

Communication

# Methylenealkane-Based Low-Viscosity Ester Oils: Synthesis and Outlook

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**Abstract:** Both Group 4 poly- $\alpha$ -olefin (PAO) and Group 5 ester oil basestocks are used in formulations of synthetic engine oils, transmission fluids, and lubricants with leading characteristics such as low viscosity (providing fuel saving), high stability, and environmental safety. The modern technologies of the production of PAOs use catalytic oligomerization of  $\alpha$ -olefins, which is complicated by the formation of low-molecular-weight  $\alpha$ -olefin dimers (methylenealkanes) as imminent side products. The use of methylenealkanes as raw materials for the synthesis of Group 5 base stocks appears to be highly promising. In the present work, we report the use of methyl 3-butylnonanoate and methyl 3-hexylundecanoate, the products of catalytic methoxycarbonylation of hex-1-ene and oct-1-ene dimers, in the synthesis of two series of branched isomeric esters. These esters demonstrated excellent rheological behavior and may be considered as low-viscosity engine oils with leading characteristics.

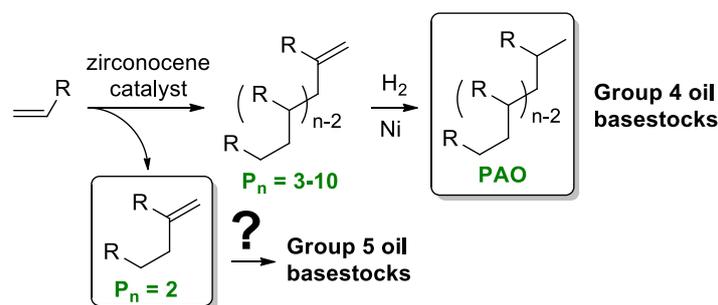
**Keywords:** kinematic viscosity; methoxycarbonylation; methylenealkanes; polyesters; synthetic oils; transesterification

## 1. Introduction

Low-viscosity engine oils, transmission and hydraulic fluids have the potential to substantially increase the energy performance of machines and mechanisms [1–5]. The development of new synthetic approaches to novel types of oils and lubricants with leading characteristics is a relevant task of applied chemistry [6]. The objective requirements for these materials are, in particular, the ability to flow at sub-zero temperatures, maintaining lubrication properties at elevated temperatures, low volatility, as well as high chemical and thermal stability [7]. During the operation of combustion engines, up to half of the motor oil enters the environment, and it is therefore desirable for high-quality oils and lubricants to be biodegradable and non-toxic materials [8].

These actual requirements define two main pathways in the development of the modern oils. The first approach is based on efficient utilization of renewable sources such as vegetable oil, biomass, etc. In this case, the possible imperfection in the product characteristics is compensated by the availability and low price of the raw materials [8–22]. The second approach uses the rational design of the molecular structure of the oil base stocks [23,24]—this is the direction taken by the leading chemical companies in the development of Group 4 poly- $\alpha$ -olefin oils (PAOs). The modern PAOs are hydrogenated  $\alpha$ -olefin oligomers and produced in two stages by metallocene-catalyzed oligomerization of  $\alpha$ -olefins followed by the catalytic hydrogenation of structurally uniform oligomers

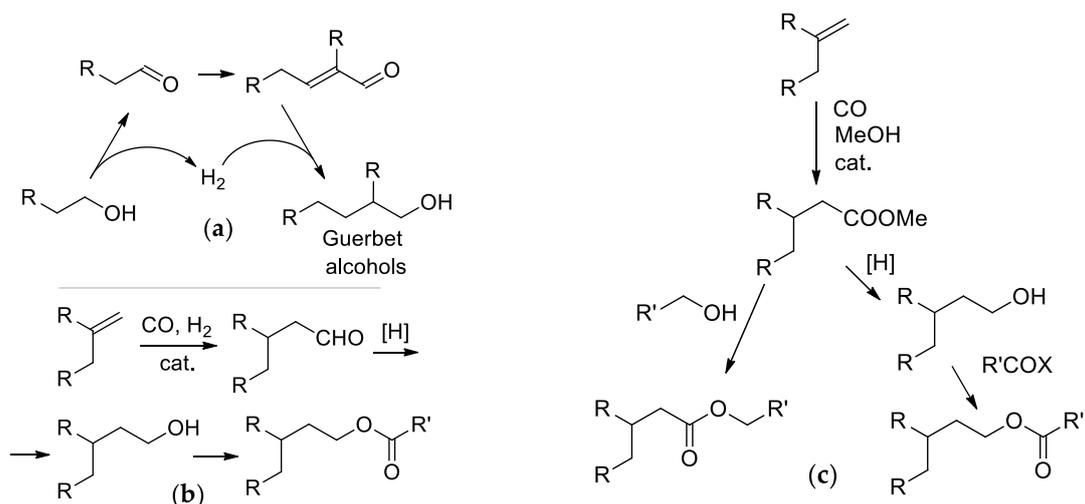
(Scheme 1) [25–31]. However, the first stage of this process is accompanied by the formation of  $\alpha$ -olefin dimers—methylenealkanes [25,32–37]—using a highly efficient heterocene catalyst [31].



**Scheme 1.** The modern synthesis of Group 4 oil basestocks and the problem of methylenealkanes.

Therefore, the problem of the utilization of methylenealkanes that are unavoidable by-products of  $\alpha$ -olefin oligomerization is of great relevance and importance. In view of the fact that high-quality engine oils contain both Group 4 and Group 5 base stocks, the idea of using these methylenealkanes in the production of Group 5 oils is economically attractive.

The branched structure of methylenealkanes offers hope for superior viscosity characteristics of their derivatives, for example, esters. The prospects of structurally-similar Guerbet alcohols in the synthesis of the Group 5 oils have been demonstrated earlier [38–40]. Thus, the synthetic approach to obtain homologs of these alcohols using methylenealkanes seems to be highly prospective, bearing in mind only moderate product yields in the dimerization of 1-alkanols according to a Guerbet reaction [41,42] (Scheme 2a). The synthesis of branched alcohols from methylenealkanes via hydroformylation with subsequent reduction was performed earlier by Patil et al. (Exxon) [43,44] and by Kashiwamura et al. (Idemitsu) [45]. These alcohols were used in the synthesis of branched esters with promising viscosity characteristics (Scheme 2b).



**Scheme 2.** (a) Synthesis of Guerbet alcohols; (b) Hydroformylation of methylenealkanes followed by reduction and esterification [43–45]; (c) Methoxycarbonylation of methylenealkanes followed by preparation of isomeric esters (this work).

Recently [46], we reported an efficient method of catalytic methoxycarbonylation of methylenealkanes with regioselective formation of the corresponding methyl esters (Scheme 2c). In contrast with the hydroformylation/reduction sequence reported earlier [43–45] (Scheme 2b), our approach (Scheme 2c) allows obtaining the esters that contain methylenealkane-derived branched alkyl in acid or in alcohol fragment of the molecule. In that way, we can synthesize isomeric esters in

order to establish the molecular structure that provides the best viscosity characteristics. In the present paper, we report the preliminary results on the synthesis and comparative study of the esters based on 5-methyleneundecane and 7-methylenepentadecane (dimers of hex-1-ene and oct-1-ene) as prospective Group 5 base oils.

## 2. Materials and Methods

### 2.1. General Experimental Remarks

Triisobutylaluminium (TIBA, 1 M solution in hexane, Merck, Kenilworth, NJ, USA), modified methylalumoxane (MMAO-12, 1.52 M solution in toluene, Merck), and  $\text{CDCl}_3$  (99.8%  $^2\text{H}$ , Cambridge Isotope Laboratories Inc., Tewksbury, MA, USA) were used as purchased. Oct-1-ene (Merck) was stored over Na wire and distilled under argon. Toluene and *o*-xylene were refluxed over Na/benzophenone and distilled before use. Methanol (Merck) was dried over CaO and distilled under argon. Hydrogen (99.999%, Linde Gas Rus, Balashikha, Russia) was used without purification.

Diphosphine ligand 2,3-bis((diphenylphosphino)methyl)bicyclo[2.2.1]heptane (*trans*-isomer) [47], 2-ethylhexanoyl chloride [48], 5-methyleneundecane, 7-methylenepentadecane [49] and hydrogenated trimers of oct-1-ene and dec-1-ene [31] were synthesized according to previously reported procedures.

The  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz, Bruker, Billerica, MS, USA) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks. GC analysis was carried out with a Crystallux-4000M chromatograph with a flame ionization detector (Meta-Chrom Ltd, Yoshkar-Ola, Russia). Analysis was carried out using 30,000  $\times$  0.32 mm fused silica columns with stationary phase poly[methyl(95)phenyl(5)] siloxane (film thickness 0.25  $\mu\text{m}$ ) at a carrier gas (argon) flow rate of 1 mL/min, split ratio 1:50, detector and injection port temperature of 300 °C in the isothermal mode of 150 °C. Injection volume was 0.4  $\mu\text{L}$ . The chromatographic peaks of the reactants, isomeric alkenes, and products were identified based on their retention times, and the content of each component was determined by GC of artificial mixtures of known concentrations. Elemental analysis (C, H, N, O) was performed using a Perkin Elmer Series II CHNS/O Analyzer 2400 (Perkin Elmer, Waltham, MA, USA).

### 2.2. Methoxycarbonylation of Methylenealkanes

The diamagnetic steel autoclave with thermostated jacket was equipped with magnetic stirrer and separate CO and  $\text{H}_2$  high-pressure lines. The reaction temperature was monitored by a precalibrated Chromel-Copel thermocouple. A constant temperature was maintained with an accuracy of  $\pm 0.5$  °C by circulating a high-temperature bath fluid (polydimethylsiloxane) through the reactor jacket. The autoclave pressure was measured by a standard pressure gauge attached to the lid. All experiments were carried out with a stirrer rotation speed of 600 rpm.

A mixture of methylenealkane (60 mmol), methanol (3.88 mL, 96 mmol), *o*-xylene (1 mL),  $\text{PdCl}_2$  (0.6 mmol), diphosphine (1.32 mmol) and toluene (added to the total volume of 200 mL) was placed in an autoclave. The autoclave was purged three times with  $5 \times 10^5$  Pa of CO and then pressurized to  $1 \times 10^6$  Pa at room temperature. The autoclave was heated to 115 °C, and the pressure was increased to  $2 \times 10^6$  Pa by CO feed, then to  $2.6 \times 10^6$  Pa by hydrogen feed and finally to  $3.2 \times 10^6$  Pa by CO feed. The constant pressure was maintained by CO feed. After 20 h, the autoclave was cooled to room temperature and vented. The reaction mixture was filtered, evaporated under reduced pressure, and the residue was distilled in vacuo. Boiling points and isolated yields of the esters are given below, while NMR spectra are presented in Supplementary Figures S1 and S2.

Methyl 3-butylnonanoate: B. p. 89–91 °C (1 Torr). The yield was 11.1 g (81%). Elemental Analysis: for  $\text{C}_{14}\text{H}_{28}\text{O}_2$  Calc., %: C, 73.63; H, 12.36; O, 14.01. Found, %: C, 73.69; H, 12.37; O, 13.94.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 20 °C)  $\delta$ : 3.65 (s, 3H); 2.22 (d,  $^3J = 6.8$  Hz, 2H); 1.83 (br, 1H); 1.28 (br, 16H); 0.873 (t,  $^3J = 6.8$  Hz, 3H); 0.867 (t,  $^3J = 6.8$  Hz, 3H).

Methyl 3-hexylundecanoate (E1): B. p. 95–97 °C (0.1 Torr). The yield was 12.9 g (76%). Elemental Analysis: for  $C_{18}H_{36}O_2$  Calc., %: C, 76.00; H, 12.75; O, 11.25. Found, %: C, 76.04; H, 12.80; O, 11.16.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 20 °C)  $\delta$ : 3.65 (s, 3H); 2.23 (d,  $^3J = 6.8$  Hz, 2H); 1.83 (br, 1H); 1.25 (broad, 24H); 0.87 (t,  $^3J = 6.7$  Hz, 6H).

### 2.3. Synthesis of Branched Alcohols and Esters E2–E5

#### 2.3.1. 3-Butylnonan-1-ol

Methyl 3-butylnonanoate (11.4 g, 50 mmol) in  $Et_2O$  (25 mL) was added dropwise to cooled (0 °C) suspension of  $LiAlH_4$  (1.14 g, 30 mmol) in  $Et_2O$  (200 mL). The mixture was allowed warming to room temperature, stirred for 1 h, cooled to 0 °C, and 5% aq. solution of NaF (50 mL) was added. Organic phase was separated, dried over  $MgSO_4$ , evaporated and distilled in vacuo, b.p. 88–90 °C at 0.5 Torr. The yield was 8.2 g (82%), colorless liquid. Elemental analysis: for  $C_{13}H_{28}O$  Calc., %: C, 77.93; H, 14.09; O, 7.99. Found, %: C, 77.90; H, 14.13; O, 7.97.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 20 °C)  $\delta$ : 3.62 (t, 2H); 1.57 (bs, 1H); 1.51 (q, 2H); 1.40 (br, 1H); 1.25 (bs, 16H); 0.87 (t, 6H).

#### 2.3.2. 3-Hexylundecan-1-ol

This compound was obtained by the same manner from methyl 3-hexylundecanoate (14.2 g, 50 mmol). B.p. 120–123 °C at 0.5 Torr. The yield was 10.8 g (84%), colorless liquid. Elemental analysis: for  $C_{17}H_{36}O$  Calc., %: C, 79.61; H, 14.15; O, 6.24. Found, %: C, 79.70; H, 14.18; O, 6.12.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 20 °C)  $\delta$ : 3.64 (t, 2H); 1.62 (br, 1H); 1.51 (q, 2H); 1.40 (br, 1H); 1.24 (bs, 24H); 0.87 (t, 6H).

#### 2.3.3. 3-Butylnonyl 2-ethylhexanoate (E2)

2-Ethylhexanoyl chloride (3.25 g, 20 mmol) was added dropwise at 0 °C to the solution of 3-butylnonan-1-ol (3.73 g, 20 mmol) and pyridine (1.6 mL, 20 mmol) in dry  $CHCl_3$  (50 mL). After 12 h of stirring at room temperature, the mixture was poured into ice water/HCl (50/10 mL), organic phase was separated, aqueous phase was extracted by  $CHCl_3$ . Combined organic fractions were washed by brine, dried over  $MgSO_4$  and evaporated under reduced pressure. The residue was distilled in vacuo, b.p. 130–132 °C at 0.51 Torr. The yield was 5.06 g (81%), colorless liquid. Elemental analysis: for  $C_{21}H_{42}O_2$  Calc., %: C, 77.24; H, 12.96; O, 9.80. Found, %: C, 77.30; H, 12.98; O, 9.72.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 20 °C)  $\delta$ : 4.09 (t, 2H); 2.23 (m, 1H); 1.56 (q, 2H); 1.42 (m, 1H); 1.25 (br, 24H); 0.90–0.85 (gr. t, 12H).

#### 2.3.4. 3-Hexylundecyl 2-ethylhexanoate (E3)

This compound was obtained by the same manner from 3-hexylundecan-1-ol (4.85 g, 20 mmol). B.p. 170–172 °C at 0.5 Torr. The yield was 5.68 g (77%), colorless liquid. Elemental analysis: for  $C_{25}H_{50}O_2$  Calc., %: C, 78.47; H, 13.17; O, 8.36. Found, %: C, 78.50; H, 13.22; O, 8.28.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 20 °C)  $\delta$ : 4.09 (t, 2H); 2.23 (m, 1H); 1.56 (q, 2H); 1.45 (m, 1H); 1.25 (br, 36H); 0.90–0.85 (gr. t, 12H).

#### 2.3.5. Octyl 3-hexylundecanoate (E4)

Sodium methoxide (0.11 g, 2 mmol) was added to stirred mixture of methyl 3-hexylundecanoate (5.4 g, 20 mmol) and octan-1-ol (11.6 g, 100 mmol). After 10 h of heating to 100 °C the mixture was cooled,  $H_2O$  (10 mL) was added. The mixture was extracted by *n*-hexane (520 mL), combined organic fractions were dried over  $MgSO_4$  and evaporated under reduced pressure. The residue was distilled in vacuo, b.p. 175–177 °C at 0.5 Torr. The yield was 4.9 g (66%), colorless liquid. Elemental analysis: for  $C_{25}H_{50}O_2$  Calc., %: C, 78.47; H, 13.17; O, 8.36. Found, %: C, 78.50; H, 13.20; O, 8.30.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 20 °C)  $\delta$ : 4.05 (t, 2H); 2.21 (d, 2H); 1.83 (m, 1H); 1.61 (m, 2H); 1.25 (br, 34H); 0.87 (t, 9H).

### 2.3.6. 2-Ethylhexyl 3-hexylundecanoate (E5)

This compound was obtained by the same manner from methyl 3-hexylundecanoate (5.4 g, 20 mmol) and 2-ethylhexan-1-ol (11.6 g, 100 mmol). B.p. 170–172 °C at 0.5 Torr. The yield was 5.1 g (69%), colorless liquid. Elemental Analysis: for  $C_{25}H_{50}O_2$  Calc., %: C, 78.47; H, 13.17; O, 8.36. Found, %: C, 78.55; H, 13.26; O, 8.19.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 20 °C)  $\delta$ : 3.97 (dd, 2H); 2.22 (d, 2H); 1.83 (m, 1H); 1.55 (m, 1H); 1.25 (br, 32H); 0.90–0.85 (gr. t, 12H).

NMR spectra are presented in Supplementary Figures S3–S8.

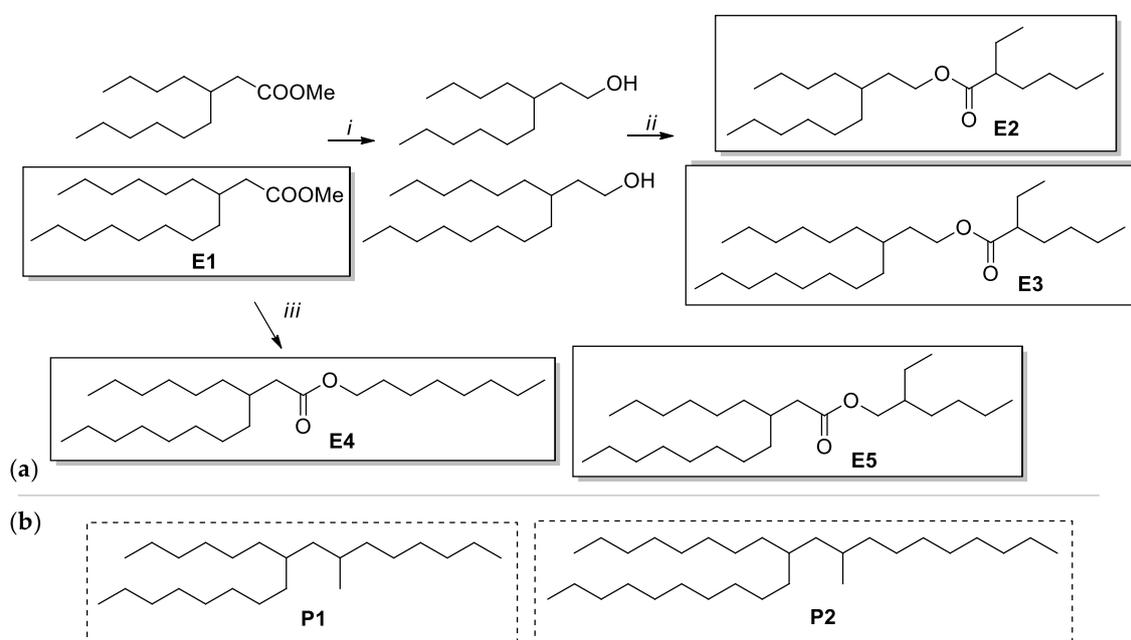
### 2.4. Viscosity Measurements

Viscosity properties of the samples of prospective oil base stocks were studied using rotational rheometer DHR-2 (TA Instruments, New Castle, DE, USA) with cone-plate geometry (cone diameter 40 mm, cone/plate angle 2°). Viscosity–temperature correlations were obtained with the temperature change rate of 5 °C/min and constant shear stresses of 1 and 100 Pa for temperatures above and below 25 °C, respectively.

## 3. Results

### 3.1. Synthesis of Branched Esters

Synthetic routes used for the synthesis of branched alcohols and esters **E1**–**E5** are presented in Scheme 3. The reduction of methyl 3-butylnonanoate and methyl 3-hexylundecanoate resulted in the corresponding branched alcohols with more than 80% isolated yields. Branched esters **E2** and **E3** were obtained by the reaction of these alcohols with 2-ethylhexanoyl chloride. Esters **E4** and **E5** were obtained by transesterification of the methyl ester **E1** with octan-1-ol and 2-ethylhexan-1-ol, respectively. Sodium methoxide was used as a catalyst of transesterification. Branched alcohols and esters **E2**–**E5** were separated by distillation in vacuo without thermal degradation and isomerization.

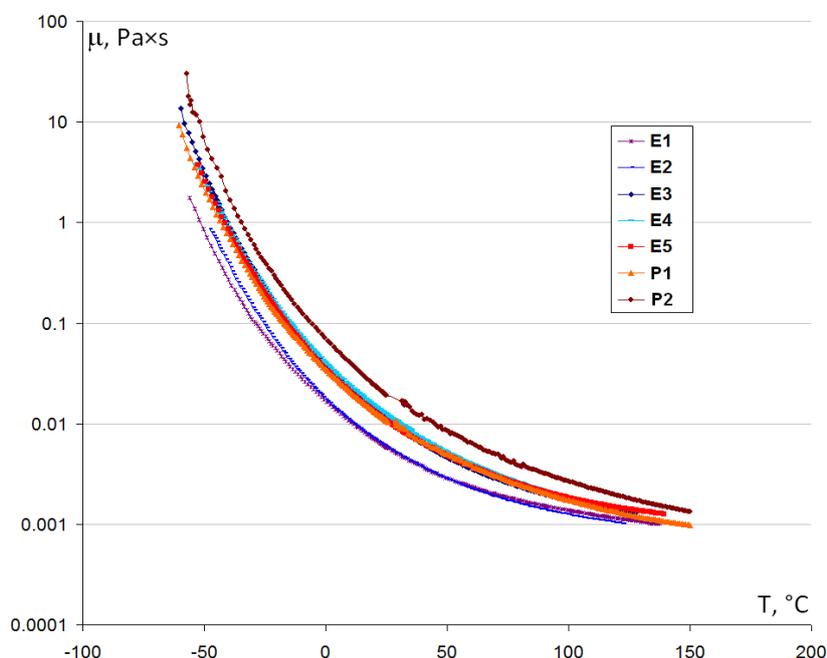


**Scheme 3.** (a) Synthesis of branched alcohols and branched esters, (i)  $LiAlH_4/Et_2O$ , then hydrolysis; (ii) 2-ethylhexanoyl chloride, pyridine,  $CHCl_3$ ; (iii) 1-octanol or 2-ethylhexanol, NaOMe, 100 °C; (b) Low-viscosity PAO basestocks that were used as a benchmark.

### 3.2. Viscosity of Branched Esters

Viscosity of the esters obtained was studied for the compounds **E1–E5** (see Scheme 3, selected by the frames). Methyl 3-butylnonanoate was excluded from our selection as unimportant for lubrication use due to its low viscosity at 100 °C (0.98 cSt). For comparison, we also studied hydrogenated trimers of oct-1-ene and dec-1-ene (**P1** and **P2**, respectively) as Group 4 oil base stocks with close molecular weights.

The viscosity index (VI) is a commonly used characteristic of base oils and lubricants that reflects the abilities of the oil to flow at low temperatures and to keep lubrication properties at elevated temperatures. However, VI is not applicable for low-viscosity oils. In addition, the temperature interval for the determination of VI is 0–100 °C, which does not fully cover the operating temperatures of machineries. The pour point is another characteristic of base oils that is essential for the estimation of their applicability at sub-zero temperatures. Nevertheless, even these two characteristics, supplemented with the data on the viscosity at –40 °C, do not represent the full picture of the viscosity–temperature relationships. In our study, we have measured and analyzed the viscosities of **E1–E5**, **P1** and **P2** in the temperature interval from –60 to 150 °C (Figure 1).



**Figure 1.** The temperature dependence of the dynamic viscosity for **E1–E5**, **P1** and **P2**.

The common empirical temperature–viscosity correlation is a two-parameter exponential known as an Andrade Equation (1) [50].

$$\mu = Ae^{\frac{E_a}{RT}}, \text{ or } \ln \mu = \ln A + \frac{E_a}{RT} \quad (1)$$

where  $\mu$  is dynamic viscosity,  $A$  is an empirical parameter,  $R$  is the gas constant,  $T$  is temperature, and  $E_a$  is a viscosity activation energy.

This Arrhenius-like correlation is not applicable for the temperatures near the glass transition point. Given the importance of the viscosity of base oils at both high and low temperatures, Equation (2) could be proposed.

$$\ln \mu = \frac{T \ln \mu_{T \rightarrow \infty} + \frac{E'_a}{R}}{T - T_{\mu \rightarrow \infty}} \quad (2)$$

This equation is based on assumptions about the constant viscosity at high temperatures ( $T \rightarrow \infty$ ) and infinitely high viscosity ( $\mu \rightarrow \infty$ ) at a low temperature that is close to glass transition point. If  $T \gg T_{\mu \rightarrow \infty}$ , Equation (2) becomes the Andrade Equation (1). The results of the approximations of the experimental data on the thermal dependences of dynamic viscosities of **E1–E5**, **P1** and **P2** by Equation (2) are presented in Table 1. Note that such an approximation was in good agreement with the experimental results ( $R^2 > 0.999$ ).

**Table 1.** The key experimental and calculated (Equations (1) and (2)) characteristics of **E1–E5**, **P1** and **P2**.

Oil Basestock	Dynamic Viscosity, at $T$ (°C), mPa·s				Pour Point, °C	$E_a$ , <sup>1</sup> kJ/mol	$E'_a$ , <sup>2</sup> kJ/mol	$T_{\mu \rightarrow \infty}$ , <sup>2</sup> °C	$\mu_{T \rightarrow \infty}$ , <sup>2</sup> mPa·s
	−40	25	40	100					
<b>E1</b>	267	5.86	3.75	1.38	−58	15.7	17.5	−116.3	0.076
<b>E2</b>	392	5.93	3.67	1.25	−56	17.6	18.4	−114.2	0.056
<b>E3</b>	893	11.5	6.28	1.73	−60	20.7	20.3	−130.4	0.027
<b>E4</b>	910	12.4	7.16	1.88	−53	21.4	20.1	−134.2	0.029
<b>E5</b>	852	10.9	6.41	1.83	−60	20.3	19.2	−125.7	0.045
<b>P1</b>	725	10.7	6.57	1.75	−62	19.1	19.6	−132.6	0.034
<b>P2</b>	1850	19.2	11.7	2.67	−57	21.4	20.0	−129.8	0.041

<sup>1</sup> Based on experimental data for temperature interval 40–120 °C, Equation (1); <sup>2</sup> Calculated parameters of the Equation (2).

#### 4. Discussion

The value of  $\mu_{T \rightarrow \infty}$ , which can be interpreted as a viscosity at the temperature close to the boiling point, correlates to the volatility of the compound under study: it may be assumed that, all other things being equal, the lower this viscosity, the higher the boiling point and therefore the lower the evaporation rate. The pour point of base oils is close to a temperature of their either crystallization or glass transition depending on their nature and ability to crystallize. In the first case, the oils lose their fluidity instantly [51], while in the second one, it happens gradually when the viscosity reaches about 500–1000 Pa·s [52].  $T_{\mu \rightarrow \infty}$  should correlate with glass transition temperature. In our case,  $T_{\mu \rightarrow \infty}$  is far below the pour point; in addition, viscosity at a temperature slightly below the pour point is 1–30 Pa·s. Thus, the loss of fluidity of ester oils and hydrogenated  $\alpha$ -olefin trimers is due to their crystallization. This means that there is potential for lowering the pour point of these oils (down to  $-(80\text{--}100)$  °C) by optimizing their structure or introduction of additives that inhibit crystallization.

A few other important observations and findings could be drawn from the data presented in Table 1. Methyl ester **E1** is characterized by low viscosity at 100 °C and potentially high volatility, and therefore could hardly be regarded as a base stock of the engine oil. The same is true for the derivative of hex-1-ene dimer, 3-butylnonyl 2-ethylhexanoate **E2**: this compound with higher molecular weight in comparison with **E1** is characterized by higher viscosity at  $-40$  °C and lower viscosity at 100 °C. The derivatives of oct-1-ene dimer **E3–E5** seem to be substantially more promising oil base stocks, bearing in mind the characteristics of high-quality Group 4 oil benchmarks **P1** and **P2**. The esters **E3–E5** have equal molecular weight, and the comparison of their viscosity characteristics may allow us to find optimal type of the molecular structure of the promising Group 5 basestock based on  $\alpha$ -olefin dimer.

Among these three esters, compound **E5** has the minimal low-temperature viscosity and satisfactory value of the dynamic viscosity at 100 °C. The efficient viscosity activation energy  $E'_a$  for **E5** was also lowest among the basestocks under study. Taking into account the low value of the pour point, **E5** can be regarded as a prospective prototype for the further design of the formulation of Group 5 ester oils based on by-products of the synthesis of Group 4 poly- $\alpha$ -olefin oils.

The global task of the energy efficiency and saving within the context of the machine's exploitation will require the consideration of both viscosity reduction and oil drain interval extension [5]. Minimization of the environmental pollution should also be taken into account [4]. In this regard, the development of efficient synthetic approaches to Group 5 oil basestocks appears to be a promising area of the advanced applied chemistry. The utilization of  $\alpha$ -olefin dimers, which are by-products of

the modern Group 4 oil technology, with the obtaining of Group 5 oil basestocks that are not inferior in their characteristics to the best PAO oils, seem to us evidence-based and economically beneficial. We therefore hope that the results of our preliminary study could contribute to development of the modern non-waste  $\alpha$ -olefin-based technologies of engine oils and lubricants.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2075-4442/8/5/50/s1>, Figures S1–S8: NMR spectra of the branched esters and alcohols, Tables S1–S7: the data on temperature dependence of dynamic viscosity for E1–E5, P1 and P2.

**Author Contributions:** Conceptualization, I.N., S.I. and P.I.; methodology, S.I.; software, S.I.; validation, S.I. and Alexey V.; formal analysis, S.I.; investigation, V.B., A.V. (Alexander Vinogradov), A.V. (Alexey Vinogradov) and S.I., N.S. and S.B.; resources, S.I.; data curation, S.I.; writing—original draft preparation, P.I.; writing—review and editing, S.I. and P.I.; visualization, P.I.; supervision, I.N.; project administration, A.V. (Alexander Vinogradov); funding acquisition, A.V. (Alexander Vinogradov). All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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