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Behavior of protonated cyclopropyl intermediates during polyalphaolefin synthesis: Mechanism and predicted product distribution

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A new mechanism for the origin of multiple skeletal isomers observed in the cationic dimerization of 1-decene is proposed, and products that should form based on this mechanism are predicted. A protonated cyclopropyl intermediate appeared to form directly from combination of 2-decyl carbocation with 1-decene; formation of this intermediate did not appear to occur via ring closure of a branched secondary carbocation. The authors propose that rapid, repeated isomerizations of the protonated cyclopropyl intermediates lead to multiple skeletal isomers in decene dimers. The proposed mechanism can account for structures previously identified in mixtures of decene dimers and butene dimers. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: carbenium ion; carbocation rearrangement; cationic oligomerization; protonated cyclopropyl intermediate; polyalphaolefin; skeletal isomerization mechanism

INTRODUCTION

The mechanism of alpha olefin oligomerization to make polyalphaolefins (PAO) has been a subject of much investigation for some time.[1–4] Of chief interest is an explanation for the origin of multiple skeletal isomers. Nuclear magnetic resonance (NMR) evidence has shown that most of the oligomers contain one more methyl group than a simple mechanism would predict, and Shubkin and coworkers proposed a protonated cyclopropyl intermediate at the dimerization stage to account for skeletal isomerization that could produce an additional methyl group.[1,4] Other workers have also proposed that double bond isomerization in the 1-decene monomer could account for structures present in the products.[2,3] Indeed, detailed NMR[5] and gas chromatography/mass spectrometry (GC/MS)[6] work have provided much information about the structures of products in the saturated dimer fraction (C20 isomers or "PAO 2") isolated from 1-decene oligomerization.

A typical PAO manufacturing process involves the use of BF_3 or other Lewis acid, in combination with a protic source such as an alcohol or water, to induce cationic oligomerization of 1-decene or other linear alpha olefin.[7,8] These conditions produce a mixture of branched oligomers with a distribution that peaks around trimer. The hydrogenated products, once fractionated into different viscosity/molecular weight fractions, are outstanding lubricants. Their structures impart excellent viscosity indices and low pour points, as well as outstanding oxidative stabilities.

The simple mechanism for cationic oligomerization[9] (Fig. 1) does not explain the high number of isomers observed in these products. Chromatographic analysis of the hydrogenated dimer fraction shows well over 50 different isomers.[2,6] NMR analyses on dimer and other fractions have shown that all of the skeletal rearrangement may occur at the dimerization stage,[1] and much analytical work has focused on the dimer fraction.

The high number of isomers observed in the saturated dimer fraction indicates that some type of carbenium ion isomerization has occurred that is extremely rapid relative to both proton elimination and reaction with monomer (to make trimer). Previous investigators have suggested that rapid double bond isomerization occurs in the monomer and that reaction of internal carbenium ions with 1-decene leads to the formation of multiple isomers in the C20 fraction.[3] Our observations do not support this conclusion.

EXPERIMENTAL

Oligomerization reactions. In a typical oligomerization reaction, 5.0 g of olefin, 0.3 g of n-nonane internal standard, and 0.050–0.12 g of $AlCl_3$ or $AlBr_3$ were combined in a 20 ml glass bottle with magnetic stir bar. Sometimes, 1-butanol (0.3 mole 1-butanol per mole AlX_3) was included, but the 40–100 ppm water in the olefin samples was enough to generate an active catalyst. The bottle was placed in a heated metal block inside a glove box having dry nitrogen atmosphere. Mixtures stirred at 300 rpm and 25 °C or 90 °C. Reaction mixtures were periodically sampled by withdrawing a few drops of liquid using a glass pipette and adding them to 0.5 ml of cyclohexane solvent. Outside the glove box, mixtures were quenched with a few drops of isopropanol and analyzed by gas chromatography. From the chromatographic data, percent conversion of monomer to oligomer was calculated, as well as oligomer carbon number distributions. Skeletal isomerization in monomer was detectable, and the number and width of peaks for dimer and heavier products was a qualitative measure of the variety of isomers present. The 1-decene was from Chevron Phillips Chemical Company (The Woodlands, TX USA). Aluminum chloride and aluminum bromide were from Sigma-Aldrich (St. Louis, MO USA).

Gas chromatographic analyses. The method was split injection on a gas chromatograph with a flame ionization detector (FID). Initial oven temperature was 70 °C and increased 5 °C/min to 130 °C, then 20 °C/min to

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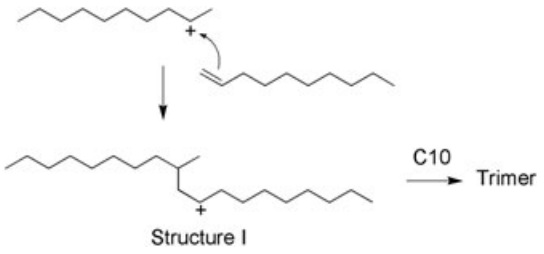

Figure 1. Simple mechanism accepted for cationic polymerization

300 °C for 20 min. The column was an Alltech FSOT capillary column, 30 m × 0.25 mm × 0.25 μm. Data analyses were performed using Chemstation® software. This method was appropriate for determining overall conversion to oligomer, for tracking any potential isomerization in monomer, and for confirming broad isomer distributions in dimer.

Synthesis of 2-octyl-1-decene. In a round-bottomed flask, 105.5 g of tri-n-octyl aluminum, 1364.3 g of 1-octene, and 733.1 g of 1-decene were combined. The mixture was heated and stirred under nitrogen at 120 °C for 9.7 days, then was quenched at 80 °C with 500 ml of aqueous NaOH (25 wt %). By GC/FID, the organic phase was 10.8 wt % octenes, 6.2 wt % decenes, 39.2 wt % hexadecenes, 35.6 wt % octadecenes, and 8.3 wt % eicocenes; the C16 and C18 fractions were about 95% vinylidene : 5% internals. The 2-octyl-1-decene was isolated by vacuum distillation.

Synthesis of 7-methyl-4/5-undecenes. This mixture was prepared by dimerization of 1-hexene (Chevron Phillips Chemical Company, The Woodlands, TX USA), according to procedures described previously.[10] Hydrogenation of the product mixture[11] showed the C12 paraffinic product to be 65% 5-methyl undecane and 30% n-dodecane. Double bond placement[12] in the dodecenes showed that 45% of the double bonds were between C4 and C5, while 55% were between C5 and C6. The mixture was therefore about 29 wt % 7-methyl-4-undecenes, 36 wt % 7-methyl-5-undecenes, 15 wt % 4-dodecenes, and 15 wt % 5-dodecenes, with 5% other C12 isomers.

Computer model. Original source code for the computer model was written using the Delphi® XE Windows® development environment from Embarcadero (San Francisco, CA USA).

RESULTS AND DISCUSSION

We conducted a number of small-scale reactions using $AlCl_3$ or $AlBr_3$, along with trace water or 1-butanol, to oligomerize several different olefin monomers. Mixtures of 1-decene dimers appeared to contain the same products, regardless of whether we used aluminum halide or BF_3 as the dimerization catalyst. We chose solid aluminum halides for our work, because solid catalysts were easier to use than gaseous BF_3 on a small scale. (We did not have to regulate pressure.) NMR data indicated that decene dimers made using aluminum halide had 3.7 methyl groups per molecule, in close agreement with 3.8 methyl groups reported for decene dimers made using BF_3,[1–5] and decene dimers from either BF_3 or aluminum halide catalysis, gave the same peaks (but not the same relative peak heights) in standard proton decoupled ^{13}C NMR spectra. We therefore expect that BF_3 and aluminum halides oligomerize 1-decene by common mechanisms. Reactions were batch (not continuous) and allowed us to sample reaction mixtures at a number of reaction times and levels of monomer conversion.

Reactions with 1-decene were instructive. Figure 2 shows chromatograms of the C20 olefin fractions at 47% and 75% conversion during a representative 1-decene oligomerization. A large number of C20 isomers are detectable in both samples, and both chromatograms appear to show similar peaks for the C20 products. At 47% conversion, 93% of the unconverted

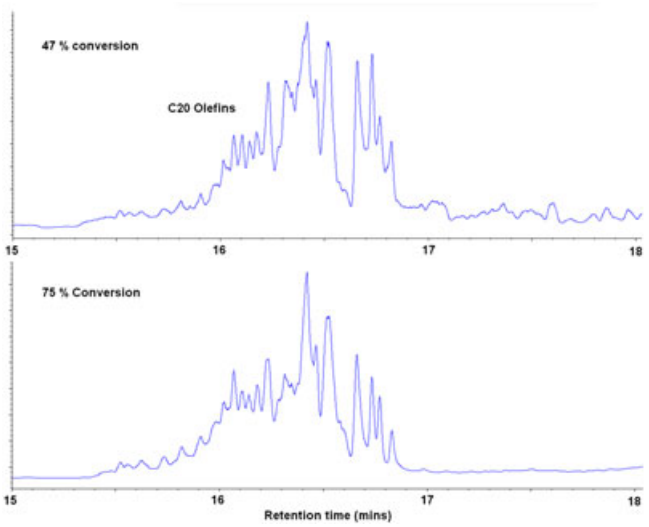

Figure 2. Gas chromatograms showing peaks for C20 olefin isomers at 47% and 75% conversion during 1-decene oligomerization

decene was still 1-decene; at 75% conversion, 65–70% of the unconverted decene was still 1-decene. If rapid double bond isomerization in the decene fraction is necessary to form many different C20 isomers, then we would expect to see substantial double bond isomerization in the decene fraction early in the oligomerization process, but we do not.

Table 1 shows the distribution of olefin isomers in the decene fraction recovered from a reaction mixture having 75% decene conversion to oligomer. We used a previously reported analytical method[12] to determine this distribution. The double bond is clearly moving in a stepwise manner toward the internal positions, as 2-decene makes up almost half of the internal olefin. Table 1 also shows data for the distribution of decene isomers recovered from a typical BF_3-catalyzed oligomerization. We draw similar conclusions from both samples: Double bond isomerization in the decene fraction is clearly slow, relative to oligomerization, and skeletal isomerization has not occurred in the monomer fraction.

If 1-decene isomerized to internal olefins that oligomerized faster than 1-decene, we might not detect the internal decenes. However, we have observed that a mixture of internal decenes oligomerizes at a much slower rate than 1-decene, in agreement with previous reports.[4] We isomerized 1-decene to a mixture of linear internal decenes on a silicoaluminophosphate (SAPO) catalyst.[11] This mixture required 18 h to achieve 44% conversion to oligomer, while 1-decene achieved 72% conversion in about half an hour, under the same oligomerization conditions. Furthermore, in a competitive oligomerization with 1-tetradecene, internal decenes were less reactive than the alpha olefin. We began with a mixture of 50 mole % internal decenes and 50

Table 1. Double bond positions in residual decenes

Decene isomer	AlX_3 catalysis	BF_3 catalysis
1-decene	69.0%	76.3%
2-decenes	15.0%	9.4%
3-decenes	6.1%	5.4%
4-decenes	7.0%	5.4%
5-decenes	2.9%	3.4%

Journal of Physical Organic Chemistry

mole % 1-tetradecene. When 39% of the C14 monomer had converted to oligomers, only 24% of the C10 monomer had converted to oligomers. Extensive skeletal isomerization in the dimer fraction does not require extensive double bond isomerization in the monomer.

Skeletal rearrangements evidently do not occur in the monomer, but some type of rapid isomerization clearly occurs during formation of dimer. There must be a rearrangement mechanism open to the dimer that is not open to the monomer. The original Shubkin mechanism (Fig. 3) proposes a protonated cyclopropyl intermediate that can open to a tertiary carbenium ion. Rearrangement to this tertiary carbenium ion may be favorable, but one such isomerization does not immediately explain the steps involved in producing fifty or more C20 isomers, as there appears to be no clear reason why the tertiary carbenium ion in Fig. 3 would continue to isomerize to other carbenium ions faster than it would either eliminate a proton to form olefin or react with 1-decene to make trimer. Moreover, if this tertiary carbenium ion did react with 1-decene to make trimer, the trimer would contain a quaternary carbon, which is not observed in the product mixtures.[5]

We subjected 2-octyl-1-decene to oligomerization conditions with $AlBr_3$. This olefin should form a tertiary carbocation immediately upon contact with catalyst. While we observed double bond isomerization and oligomerization in this reaction mixture, the monomer showed no evidence of skeletal isomerization. Formation of a tertiary carbenium ion evidently did not immediately lead to extensive skeletal isomerization in the monomer.

To model Structure I in Figs. 1 and 3, we prepared a mixture containing about 29 wt % 7-methyl-4-undecenes, 36 wt % 7-methyl-5-undecenes, 15 wt % 4-dodecenes, and 15 wt % 5-dodecenes, with 5% other C12 isomers. Under oligomerization conditions, half the 7-methyl-5-undecenes and half the 7-methyl-4-undecenes (~32% of total monomer) should immediately generate carbocations with methyl groups two carbons away from the centers of positive charge (Fig. 4). If Structure I represents the first intermediate along the route to skeletal rearrangement in the PAO dimer fractions, then this C12 monomer should undergo skeletal rearrangement under oligomerization conditions. It did not. In a competing oligomerization with linear internal decenes, these C12 isomers formed oligomers at a rate comparable to that of internal decenes, but the C12 isomers underwent no observed skeletal isomerization. Figure 5 shows the gas chromatograms for the C12 isomers before and after treatment with $AlBr_3$ for several hours. These observations argue that Structure I in Figs. 1 and 3 does not undergo skeletal isomerization during PAO synthesis. Figure 6 summarizes our findings regarding which types of carbocations do not appear to skeletally isomerize in PAO synthesis.

We propose that 2-decyl carbocation combines with 1-decene to form a protonated cyclopropyl intermediate directly and that Structure I in Figs. 1 and 3 is not an intermediate in the formation of the protonated cyclopropyl intermediate. At least one previous report has suggested a similar interaction between olefins and carbocations,[13] but we are unaware of previous reports of rapid, multiple skeletal isomerizations from such intermediates. Examples of cyclopropanation reactions are known[14] but do not appear to occur by direct interaction of a carbocation with an olefin.

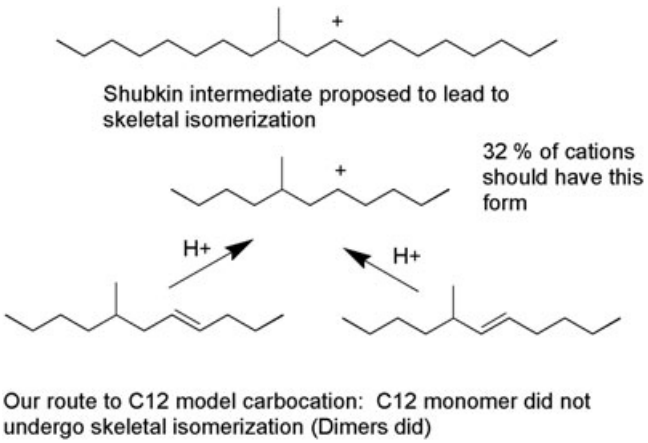

Figure 4. Comparison of Shubkin's proposed C20 intermediate with C12 carbocation expected to form from methyl undecenes

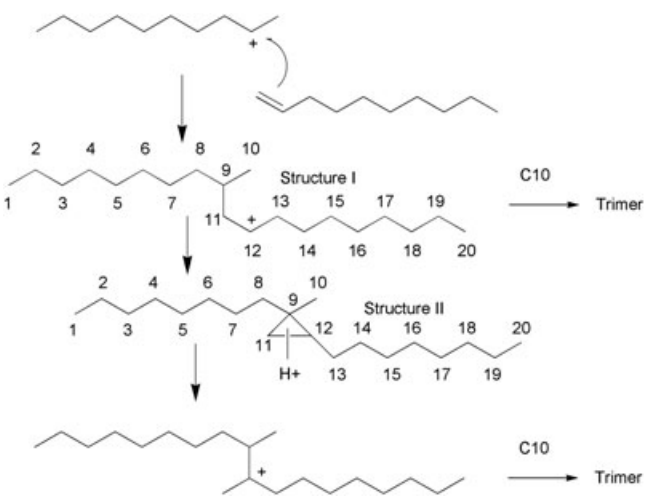

Figure 3. Shubkin mechanism showing protonated cyclopropyl intermediate

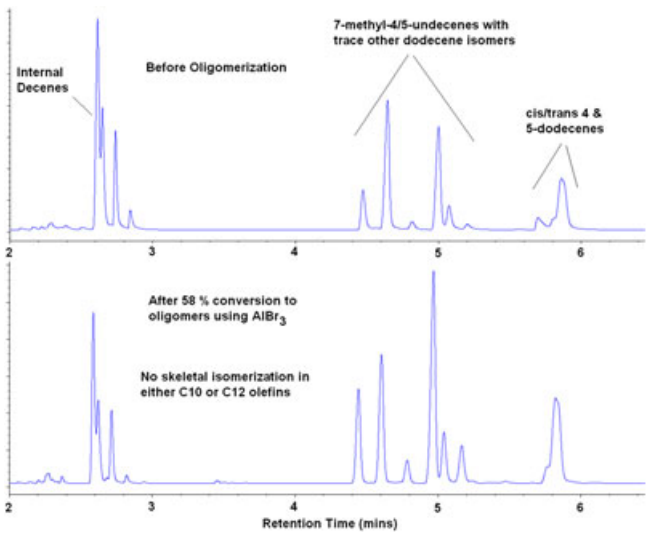

Figure 5. Gas chromatograms of C10 and C12 olefins before and after treatment with $AlBr_3$ for oligomerization

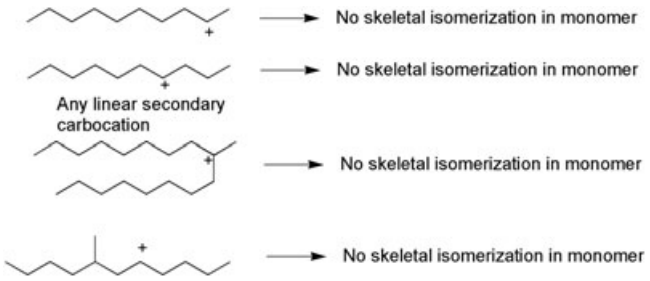

Figure 6. Carbocations that do not skeletally isomerize during PAO synthesis

There is precedent to support the proposal that a protonated cyclopropyl intermediate can undergo rapid skeletal isomerization and thus lead to the multiple skeletal isomers observed in PAO synthesis. We recently reported observations on the double bond and skeletal isomerization of linear olefins on a SAPO catalyst.[11] On this catalyst, double bonds migrated in a step-wise manner. Additionally, skeletal isomerization to methyl substituted olefins occurred, presumably through a protonated cyclopropyl intermediate.[15–20] During skeletal isomerization, the methyl groups formed at nearly random positions along the carbon chain, regardless of the double bond location in the starting olefin, and the catalyst was inactive towards linear alkanes under the conditions of our experiments. We concluded that the intermediate protonated cyclopropyl intermediate isomerized extremely rapidly (and repeatedly), essentially to an equilibrium distribution of cyclic isomers, before it opened to form the methyl substituted product. If this protonated cyclopropyl intermediate isomerizes extremely rapidly, then perhaps the protonated cyclopropyl intermediate proposed by Shubkin in PAO synthesis isomerizes in a similar fashion. If it does, then we can predict what structures should form from such a mechanism.

Figure 3 shows the initial steps of Shubkin's proposed mechanism and the first protonated cyclopropyl intermediate (Structure II). Our data in Fig. 5 demonstrate that the mechanism shown in Fig. 3 is not entirely correct: Structure I in Fig. 3 apparently does not lead to skeletal isomerization in the dimer. However, protonated cyclopropyl intermediates are broadly accepted as intermediates during skeletal isomerization, and we propose that Structure II in Fig. 3 forms directly from combination of 2-decyl carbocation and 1-decene. Previous observations regarding skeletal isomerization of linear olefins[11] suggest that carbons alpha to the ring in Structure II/Fig. 3, such as carbons 8, 10, and 13, can form new cyclopropyl rings by binding with either of the two carbons on the opposite side of the cyclopropyl ring. This type of binding is consistent with the observations long reported for the interactions of a cyclopropane ring with an alpha carbon,[21–27] and isotopic scrambling experiments[28,29] show that such interchanges are rapid for a sec-butyl cation. Indeed, there are numerous reports of rapid migrations involving three-membered rings within cyclic systems,[30–35] and the skeletal isomerization route we are proposing for PAO may simply be an extension of these transformations to intermediates that do not have a large ring system. The well-known investigations of the 2-norbornyl cation[36–40] also demonstrate the stabilizing effects of corner-protonated cyclopropyl species.

Structure II/Fig. 3 therefore has six different modes for extremely rapid isomerization to a new cyclopropyl intermediate:

1. Carbon 8 binds with carbon 11
2. Carbon 8 binds with carbon 12
3. Carbon 10 binds with carbon 11
4. Carbon 10 binds with carbon 12
5. Carbon 13 binds with carbon 9
6. Carbon 13 binds with carbon 11

Each of these options appears to be a concerted step akin to an S_N2 reaction, in which the alpha carbon acts as a nucleophile and a protonated corner carbon acts as a leaving group.

Figure 7 shows our proposed mechanism for the origin of skeletal isomerization in PAO synthesis. A protonated cyclopropyl intermediate forms and then begins rapid isomerizations. These isomerizations may not all be equally fast: Route 1 above may be faster than route 2, for example, if binding with a secondary ring carbon is faster than binding with a tertiary ring carbon. In fact, constraints of the zeolitic cage in the SAPO catalyst prevent isomerizations that would result in alkyl branches larger than a methyl group, so all isomerization steps on the SAPO catalyst involve a secondary ring carbon. We assume this constraint does not apply to the current homogeneous reaction. (Following this mechanism, internal decene monomers cannot form protonated cyclopropyl intermediates having methylene carbons in the rings, but internal olefins still show extensive skeletal isomerization at the dimer stage.)

The intermediates in Fig. 7 can then either isomerize again, react directly with monomer to make trimer, or they can open to form carbenium ions that eliminate a proton to form C20 olefins. Rings that open have three different bonds that can break, so on first thought, each cyclopropyl intermediate appears capable of forming up to three different skeletal isomers. However, our previously reported SAPO observations[11] suggest that some ring opening mechanisms are much more likely than others.

Figure 8 shows a typical protonated cyclopropyl intermediate expected to form during the skeletal isomerization of a linear olefin on a SAPO or other solid acid catalyst. We think the

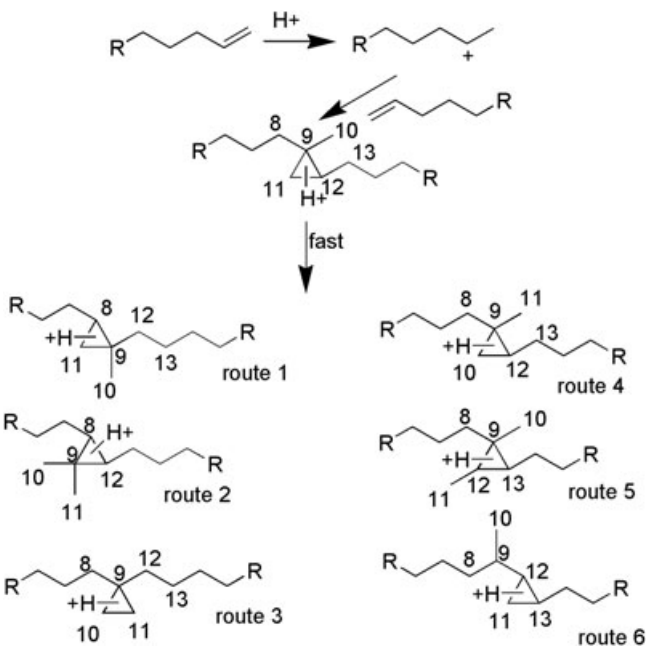

Figure 7. Proposed rapid isomerization of protonated cyclopropyl intermediates

Journal of Physical Organic Chemistry

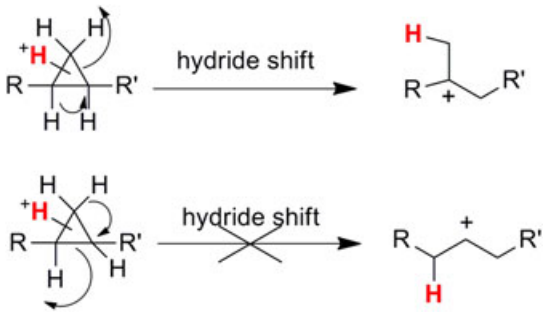

Figure 8. Ring opening mechanism for skeletal isomerization of linear olefins observed on SAPO catalyst (Tertiary carbenium ion highly preferred)

intermediates in our previous experiments opened by 1,2 hydride shifts that led always (or almost always) to a tertiary rather than a secondary carbenium ion. The acidic proton associated with such cyclopropyl intermediates appears to protonate either edge-wise[16,18] on one of the carbon–carbon bonds or on a corner carbon[19,20] of the ring and is rapidly mobile. Calculations have indicated that corner-protonated species are slightly more stable than edge-protonated species and that proton migration occurs rapidly through the edge-protonated intermediate.[41] The carbon–carbon bond that breaks upon ring opening is likely one of the carbon–carbon bonds associated with a protonated corner carbon. If the rapidly migrating rings opened to secondary carbenium ions, then the ring isomerizations could serve as a route to rapid, non-stepwise double bond isomerization, which we did not observe in those experiments. The protonated cyclopropyl intermediates appeared to open only to the tertiary carbenium ions shown in Fig. 8; opening to the secondary carbenium ion apparently did not occur. We therefore think that ring openings for intermediates like those in Fig. 7 should follow routes like those shown in Fig. 9.

We think trimer likely forms by direct reaction between 1-decene and a protonated cyclopropyl intermediate. Our proposed mechanism requires that the protonated cyclopropyl intermediates open to tertiary carbenium ions. If 1-decene reacted with a tertiary carbenium ion in a propagation step, a quaternary carbon would result in the product, and NMR analyses have not revealed quaternary carbons in PAO samples.[5] Direct reaction of 1-decene with a protonated cyclopropyl intermediate, however, permits the formation of trimer molecules without quaternary carbons (See Fig. 10).

Explaining the mechanism of propagation beyond the trimer stage is problematic. If propagation continued via the simple cationic mechanism, there would be no further skeletal isomerization in the growing chain, consistent with actual NMR data reported for samples of trimer and tetramer.[1] This observation argues that carbocations at the trimer stage do not combine with monomer directly to make protonated cyclopropyl intermediates that introduce additional methyl groups. We have no satisfactory explanation for this behavior, except to suggest that the branched structures formed at the dimerization stage sterically inhibit direct formation of another protonated cyclopropyl intermediate.

We constructed a computer model to predict the structures of C20 isomers expected after a number of repeated isomerizations of Structure II in Fig. 3. The model started with 3000[42] intermediates like Structure II/Fig. 3. For each "molecule," the computer selected a random, allowed mode of isomerization and

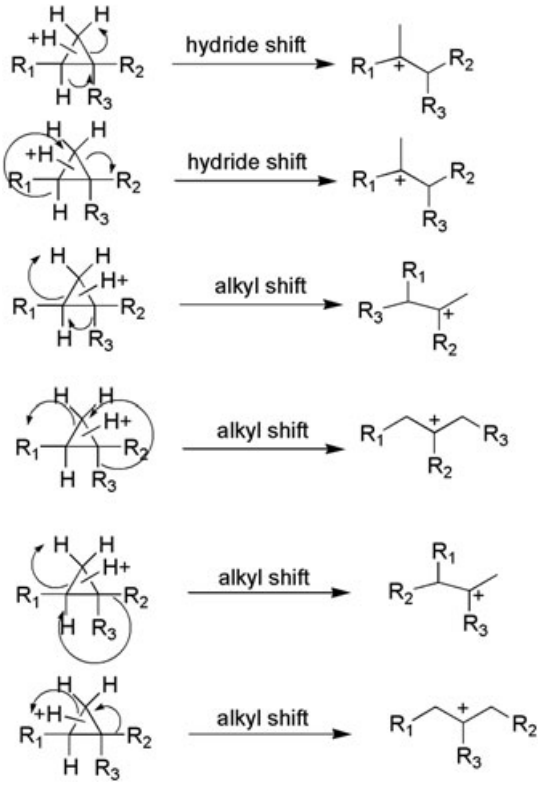

Figure 9. Expected ring opening mechanisms allowed during PAO synthesis

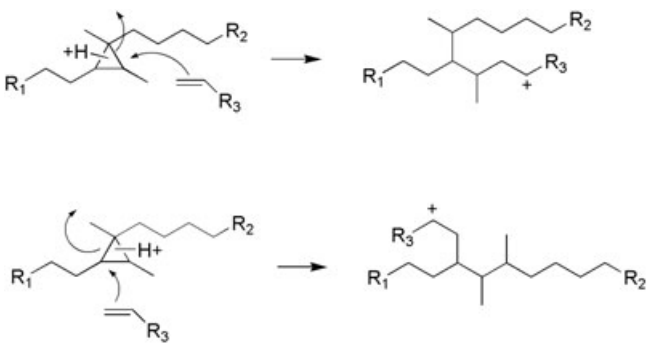

Figure 10. Direct reaction of protonated cyclopropyl intermediate with monomer

Table 2. Simulation results for random isomerizations of Structure II/Fig. 3

# Isomerizations	# C20 Isomers	% as Vicinal dimethyl
1	11	36.3
2	23	33.6
3	44	30.9
4	63	27.6
5	85	24.9
10	189	14.6
25	368	6.4
50	463	3.6

replaced the starting structure with the resulting new one. (In this approach, all isomerizations were equally probable, which may not reflect reality.) We could repeat this process any desired number of times, thus simulating different rates of isomerization. At the end of all the isomerizations, the computer selected a random, allowed mode of ring opening for each cyclopropyl intermediate. The resulting carbenium ion eliminated a proton to give an olefin that, upon hydrogenation, gave the observed C20 paraffin.

Table 2 shows the number of skeletal isomers predicted for a number of different random isomerizations per cyclopropyl intermediate. The number of isomers listed does not include stereoisomers. GC/MS data have been consistent with the presence of resolvable diasteromers,[6] and we could add R and S options for each asymmetric carbon present in these structures, thus increasing the actual number of unique structures that one might detect in a detailed chromatographic analysis.

Table 3. Product distribution predicted for three random isomerizations of Structure II/Figure 3

					One possible route for new C–C bonds at each ring isomerization		
Rank	Isomer type	Main chain	%	Running total	Step 1	Step 2	Step 3
1	9,10-Dimethyl	Octadecane	21.7	21.7	13 to 11	11 to 9	12 to 10
2	8,9-Dimethyl	Octadecane	8.8	30.5	12 to 8	10 to 8	9 to 7
3	9-Isopropyl	Heptadecane	8.5	39.0	11 to 10	12 to 10	12 to 11
4	8,10-Dimethyl	Octadecane	7.3	46.3	12 to 10	12 to 11	13 to 11
5	8-Ethyl-9-Methyl	Heptadecane	6.0	52.3	13 to 9	12 to 10	13 to 12
6	8-(2-Methylpropyl)	Hexadecane	5.8	58.1	12 to 8	13 to 9	14 to 12
7	10-Methyl	Nonadecane	5.6	63.8	12 to 8	11 to 8	11 to 10
8	9-Ethyl	Octadecane	5.4	69.2	13 to 9	12 to 10	11 to 9
9	9-Methyl	Nonadecane	5.0	74.2	11 to 8	12 to 11	11 to 10
10	9-Ethyl-8-Methyl	Heptadecane	4.7	78.9	13 to 9	13 to 10	14 to 9
11	8-Isopropyl	Heptadecane	4.5	83.4	12 to 10	11 to 10	10 to 8
12	7,10-Dimethyl	Octadecane	2.4	85.8	13 to 11	14 to 12	15 to 13
13	7-Ethyl-9-Methyl	Heptadecane	2.1	87.9	13 to 9	14 to 9	15 to 13
14	7,9-Dimethyl	Octadecane	1.5	89.4	12 to 8	11 to 8	11 to 7
15	8-Methyl-7-Propyl	Hexadecane	1.1	90.5	13 to 11	14 to 12	14 to 9
16	7-(3-Pentyl)	Pentadecane	1.0	91.5	13 to 9	13 to 10	14 to 9
17	7-Ethyl-8-Methyl	Heptadecane	1.0	92.5	11 to 8	9 to 7	9 to 6
18	7-(2-Butyl)	Hexadecane	0.8	93.4	11 to 10	10 to 8	9 to 7
19	7-Methyl-8-Propyl	Hexadecane	0.8	94.2	12 to 10	13 to 9	14 to 9
20	6-Ethyl-9-Methyl	Heptadecane	0.7	94.9	13 to 11	14 to 11	15 to 13
21	9-Propyl	Heptadecane	0.7	95.6	13 to 11	13 to 9	13 to 10
22	6,10-Dimethyl	Octadecane	0.6	96.1	13 to 11	14 to 11	15 to 11
23	8-Ethyl-7-Methyl	Heptadecane	0.5	96.6	11 to 8	11 to 7	9 to 7
24	8-(3-Methylbutyl)	Pentadecane	0.4	97.0	12 to 8	12 to 7	13 to 7
25	7-Isopropyl	Heptadecane	0.3	97.4	11 to 8	12 to 8	9 to 7
26	7,8-Dimethyl	Octadecane	0.3	97.7	11 to 8	12 to 8	9 to 7
27	9-Ethyl-7-Methyl	Heptadecane	0.3	97.9	13 to 9	13 to 10	14 to 10
28	8-Methyl-6-Propyl	Hexadecane	0.2	98.2	13 to 11	14 to 12	15 to 12
29	7,8-Diethyl	Hexadecane	0.2	98.4	13 to 9	13 to 10	14 to 9
30	6-Ethyl-8-Methyl	Heptadecane	0.2	98.6	11 to 8	9 to 7	8 to 6
31	8-Ethyl	Octadecane	0.2	98.8	11 to 8	9 to 7	10 to 7
32	6-Butyl-7-Methyl	Pentadecane	0.2	99.0	13 to 9	14 to 9	15 to 9
33	7-Butyl -6-Methyl	Pentadecane	0.1	99.1	13 to 9	14 to 9	15to 9
34	6-(3-Methylbutyl)	Pentadecane	0.1	99.2	12 to 8	12 to 7	12 to 6
35	8-Propyl	Heptadecane	0.1	99.4	11 to 8	9 to 7	10 to 7
36	6,9-Dimethyl	Octadecane	0.1	99.5	11 to 8	11 to 7	11 to 6
37	6-(2-Methylpropyl)	Hexadecane	0.1	99.6	12 to 8	12 to 7	8 to 6
38	8-Butyl	Hexadecane	0.1	99.7	13 to 9	14 to 9	14 to 10
39	6,7-Dimethyl	Octadecane	0.1	99.8	12 to 8	9 to 7	9 to 6
40	6-Isopropyl	Heptadecane	0.1	99.9	12 to 8	9 to 7	9 to 6
41	6-Methyl-7-Propyl	Hexadecane	0.0	99.9	11 to 8	9 to 7	9 to 6
42	5-Methyl-6-Pentyl	Tetradecane	0.0	99.9	13 to 9	14 to 9	15 to 9
43	9-Methyl -8-Propyl	Hexadecane	0.0	100.0	13 to 9	14 to 9	14 to 8
44	8-Methyl-9-Propyl	Hexadecane	0.0	100.0	13 to 9	14 to 9	13 to 8
45	6-(2-Hexyl)	Tetradecane	0.0	100.0	13 to 9	14 to 9	15 to 9

Journal of Physical Organic Chemistry

Table 2 also shows the percent of products that were vicinal dimethyl octadecanes. Previous investigators have reported that up to about 30% of the C20 products could be vicinal dimethyl octadecanes.[6] If that report be correct, then about three isomerizations per intermediate would be enough to account for the level of vicinal dimethyl octadecanes and the presence of more than 40 skeletal isomers. In our SAPO work on skeletal isomerization of linear olefins, the rings appeared to isomerize fast enough to yield equal populations of nine different cyclic intermediates before opening to a methyl substituted chain: We observed the isomerization of 11-dococene to nearly equal quantities of 2, 3, 4, and 5+-methyl substituted chains. Our kinetic calculations have shown that the rate of ring isomerization must have been at least 500 times faster than the rate of ring opening to account for this observation.

Table 3 shows a typical product distribution predicted from a simulation that used three random isomerizations for each Structure II in Fig. 3. The model assumes that all the cyclic intermediates open equally fast to form C20 isomers and that they all react equally fast with 1-decene to make trimer. The distribution has many products previously suggested to be present in PAO 2. Noteworthy is the prediction of 9,10-dimethyl octadecane as the product of highest concentration, which previous work has suggested is the structure present in highest quantity.[5,6] Additionally, this product mixture shows an average of 3.7 methyl groups per chain, consistent with NMR data on real samples.[1–5] We note, however, that this distribution contains some structures having isopropyl groups, which previous NMR analyses have failed to detect.[5] The evidence for there being no isopropyl isomers in PAO 2 appears to be the absence of a predicted methyl peak in the ^{13}C NMR spectra of PAO 2 samples. This predicted methyl peak might be overwhelmed by nearby methylene peaks, so the evidence against isopropyl isomers might not be conclusive. If isopropyl isomers are not actually present in PAO 2, some isomerizations we propose may be less likely than others. For example, formation of much isopropyl substituted product would require that carbon 8 in Structure II/Fig. 3 bind with carbon 12 at a similar rate as binding at carbon 11, which might very well be unlikely.

In the event of 1-decene isomerization to 2-decenes, we have the possibility that a 3-decyl carbenium ion reacts with 1-decene to make the cyclic intermediate having an ethyl rather than a methyl substituent on carbon 9 in Structure II/Fig. 3. Simulations showed that products derived from this intermediate were essentially the same as those derived from Structure II, although the predicted distribution of those products was not the same. Double bond isomerization in the monomer therefore appears to affect the possible distribution of dimeric products but not the list of available structures. As an illustration, Fig. 11 shows an example mechanistic route to 7-butyl-6-methyl pentadecane, a structure difficult to explain by other mechanisms.

Table 4 lists products that previous workers have identified in PAO 2.[5,6] We can account for the formation of every one of them using the current mechanism operating on Structure II/

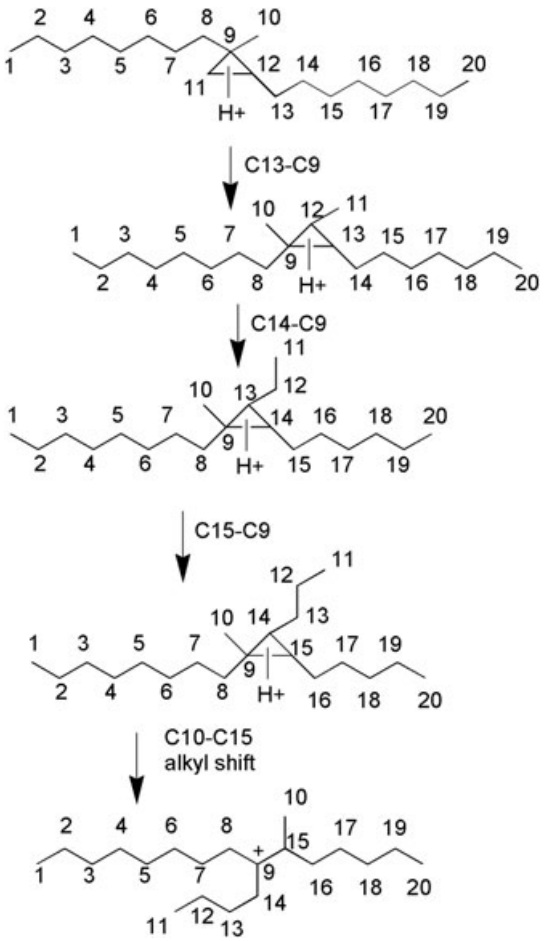

Figure 11. Example mechanistic route to 7-butyl-6-methyl pentadecane

Table 4. Products previously identified in PAO 2 and predicted by proposed mechanism

		Reference #
2,3-dimethyl	Octadecane	6
3,4-dimethyl	Octadecane	6
4,5-dimethyl	Octadecane	6
5,6-dimethyl	Octadecane	6
6,7-dibutyl	Dodecane	6
6,7-dimethyl	Octadecane	6
6-butyl	Hexadecane	6
6-butyl-7-ethyl	Tetradecane	6
6-butyl-7-propyl	Tridecane	6
6-ethyl-7-pentyl	Tridecane	6
6-pentyl-7-propyl	Dodecane	6
7-methyl -6-propyl	Hexadecane	6
7,10-dimethyl	Octadecane	5
7,8-dimethyl	Octadecane	6
7,8-dipropyl	Tetradecane	6
7-butyl-8-methyl	Pentadecane	5
7-propyl	Heptadecane	6
8,10-dimethyl	Octadecane	5
8,9-diethyl	Hexadecane	5
8,9-dimethyl	Octadecane	6
8-ethyl	Octadecane	6
9-ethyl -8-methyl	Heptadecane	5
8-methyl-9-propyl	Hexadecane	5
9,10-dimethyl	Octadecane	5,6
9-methyl	Nonadecane	5,6
butyl (5,7, and 8)	Hexadecanes	6

Table 5. Previously identified octane isomers from butene dimerizations

Products from dimerization of 1-butene and cis-2-butene[2]	Identified in mixture	Quaternary carbon	Predicted by simple mechanism if isobutene forms	Predicted by new proposed mechanism
2,2,4-trimethyl pentane	Yes	Yes	Yes	
2,2-dimethyl hexane	Yes	Yes	Yes	
2,2,3-trimethyl pentane	Yes	Yes	Yes	
3,3-dimethyl hexane	Yes	Yes		
2,3,3-trimethyl pentane	Yes	Yes	Yes	
3-methyl-3-ethyl pentane	Yes	Yes		
3,4-dimethyl hexane	Yes		Yes	Yes
2,3-dimethyl hexane	Yes			Yes
2,4-dimethyl hexane	Yes		Yes	Yes
2-methyl-3-ethyl pentane	Yes			Yes
3-methyl heptanes	Yes		Yes	Yes
4-methyl heptanes	Yes			Yes
2,5-dimethyl hexane	Yes			Yes
2-methyl heptanes	Yes			Yes
2,3,4-trimethyl pentane	Yes		Yes	
3-ethyl hexane				Yes

Fig. 3. The minimum number of random isomerizations required to obtain a distribution that includes all the products listed in Table 4 results in a mixture that has substantially less than 30% vicinal dimethyl products, suggesting that some isomerizations are probably faster than others or that some dimer intermediates react with 1-decene faster than others. Alternatively, low levels of some of these products could result from reactions involving internal decenes.

Onopchenko, *et al*. reported a list of 15 products they identified in the octane fractions isolated after dimerization of 1-butene and of cis-2-butene.[2] Their catalyst was a complex of BF_3 and mannitol, because they were unable to isolate dimer fractions when they used other BF_3 catalysts. They identified six products having quaternary carbons, which they thought had originated after skeletal isomerization of monomer to isobutene. Of the nine remaining products, our proposed mechanism predicts eight of them, and one product predicted by our mechanism is not listed among Onopchenko's products. Our model predicts five identified products that appear to have no other explainable origin (Table 5). The new mechanism predicts that 1-butene and 2-butene should give rise to the same products but not in the same distributions, consistent with Onopchenko's reported results.

CONCLUSIONS

The structures predicted by this model appear to be in accord with the types of structures suggested previously for PAO 2, and the model predicts products previously identified in mixtures of butene dimers and decene dimers. Three repeated isomerizations of the initial protonated cyclopropyl intermediate are enough to generate enough isomers to account for the variety of structures present in the C20 fraction isolated from commercial PAO processes. This rapid isomerization of protonated cyclopropyl intermediates, previously reported for skeletal isomerization of linear olefins, is a possible explanation for the large number of skeletal isomers observed in commercial PAO. This intermediate appears to form directly from combination of 2-decyl carbocation with 1-decene.

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