methyl-1-pentene	$SnCl_2$+ CH_3NO_2	3.02	26
2-methyl-1-butene	$AlCl_3$	12-18	3-15
	$SnCl_2$+ CH_3NO_2	4.66	52
Isobutylene	$AlCl_3$	14-31	58-71
	Aluminum alkyls + alcohols; $SnCl_2$ + modifiers	2.63-64.62	90-114
	Aluminum alkyls + alcohols + $CoCl_2$ + modifiers	3.01	125
Octene or Decene*	$AlCl_3$	18	111
	$AlCl_3$, BF_3, or $AlCl_3$ + $TiCl_4$ with polar modifiers	4.84-5.83	116-122
	Thermally-initiated free radical	7.39	126
	Chemically-initiated free radical	9.12	137
	$AlCl_3$ or $AlCl_3$ + $TiCl_4$ with alkyls or non-polar modifiers	5.20-37.72	132-137
	$TiCl_4$ + $Al_2Et_3Cl_3$ + Propylene Oxide	18.2-20.7	151-153

*These monomers are equivalent as far as VI is concerned.

TABLE A-4

VISCOSITY PROPERTIES OF LIGHT-ENDS STRIPPED OILS ETHYLENE/PROPYLENE COPOLYMER

Catalyst	KV_{210}(cSt)	VTF-VI
Ziegler-Natta + BF_3 (Mobil)	9.73	99
Ziegler-Natta (Mobil)	21.70	138
Ziegler-Natta (Sun)	6.80	140

TABLE A-5

VISCOSITY PROPERTIES OF LIGHT-ENDS STRIPPED OILS ZIEGLER-NATTA + BF_3 AS CATALYST FOR ETHYLENE/PROPYLENE COPOLYMER

Added Monomer	KV_{210}(cSt)	VTF-VI
None	9.73	99
Butene	8.93	106
Hexene	8.50	117
Decene	7.77	119

TABLE A-6

PROPERTIES OF LIGHT-ENDS STRIPPED PRODUCTS

MONOMER	CATALYST	KV_{210}(cSt)	VTF-VI
Ethylene/Propylene	Ziegler-Natta + BF_3 (Mobil)	9.73	99
	Ziegler-Natta (Mobil)	21.70	138
	Ziegler-Natta (Sun)	6.80	140
E/P + Butene	Ziegler-Natta + BF_3 (Mobil)	8.93	106
	Ziegler-Natta (Mobil)	47.59	143
E/P + Hexene	Ziegler-Natta + BF_3 (Mobil)	8.50	117
	Ziegler-Natta (Mobil)	29.35	149
E/P + Decene	Ziegler-Natta + BF_3	7.77	119
Linear α-olefins C_6-C_{14} (around C10)	BF_3 + modifiers, $AlCl_3$ + $TiCl_4$ + modifiers	4.09-6.55	100-121
	Chemically-initiated free radical	40.35	141
Olefins from wax-cracking C_5-C_{20} (around C_{10})	Thermally-initiated free radical	46.3	112
	BF_3 + H_2O	3.23-5.39	119-120

This trend is counter to the trend for viscosity index. It is, thus, evident that some form of compromise is always made between pour point and viscosity index.

Another low temperature property is kinimatic viscosity at -40°F. This is obviously related to pour point inasmuch as oils which have a pour point above -40°F are going to have a very high viscosity at that temperature.

The difference between pour point vs. VTF-VI and KV_{-40} vs. VTF-VI is that the viscosity index and the low temperature viscosity both become worse with branching, while the pour point may improve.

The variation of pour point and VTF-VI with branching and straight chain content for a C_{30} hydrogenated ethylene/propylene copolymer is shown in Table A-7. The copolymer with higher percent ethylene is logically assumed to have longer straight chain portions and a lower degree of branching. The exception to the rule is pure propylene oil, which has a fair degree of crystallinity and, therefore, has both a high pour point and a low VTF-VI.

The variation of KV_{-40} and VTF-VI with branching for a C_{30} hydrocarbon is shown in Table A-8.

Thermal and oxidation stability are important properties which distinguish synthetic hydrocarbons from mineral oil lubricants. Under most conditions, oxidation stability is more important because operating conditions do not create thermal stress.

Data (4) are available on the 400°F oxidative stability and the 700°F thermal stability of hydrogenated poly- α -olefins and ethylene/propylene copolymer oils. The percent viscosity change after both tests is greater

TABLE A-7

VTF-VI AND POUR POINT VS. % ETHYLENE IN E/P OIL

% Ethylene	VTF-VI	Pour Point (°F)
0	79	95
46	125	-65
48	124	-60
52.5	126	-20
56.5	131	-15
58.5	131.5	-15
71	138	70
83	140	115
100	144	169

TABLE A-8

VTF-VI AND KV_{-40} VS. MONOMER (BRANCHING) AT A SIMILAR MOLECULAR WEIGHT

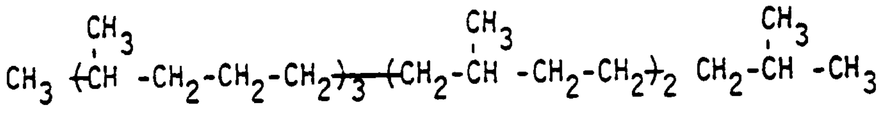
Oil	Carbon #	VTF-VI	KV_{-40}(cSt)
Decene Trimer	30	119	2070
Octene Tetramer	32	101	4750
Hexane Pentamer	30	97	7850
Propylene Decamer	30	62	>99M

for the poly-α-olefin than for the ethylene/propylene copolymer, but the total acid number (TAN) after the oxidation test is the same for both. Since the structures of these two oils, in general, should give similar products for each oxidative cleavage, one is left with the impression that the actual number of breaks is the same, but that the viscosity gain per break is greater for poly-α-olefins. The viscosity change per break can be explored by examining the effects of the most probable thermal cleavages on the viscosity of the two oils.

A very primitive calculation shows that the expected percent viscosity change is, in fact, greater for poly-α-olefin than for ethylene/propylene copolymer for the same number of breaks per molecule. Figure A-1 illustrates the model compounds used in the calculations. Tables A-9-A-11 contain the details of these calculations.

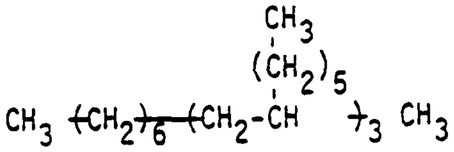
This method applied to polyisobutylene oil would predict the percent change in viscosity in the thermal test to be smaller than that for ethylene/propylene oil. This is contrary to experimental results[5]. The explanation lies in the fact that polyisobutylene contains primarily 4° carbons as opposed to the 3° carbon in the other two oils. Polyisobutylene is known[6] to undergo an unzipping reaction to monomer which is possible because of the 3° radicals formed on initial thermal cleavage. The poly-α-olefins and ethylene/propylene copolymers form only 2° radicals which are not stable enough to undergo further breakdown. Data on the acid number of polyisobutylene oil after oxidative testing is not comparable with the other two oils because a different test was used, so the number of breaks per molecule in the oxidation test cannot be compared.

ETHYLENE/PROPYLENE OIL



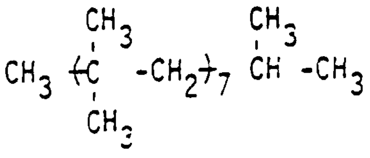
$$CH_3 \left(\overset{\substack{CH_3\\ |}}{CH} -CH_2-CH_2-CH_2 \right)_3 \left(CH_2-\overset{\substack{CH_3\\ |}}{CH} -CH_2-CH_2 \right)_2 CH_2-\overset{\substack{CH_3\\ |}}{CH} -CH_3$$

POLY-α-OLEFIN OIL



$$CH_3 \left(CH_2 \right)_6 \left(CH_2-\overset{\substack{CH_3\\ |\\ (CH_2)_5\\ |}}{CH} \right)_3 CH_3$$

POLY-ISOBUTYLENE OIL



$$CH_3 \left(\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}} -CH_2 \right)_7 \overset{\substack{CH_3\\ |}}{CH} -CH_3$$

FIGURE 1: MODEL COMPOUNDS

TABLE A-9

ETHYLENE/PROPYLENE OIL

Initial KV_{100} 15.5 cSt
Final KV_{100} 6.5 cSt
% Decrease 58%

Probability of Break	Fragments		Resulting KV_{100}(cSt)
1/6	29	1	13.58
1/6	27	3	9.72
1/6	24	6	7.39
1/6	22	8	3.00
1/6	19	11	3.00
1/6	17	13	2.55

WEIGHTED AVERAGE = 6.54 cSt

TABLE A-10

POLY- α -OLEFIN OIL

Initial KV_{100}	23.3 cSt
Final KV_{100}	5.6 cSt
% Decrease	76%

Probability of Break	Fragments		Resulting KV_{100}(cSt)
1/6	26	6	7.02
1/3	24	8	7.02
1/6	23	9	7.02
1/6	17	15	2.88
1/6	16	16	2.88

WEIGHTED AVERAGE = 5.64 cSt

TABLE A-11

POLY-ISOBUTYLENE OIL

Initial KV_{100}	134 cSt
Final KV_{100}	84 cSt
% Decrease	37%

Probability of Break	Fragments		Resulting KV_{100}(cSt)
17/31	31	1	129.82
1/31	29	3	121.52
2/31	28	4	49.60
1/31	27	5	23.87
1/31	25	7	23.87
2/31	24	8	18.29
1/31	23	9	18.29
1/31	21	11	16.74
2/31	20	12	16.74
1/31	19	13	16.74
1/31	17	15	3.57
1/31	16	16	3.57

WEIGHTED AVERAGE = 84.01 cSt

CORRELATIONS ON PURE COMPOUNDS

Breakdowns of some polyolefin-based lubricant property data are available to the level of carbon number (C_{30}, C_{32}, etc.)[7] but, to date, there has been no successful characterization of the chemical structures of these isomeric mixtures. Detailed structure-property correlations on acyclic saturated hydrocarbons have been limited to relatively low molecular weight and/or relatively straight chain pure compounds. The classic work on this subject is API Project 42, which contains no data on thermal or oxidative stabilities. None of these tabulations of viscosities, viscosity indices and pour points versus structure holds any surprises.

A detailed study[8] of hydrogenated aromatics and alkyl aromatics as they relate to viscosity, viscosity index, melting point and molecular structure, leads to the following conclusions:

Viscosity

A. At a given molecular weight, hydrogenation of alkylnaphthalenes causes no increase in viscosity beyond that expected for a larger molecular weight.

B. n-Alkylbenzenes and n-paraffins have about the same viscosities at a given molecular weight. However, greater number of rings (aromatic or naphthenic) and/or more complex ring fusion at constant molecular weight increase viscosity. Branched alkylbenzenes are usually more viscous than iso-paraffins of the same molecular weight.

C. Increasing alkyl branching or larger numbers of ring substituents (same total molecular weight) can result in more viscous alkyl aromatics. However, small amounts of branching in paraffins can even lead to a decrease in viscosity.

D. The position of a substituent along an alkyl chain can significantly affect viscosity. Internal phenyl substitution often gives higher viscosity than terminal substitution, but these effects vary broadly.

<u>ASTM-Viscosity Index</u>

A. In a homologous series, the viscosity index increases with increasing molecular weight. The VI's of n-alkyl aromatics are roughly the same as those of the n-paraffins, of equivilent side chain length.

B. Generally, more branching or ring substitutions for the same molecular weight lead to lower VI's. Even p-methyl ring substitutions may have significant effects. It is not always possible to predict which substitution patterns will have better viscosity-temperature relationships, but "longer and/or straighter" seems to give the best VI's, e.g., for the same substituents para better than meta better than ortho.

C. At a given molecular weight, the more cyclization and fusion in a compound, the worse the VI. However, cyclopentyl substitution appears to affect VI less than other rings; this group still contributes to a higher viscosity than five carbon paraffin substituents.

D. Compounds with two or more rings connected by alkyl bridges generally lose VI on hydrogenation. The viscosity indices of cyclohexyl compounds are often similar to those of the corresponding phenyl derivatives, although considerable variation is observed. Naphthalene systems often show VI improvement on hydrogenation.

Melting Point

A. For a given molecular weight, n-paraffins melt higher than n-alkyl-benzenes or naphthalenes.

B. Hydrogenation of phenyl rings increases the melting point slightly, but often decreases the melting points of naphthalenes.

C. While increasing molecular weight leads to higher melting points, in general, the initial substitution of short chains on aromatic rings depresses melting point.

D. Branching and ring substitution at a given molecular weight lowers melting point.

Thermal stability of pure compounds has been measured in two different ways. The recent work by Gulf[9] uses the 700°F test which measures percent loss of viscosity at 100°F after thermal degradation. One puzzling piece of data is the squalane viscosity loss. A 41.8% loss in KV_{100} is reported by Gulf for squalane as opposed to a 17.2% loss in KV_{100} reported by Sun for ethylene/propylene oil.

A paper on jet fuels[10] measures thermal stability by a different criteria which is pertinent for their uses but not applicable for ours. Monsanto measured the "thermal decomposition temperature," which is defined as the temperature in °F at which gas is evolved at 1 mole % per hour. The results of the tests clearly reflect the bias of the test in that cyclic compounds fare better than n-alkanes due to the fact that one break in a cycle will not release two smaller molecules measurable as gas evolution.

Oxidation stability has been measured in a variety of ways on pure compounds. One method[11] consists of heating the sample at 140°C under

1 atm of O_2 for 7 hours. A number of parameters were measured, including the maximum rate of O_2 consumption and the total O_2 consumption. The data, shown in Table A-12, indicate a higher level of stability for alkylated benzenes than for either straight chain or branched alkanes. This may indicate an area of interest. A second method[12] studied the rate of O_2 consumption at 110°C. A thorough product analysis was carried out. The most interesting phenomenon noted was the formation of oxidation inhibitors in naphthalene hydrocarbon oils by oxidation of a small amount of the oil.

SUMMARY

In summary, a great deal of data has been amassed on the relationship of viscosity, viscosity index and melting point to molecular structure for aromatics and alkylaromatics, naphthenics and alkylnaphthenics, and low molecular weight acyclic saturates. No suitable data has been generated on the relationship of thermal and oxidative stabilities, or responses to oxidation inhibitors, to molecular structure for any of these pure compounds. Gaps exist in the acyclic saturate data where specific products of catalytic systems are under scrutiny.

TABLE A-12

RATE OF OXYGEN CONSUMPTION AT 140°C OVER 7 HOURS, 1 ATM O_2

Sample	Maximum Rate x 10^4 mol/l sec	Total O_2 Absorption mol/l
Squalane	15.50	15.50
Hydrogenated -olefin oligomers	11.80	8.26
n-hexadecane	7.5	5.46
didodecylbenzene	1.39	1.49
dodecylbenzene	--	.92

APPENDIX I

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APPENDIX B

SYNTHESIS AND PURIFICATION OF 1-DECENE-2-^{13}C

Introduction

Synthesis of 1-decene-2-^{13}C was carried out by Dr. Allan P. Marchand at North Texas State University under subcontract.

The overall synthetic scheme is as follows:

$$\text{R-Br} \rightarrow \text{R*CO}_2\text{H} \rightarrow \text{R-*CHO} \rightarrow \text{R-*CH=CH}_2$$

where R = n-C_8H_{17}, and the asterisk indicates the position of the carbon-13 label. Initially, we envisioned that 1-decene-2-^{13}C could be prepared by a *Wittig reaction of triphenylphosphonium* methylide with pelargonaldehyde-1-^{13}C. The aldehyde, in turn, could be synthesized via Grignard reaction of 1-octyl-magnesium bromide with $^{13}CO_2$.

Discussion

All synthetic operations were first performed on nonisotopically-enriched materials, and the yield of each step was optimized. In practice, we found that while the synthesis of pelargonic acid using the Grignard procedure described above was straightforward, its reduction to pelargonaldehyde proved somewhat troublesome. Attempted reduction of pelargonic acid methyl ester with diisobutylaluminum hydride[1] afforded only mixtures of the desired pelargonaldehyde plus starting material. Increased reaction times did not markedly improve the yield of aldehyde, nor did this action result in an improved ratio of aldehyde to starting material in the product. Consequently, an alternative method was sought for the reduction of pelargonic acid to pelargonaldehyde. Of the various methods that were considered and attempted, the best procedure proved to be (i) reduction of pelargonic acid to 1-nonanol using borane-THF complex[2] followed by (ii) careful oxidation of the alcohol to pelargonaldehyde with pyridinium chlorochromate.[3]

Our four-step synthesis of 1-decene-2-^{13}C from 1-bromooctane is outlined in the Scheme. This synthetic sequence provides the desired labelled 1-decene in 57% overall yield. Our method should be applicable generally to the synthesis of terminal alkenes which are site-specifically ^{13}C-labelled in the 2-position.

SCHEME

$$\text{R-Br} \xrightarrow[(76\%)]{(a\text{-}c)} \text{R-*CO}_2\text{H} \xrightarrow[(98\%)]{(d)} \text{R-*CH}_2\text{OH} \xrightarrow[(91\%)]{(e)} \text{R-*CH=O} \xrightarrow[(84\%)]{(f)} \text{R-*CH=CH}_2$$

R = $\underline{n}$-C_8H_{17}; asterisk indicates position of ^{13}C label.

(a) Mg, dry Et_2O; (b) CO_2, 90 mol-% ^{13}C isotopic enrichment; (c) Aqueous acidic workup; (d) Borane-THF complex, 0°C; (e) Pyridinium chlorochromate, dry CH_2CL_2, room temperature; (f) methyltriphenylphosphonium bromide, dimethyl sulfoxide, room temperature.

Proton NMR spectra (60 MHz) were obtained with a Hitachi-Perkin Elmer Model R-24B NMR spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer. In all cases, signals are reported in parts per million (ppm) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer model 1330 infrared spectrophotometer. Isotopically ^{13}C-enriched carbon dioxide (90 mol-%) was purchased from Amersham Corporation, Chicago, Illinios. The reaction products (i.e., pelargonic acid, 1-nonanol, pelargonaldehyde, and 1-decene) are well known compounds which have been fully characterized in the chemical literature; the boiling points of these materials (unlabelled and ^{13}C-labelled) as synthesized in the present study agree with the corresponding literature values.

Synthesis of Pelargonic Acid-1-^{13}C - A modification of the procedure described by Marshall and coworkers[4] was employed. A 250 mL three-necked flask was fitted with a condenser, thermometer, magnetic stirring bar, and addition funnel, and an argon inlet-outlet tube was placed at the top of the condenser. The system was flame dried and maintained under argon throughout the reaction. The reaction flask was charged with magnesium metal (2.67 g, 0.11 mol), and 1-octylmagnesium bromide was prepared in the usual manner by reaction of the magnesium with a 1 M solution of 1-bromooctane in dry tetrahydrofuran (THF, 100 mL, 0.1 mol). After the formation of the Grignard reagent has been completed, the thermometer and the addition funnel were replaced with glass stoppers, and the reaction flask was placed on a volume-calibrated (mol CO_2 vs. mm Hg) vacuum line. The stopcock which connects the reaction flask to the vacuum line remained closed. The Grignard solution was frozen via application of external cooling (liquid nitrogen bath), and the reaction flask was evacuated to 0.01 mm Hg. The stopcock which connects the reaction flask to the vacuum line was again closed, and the requisite amount of $^{13}CO_2$ was bled into the precalibrated vacuum line. The stopcock was opened, allowing CO_2 to diffuse into the cooled reaction flask. The liquid nitrogen bath was replaced by a dry ice-acetone bath; once the reaction solution became liquified magnetic stirring was initiated and the reaction mixture was stirred overnight. At the conclusion of the reaction, the mixture was quenched with 18% aqueous hydrochloric acid solution (50 mL). Water (100 mL) was added and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with ether. The combined organic layers were stirred vigorously with 5% aqueous potassium hydroxide solution (300 mL) for 30 minutes. The organic layer was separated and extracted with 5% aqueous potassium hydroxide solution (2 x 50 mL). The combined aqueous layers were acidified with concentrated aqueous hydrochloric acid solution and extracted with ether. The combined organic layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford pure pelargonic acid-1-^{13}C (12.0 g, 76%); ^1H NMR ($CDCl_3$) 0.93 (t, J = <u>ca.</u> 7 Hz, 3H), 1.04-1.75 (m, 12H), 2.33 (t, J = <u>ca.</u> 7 Hz, 2H), 11.54 (s, 1H); ^{13}C NMR ($CDCl_3$) 180.36 (s), 34.04 (s), 31.77 (t), 29.16 (t), 29.16 (t), 29.06 (t), 24.67 (t), 22.56 (t), 13.89 (q); IR (neat) 2500-3400 (br, vs), 1677-1730 (br, vs), 1390-1472 (br, s), 1160-1350 (br, s), 1112 (m), 942 (s), 728 cm^{-1} (m).

Synthesis of 1-Nonanol-1-^{13}C - A modification of the procedure described by Brown and coworkers[2] was employed. A 1 M solution of borane-THF complex in dry THF (100 mL, 0.1 mol) under nitrogen was cooled to -10°C. A solution of pelargonic acid-1-^{13}C (11.87 g, 0.075 mol) in dry THF (60 mL) was added to the borane-THF complex under nitrogen in such a manner that the temperature of the solution never exceeded 0°C. After addition of the pelargonic acid had been completed, the reaction mixture was stirred at 0°C (15 minutes). The resulting mixture was warmed to room temperature and stirred for an additional 3 hours. Aqueous sodium bicarbonate solution (5%) was added (200 mL), whereupon stirring was continued for an additional 30 minutes. The organic layer was separated, and the aqueous layer was extracted with ether. Combined ether layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford pure 1-nonanol-1-^{13}C (0.70 g, 98%); ^{1}H NMR ($CDCl_3$) 1.42 (t, J = *ca.* 6 Hz, 3H), 1.63-2.4 (m, 15H), 4.17 (t, J = *ca.* 7 Hz, 2H); ^{13}C NMR ($CDCl_3$) 62.78 (t), 32.88 (t), 32.07 (t), 29.80 (t), 29.63 (t), 29.47 (t), 26.00 (t), 22.81 (t), 14.14 (q); IR (neat) 3360 (br, s), 2930 (s), 2858 (s), 1470 (s), 1422 (s), 1338 (s), 1058 cm^{-1} (s).

Synthesis of Pelargonaldehyde-1^{13}C - A modification of the procedure of Corey and Suggs[3] was employed. To a vigorously stirred solution of pyridinium chlorochromate (27.91 g, 0.13 mol) in dry methylene chloride (175 mL) was added all at once a solution of 1-nonanol-1-^{13}C

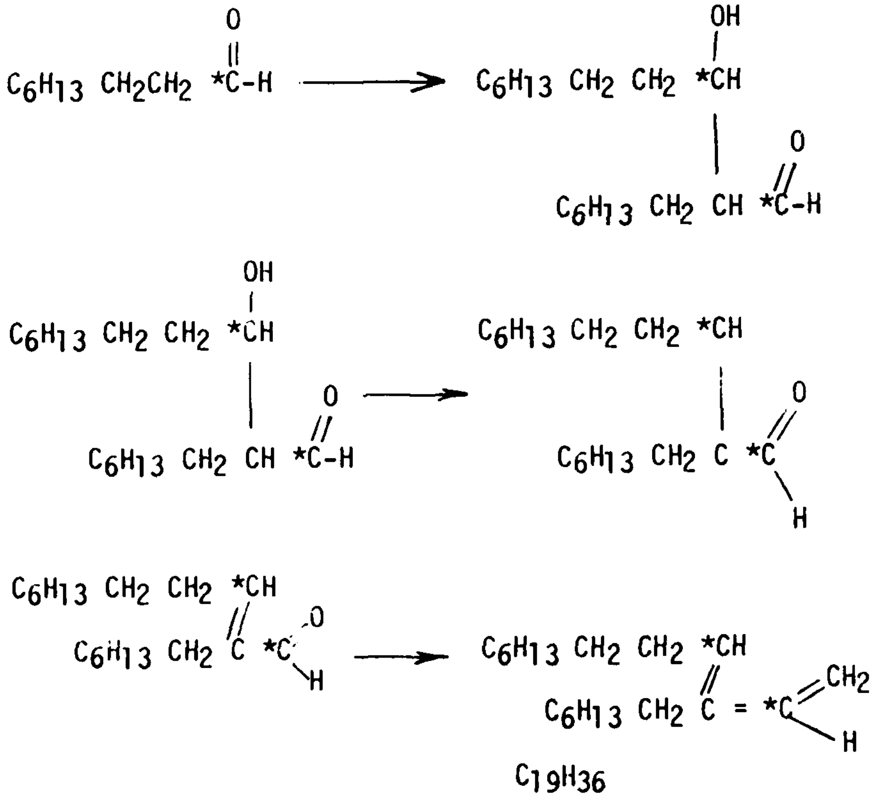
(10.67 g, 0.074 mol) in methylene chloride (20 mL). The resulting mixture was stirred at room temperature (3 hr) then diluted with ether (200 mL). The reaction mixture was then filtered through a short pad of Fuller's earth; the pad was washed thoroughly with ether, and the washings were added to the filtrate. The filtrate was concentrated in vacuo to afford pelargonaldehyde-1-^{13}C (9.62 g, 91%); ^{1}H NMR (CDCl$_3$) 0.88 (t, J = 5.5 Hz, 3H), 1.17- 1.86 (m, 12H), 2.37 (q, J = 7 Hz, 2H), 9.74 (t, J = 2 Hz, 1H); ^{13}C NMR (CDCl$_3$) 202.45 (d), 43.99 (t), 31.96 (t), 29.47 (t), 29.25 (t), 29.25 (t), 22.75 (t), 22.26 (t), 14.09 (q); IR (neat) 2928 (s), 2865 (s), 2718 (w), 1722 (s), 1472 (m), 1418 (w), 1395 (w), 1382 (w), 730 cm^{-1} (w).

Synthesis of 1-Decene-2-^{13}C - A modification of the procedure of Corey and Chaykovsky[5] was employed. Commercial sodium hydride (50% dispersion in oil, 11.04 g, 0.21 mol) was washed with dry hexane (3 x 100 mL); after the final washing, the last traces of hexane were removed in vacuo. To the remaining dry sodium hydride was added dry dimethyl sulfoxide (150 mL), and the resulting mixture was heated gently (70-75°C) until evolution of hydrogen ceased. The mixture was cooled to 15°C. To this mixture was added a solution of methyltriphenylphosphonium bromide (76.17 g, 0.21 mol, which had previously been dried by heating overnight in vacuo at 110°C) in dry dimethyl sulfoxide (220 mL). To the reaction mixture was added a solution of pelargonaldehyde-1-^{13}C (22.76 g, 0.16 mol) in dry dimethyl sulfoxide (15 mL). The resulting mixture was stirred at room temperature (3 hr) and poured into a mixture of pentane (200 mL) and water (800 mL). This mixture was stirred (10 minutes), and the layers were separated. The aqueous layer was extracted with pentane, and the combined pentane layers were washed sequentially with water (3 x 200 mL) and with brine (200 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford crude 1-decene-2-^{13}C (22.5 g, 97%). The crude product was purified via column chromatography on silica gel (pentane eluent) to afford pure 1-decene-2-^{13}C (18.85 g, 84%); ^{1}H NMR ($CDCl_3$) 0.88 (t, 3H), 1.28 (br s, 12H), 1.77-2.17 (m, 2H), 4.81-5.11 (complex m, 2H), 5.57- 6.05 (complex m, 1H); ^{13}C NMR ($CDCl_3$) 139.17 (d), 114.09 (t), 33.91 (t), 32.02 (t), 29.58 (t), 29.42 (t), 29.25 (t), 29.09 (t), 22.75 (t), 14.09 (q); IR (neat) 3082 (w), 2961 (sh, vs), 2929 (vs), 2861 (vs), 1614 (w), 1468 (m), 1382 (w), 993 (m), 912 (s), 730 cm^{-1} (w).

Purification of 1-Decene-2-^{13}C - A 10.2 g sample of 1-decene-2-^{13}C as provided by Dr. Marchand showed the expected large peak for C=CH_2, but also showed additional structural features indicative of another enriched species. These extra peaks seemed to involve splitting due to ^{13}C-^{13}C coupling. Routine gas-liquid chromatography (GLC conditions 10 ft. x 1/8 in. column with 10% methyl silicone fluid programmed from 150°C to 300°C at 10°/minute) showed that the expected material was accompanied by several impurities, including one that amounted to 12.4% by area.

Capillary gas chromatography with mass spectrographic (GC/MS) analysis of the peaks using both electron impact and chemical ionization techniques indicated an appropriate pattern for the expected enriched decene-1, $C_{18}H_{36}$ with enriched ^{13}C, and either $C_{19}H_{38}$ with no enrichment or $C_{19}H_{36}$ with double ^{13}C enrichment.

During a telephone consultation with Professor Marchand, we agreed that the most likely explanation of the data was an aldol condensation of the aldehyde, elimination of water, and reaction of the new aldehyde to give doubly-labeled diene.



$C_{19}H_{36}$

Repurification of 1-decene-2-^{13}C was accomplished by fractionation and its identity confirmed by GC/MS analysis. ^{13}C NMR showed some interesting features, one of which is anomolous. The -CH_2- adjacent to the enriched ^{13}C is split into a doublet as expected. What was unexpected was that J-modulated spin-echo techniques[6] did not cause these -CH_2- peaks to invert as would be expected. Since there are relatively few examples of ^{13}C enriched compounds of this type, this phenomenon and the related coupling constants are worthy of further investigation and clarification.

APPENDIX II

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