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Adamantane-Containing Esters as Potential Components of Thermostable Lubricating Oils

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Abstract—Some esters of dimethyladamantanedicarboxylic acids with aliphatic alcohols and the ester of dimethyladamantanedicarbinol with an aliphatic acid have been synthesized, and their properties have been studied; their viscosity–temperature properties and thermo-oxidative stability as potential components of high-temperature lubricating oils have been examined .

Keywords: alkyladamantanes, 2,2,4-trimethylpentane, destructive alkylation, alkyladamantane oils, esters, thermostable oils

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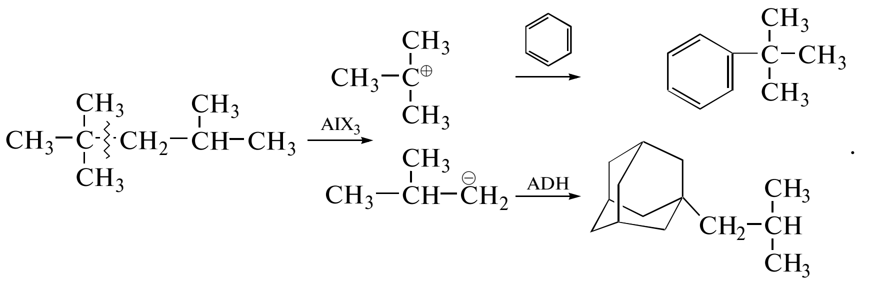
Increasing the power of engine units for modern vehicles or the output of power devices for industrial plants and equipment and simultaneous improving their efficiency, environmental safety, and dimension characteristics require continuous improving the quality of lubricants, first of all, enhancing their thermal and thermo-oxidative stabilities. The mineral oils used for the purpose, which maximum operating temperature is no more than 150°C, do not meet the demands of the current engine building industry for a long time; in this connection, thermostable synthetic oils, based on of organic acid esters with neopentyl alcohol and operable at a temperature of 200–225°C and higher are being under development now.

Among the starting compounds used for manufacturing the basestock of thermally stable lubricants, adamantane derivatives, such as higher alkyladamantanes and esters of adamantanepolyacids or adamantylpolyols, are of considerable interest [1–4]. The starting compounds adamantane and lower alkyladamantanes became quite available substances because numerous methods for their production, including industrial processes, have been worked out. To produce them by isomerization, using petrochemical feedstock (hydrogenated cyclopentadiene and methylcyclopentadiene dimers, the Schleyer method [5]) and coke byproducts (perhydroacenaphthene, perhydrofluorene, the Schneider method [6]). Both aluminum halides [5, 6] and alumina, aluminosilicates, and zeolite-containing materials [7, 8] can be used as catalysts. It is noteworthy that alkyladamantanes with alkyl (methyl and ethyl) groups at the bridgehead positions of the adamantane core are mainly produced in the former case when aluminum halide-based catalysts are used, whereas thermodynamically less stable alkyladamantane isomers bearing the alkyl groups at the secondary carbon atoms form in significant amounts along with the aforementioned compounds on solid alumina and zeolite-containing catalysts.

Higher alkyladamantanes that match oil distillates by molecular mass can be prepared using the known adamantane and lower-alkyladamantanes alkylation methods, which in particular are surveyed in the monograph [9]. One of the methods is based on the destructive adamantane alkylation reaction with isooctane in the presence of aluminum chloride, which was pioneered by E.I. Bagrii et al. [10, 11] and is essentially a version of the known Ipatieff reaction involving adamantane instead of benzene as a substrate. The difference between these versions is that *tert*-butylbenzenes are produced in the case of an aromatic substrate and *iso*-butyladamantanes in the case of adamantanes. This fact suggests that a likely alkylation agent is the carbocationic fragment of the heterolytic degradation of 2,2,4-trimethylpentane (*tert*-butyl cation) for aromatic compounds and the anionic species for adamantanes, i.e., the reaction takes place in situ immediately after the formation of the cations:



However, it should be noted that the same result will be obtained if the alkylation involves isobutylene, which is produced by stabilization of the initially generated anion: owing to the electron-donating effect of two methyl groups, a certain excess electron density concentrates on the methylene group of isobutylene and it is this group that will attacks the adamantantyl cation.

The facts that the reaction proceeds rapidly at a relatively low temperature (45–50°C) and that the products barely contain condensation or polymerization substances support the mechanism in question. However, the mechanism of this interesting reaction demands closer examination to finally elucidate the issue.

When excess isooctane is used, tri- and tetrasubstituted isobutyladamantanes bearing substituents at the tertiary carbon atoms of the core are the main products. In practical application of the reaction, it should be borne in mind that during a longer contact with the catalyst isobutyl groups isomerize to *n*-butyl groups because of a higher thermodynamic stability of *n*-butyladamantanes. It is of alkyladamantanes that the latter property is characteristic [9].

This method based on the destructive alkylation reaction of adamantane with isooctane was used by Podehradska et al [12] to build up pilot batches of triisobutyl- and tetraisobutyladamantane mixtures and to assess their potential use as lubricants. It was concluded that tetraisobutyladamantane oil could be used as cable oil owing to its high electrical insulating properties; whereas triisobutyladamantane oil was not recommended for use in freon compressors because of its insufficient thermal stability.

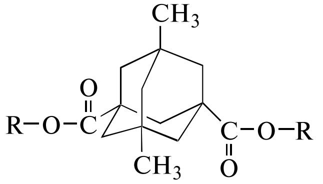
Monoesters of adamantanecarboxylic acids, lauryl alkyladamantanecarboxylates and neopentyl alkyladamantanecarboxylates, were proved to be more stable as well as methyladamantanylcarbinol monoesters (monoalkyladamantanyl)methyl laurates. In [13] one of the authors with coworkers found that monoadamantanecarboxylic acid esters are very effective antiwear additives for lubricant compositions based on polysiloxane fluids. The working capacity of lubricants in ball bearings of low-power micromotors increases owing to these additives. The positive effect is due to the fact that adamantanecarboxylic esters are adsorbed on friction surfaces to form a protective layer that prevents the friction couple from wear, thereby increasing the lubricant service life by a factor of 1.8.

In context of these results, it was interesting to examine closer the influence of the composition and structure of adamantane derivatives on their thermal stability, as well other properties, in relation to their potential use as components of thermostable lubricating oils.

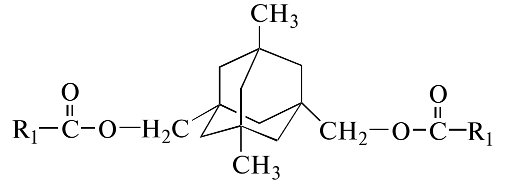
In this paper we report the results of study on the synthesis and properties of some new compounds, namely, diesters of alkyladamantanedicarboxylic acids with aliphatic alcohols and diesters of alkyladamantanedicarbinol with aliphatic acids.

EXPERIMENTAL

In this work the following two types of esters were synthesized and examined:



$R = C_4H_9$ (I); C_5H_{11} (II); C_8H_{17} (III); $C_{16}H_{33}$ (IV)



$R_1 = C_5H_{11}$ (V)

Synthesis of 5,7-Dimethyladamantane-1,3-dicarboxylic Acids (R = H)

The reaction mixture containing sulfuric acid (1000 mL, 94%) and an activator reagent (100 mL) was cooled to 28°C, and 1,3-dimethyladamantane (50 g) was slowly, portionwise added to the mixture. The reaction mixture was vigorously stirred and formic acid (100 mL, 99%) was slowly added dropwise within 2 h, then the mixture was agitated for 3 h at room temperature. The reaction mixture was poured onto ice. The precipitate formed was filtered off, washed with water until the filtrate was neutral, dried in air, and recrystallized from aqueous ethanol. The acid yield was 90% of theory. Mp 270°C. Found (%): C 66.65; H 8.03. Calculated for $C_{14}H_{20}O_4$ (%): C 66.61; H 7.94.

Di-n-butyl-5,7-dimethyladamantane-1,3-dicarboxylate (I)

In a one-neck flask fitted with a Dean–Stark trap and a reflux condenser 5,7-dimethyladamantane-1,3-dicarboxylic acid (20 g, 0.079 mol), benzene (150 mL) and *n*-butanol (12.9 g, 0.174 mol, 16 mL) were suspended, concentrated sulfuric acid (0.37 g, 0.2 mL) was added to the suspension, and the mixture was refluxed 6 h until the calculated amount of water (2.9 mL) was removed. To a benzene solution of the dibutyl ester obtained, a solution of sodium hydroxide (0.3 g, 0.0038 mol) in water (3 mL) was added, the mixture was intensively shaken, and the resulted emulsion was filtered through a layer of alumina of activity grade II ($d = 5$ cm, $h = 2$ cm) followed by elution with another portion of benzene (150 mL). The benzene solution was evaporated to dryness in vacuum, and the oily residue was distilled to isolate the main fraction with bp 126–128°C at 0.2 mmHg, affording 24.9 g (86.2%) of di-*n*-butyl 5,7-dimethyladamantane-1,3-dicarboxylate. $n_D^{20} = 1.4739$, IR spectrum: 1725 cm^{-1} (C=O). Found (%): C 73.2; H 11.7. Calculated for $C_{22}H_{36}O_4$ (%): C 72.5; H 10.0. GLC: 30 m capillary column, SE-30, 250°C (isothermal mode), $t = 460$ s.

Diamyl-5,7-Dimethyladamantane-1,3-Dicarboxylate (II)

Compound II was prepared by analogy with dibutyl ester (I) using amyl alcohol (15.4 g) instead of *n*-butanol. The yield of ester was 21.5 g (71.4%). Bp 139–140°C at 0.15 mmHg. $n_D^{20} = 1.4740$, IR spectrum: 1725 cm^{-1} (C=O). Found (%): C 73.6; H 10.6. Calculated for $C_{24}H_{40}O_4$ (%): C 73.4; H 10.3. GLC: $t = 714$ s.

Diisooctyl-5,7-Dimethyladamantane-1,3-Dicarboxylate (III)

Compound (III) was prepared by analogy with dibutyl ester (I) using isooctyl alcohol (22.7 g) instead of *n*-butanol. The yield of the isooctyl ester was 14 g (37%). Bp 240–246°C at 0.2 mmHg. $n_D^{20} = 1.4823$.

Di-n-Hexadecyl 5,7-Dimethyladamantane-1,3-Dicarboxylate (IV)

Compound IV was prepared by analogy with dibutyl ester (I) using *n*-hexadecyl alcohol (42.3 g), replacing the vacuum distillation stage by molecular sublimation in a sublimator onto a substrate cooled with liquid nitrogen, whereas temperature of a heating bath was 200°C. The yield of the *n*-hexadecyl ester was 24 g (43%). Mp 39°C.

Synthesis of Diester of 5,7-Dimethyl-1,3-Dihydroxymethyladamantane and Isovaleric Acid (V)

(A) **Dimethyl-5,7-dimethyladamantane-1,3-dicarboxylate.** In a one-neck flask fitted with a Dean–Stark trap, unpurified 5,7-dimethyladamantane-1,3-dicarboxylic acid (41 g) prepared as described above was suspended in benzene (0.4 L) and boiled for 2 h to remove the aqueous layer. Methanol (0.1 L) and oleum (0.002 L, 30%) were added and boiled for another 2 h. The solution was cooled, transferred into a separating funnel with the subsequent addition of 0.1 L of a 10% ammonium solution, and shaken; the aqueous layer was separated; the benzene layer was filtered through a Brockmann grade II alumina column ($d = 10$ cm, $h = 2$ cm); and the adsorbent was washed with 0.4 L of benzene. The combined benzene solution was evaporated to dryness in vacuum, the residue was crystallized from hexane, and dried in vacuum, to afford 34.7 g (36% based on starting 1,3-dimethyladamantane) of dimethyl 5,7-dimethyladamantane-1,3-dicarboxylate. Mp 90°C, pure for chromatography.

(B) **5,7-Dimethyl-1,3-dihydroxymethyladamantane.** Lithium aluminum hydride (11.4 g, 0.3 mol) was added within 2 h with vigorous stirring to a solution of dimethyl 5,7-dimethyladamantane-1,3-dicarboxylate (28 g, 0.1 mol) in dry ether (0.5 L) at temperature of +3 to +5°C. The solution was stirred for 3 h at room temperature, then an $AlCl_3$ saturated solution (0.2 L) was slowly added with cooling, the mixture was transferred to a separating funnel, the aqueous layer was separated, and the organic layer was washed with water (0.5 L) and dried with sodium sulfate (0.2 kg). Ether was removed to dryness in vacuum, and the residue was crystallized from *n*-heptane to obtain 20.5 g (91.4%) of 5,7-dimethyl-1,3-dihydroxymethyladamantane, which was used without further purification for preparing the isovaleric acid ester.

(C) **Diester of 5,7-dimethyl-1,3-dihydroxymethyladamantane and isovaleric acid (V).**

A one-neck round-bottom flask of a 1-L capacity was charged with 5,7-dimethyl-1,3-dihydroxymethyladamantane (15 g, 0.067 mol), isovaleric acid (20.5 g, 0.2 mol, 21.8 mL), benzene (150 mL), and toluenesulfonic acid (0.2 g). The mixture was refluxed for 4 h to remove water (2.5 g), cooled, and filtered through a column with Al_2O_3; the alumina cake was washed with benzene (150 mL). The combined benzene solution was evaporated to dryness in vacuum, the oily residue was distilled in vacuum to obtain 16.3 g (61.7%) of 5,7-dimethyldi(1,3-hydroxymethyladamantyl) diisovalerate. Bp 125°C at 0.08 mmHg. $n_D^{20} = 1.4754$. Found (%): C 73.5; H 10.7. Calculated for $C_{24}H_{40}O_4$ (%): C 73.4; H 10.8.

Table 1. ^{1}H NMR spectrum of DAADC (II)

Chemical shift, ppm	Proton quantity	Group number
0.87	12H	all CH_3 groups
1.13	2H	6
1.29	8H	$\gamma + \delta$
1.47	8H	4 + 8 + 9 + 10
1.59	4H	β
1.85	2H	2
4.02	4H	α
7.27		$CHCl_3$

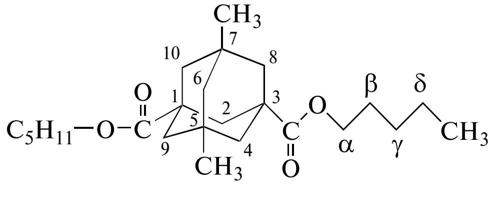
Table 2. ^{13}C NMR spectrum of DAADC (II)

Chemical shift, ppm	Group number
13.72	ε
22.03	δ
27.83 + 28.08	two methyl groups on core
29.73	5 + 7
31.13	$\beta + \gamma$
38.60	1 + 3
42.63	2
44.03	4 + 9
49.60	6
64.18	α
77.03	$CDCl_3$
176.27	COO

The chemicals used were of the analytical grade. Purity of the compounds obtained was controlled by GLC (30-m capillary column, SE-30 stationary phase, 250°C, isothermal mode). The structure of the compounds and their purity were also confirmed by spectral methods (gas chromatography–mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy). The mass spectrum and the NMR spectrum of diamyl 5,7-dimethyladamantane-1,3-dicarboxylate (DAADC) (II) as an example are given below in Tables 1 and 2, respectively. The gas chromatography–mass spectrometry study was performed on a Thermo Focus DSC2 instrument (a Varian VF-5ms capillary column, 30 m length, 0.25 mm inner diameter, 0.25 μm layer thickness, carrier gas helium, injector temperature 270°C) operating in the temperature programming mode from 30 to 30°C at a heating rate of 15°C/min with isothermal holding at the final temperature for 10 min. The mass spectrometer operating mode : ionization energy of 70 eV, source temperature of 230°C, a scan interval from 10 to 800 dalton with a scan rate of 2 scan/s, the unit mass resolution over the entire mass range.

Mass spectrum of compound II: M 392, *m/z* (abundance): 324 (16.56); 323, M-69 (89,84); 277 (38.78); 253 (100.0); 207 (26.78); 189 (22.54); 161 (41.48); 151 (18.39); 107 (21.47); 43 (19.03).

^{1}H NMR spectra were taken on a Bruker MSL-300 spectrometer (Table 1), and ^{13}C NMR spectra on a Bruker Avance-700 spectrometer, a $CDCl_3$ solution, room temperature (Table 2). The numbering of the atoms and group in II is given below:



The kinematic viscosity of the esters was determined at 100°C according to GOST (State Standard) 33-82, and the dynamic viscosity at various temperatures thermo-oxidative stability were measured according to GOST 1928-87 and GOST 23175-74, respectively [14].

RESULTS AND DISCUSSION

The viscosity properties of the adamantane-containing esters synthesized are collated in Table 3 with the known thermostable oil IPM-10, which has a close viscosity value.

As follows from these data, the compounds (samples I and II) are superior to the standard high-temperature oil IPM-10 in viscosity–temperature characteristics. The dynamic viscosity of compound II within the temperature range of +10 to –40°C increases by slightly more than a factor of 3, whereas the viscosity of the standard oil increases by a factor of 30 times; low viscosity values at negative temperatures are particularly attractive. Moreover, the sample exhibits higher thermo-oxidative stability compared with the standard oil.

It is noteworthy that small changes in the structure of the compound (on passing from compound II to compound V) prepared from adamantyl alcohol, di(hydroxymethyl)dimethyladamantane, and aliphatic acid result in sharp alteration in the pattern of change in viscosity properties; non only the absolute value of viscosity increases, but and temperature–viscosity relationship becomes much less favorable. It is interesting to compare the properties of the test compounds obtained with those of ester compounds with a close structure in which the adamantyl core is directly bound with oxygen atom (methylene linker is absent), i.e., esters of adamantanols and aliphatic acids (Table 4). Such compounds were synthesized and studied by Kosaku and Hiromichi [15].

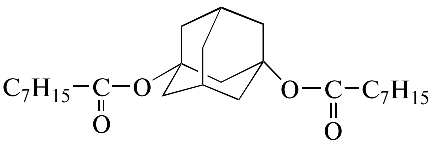
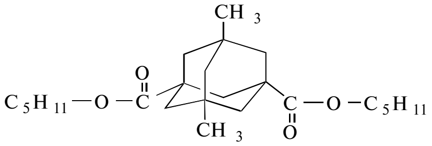
The Japanese investigators have shown that in the series of adamantyl caprylates studied, not only the absolute viscosity value of the substances increases

Table 3. Viscosity-temperature characteristics of adamantane-containing esters

Compound designation	Dynamic viscosity, mPa at *T*, °C							£[2]
	υ[1]	10	0	−10	−20	−30	−40	
I	3.08	64.28	74.02	101.3	229.8	358.4	570.7	14
II	3.61	77.91	91.55	128.5	138.3	206.5	300.2	34
V	5.77	266.8	368.65	590.2	951.0	4733	9525	26
IPM-10	3.16	31.73	51.70	90.7	173.6	397.0	960.4	25

[1] Kinematic viscosity at 100°C, mm^2/s; [2] Thermo-oxidative stability in thin layer, min.

Table 4. Properties of adamantane-containing esters

Compound	Adamantane-1,3-diol dicaprylate [15]	Diamyl-5,7-dimethyladamantane-1,3-dicarboxylate (II)
		
Molecular mass	420	392
Kinematic viscosity at 100°C, mm^2/s	5.57	3.61
DTA data: temperature of exotherm in air, °C	313	302

(with the viscosity index remaining almost unchanged), but their thermo-oxidative stability is also enhanced as the number of ester substituents at the tertiary carbon atoms of the adamantane core increases (from 1 to 3). So, the temperature of the exothermal peak in air for adamantyl mono-, di-, and tricaprylates was 223, 313, and 331, respectively.

Thus, the ester derivatives of adamantane and alkyladamantanes are quite promising as components of thermostable lubricants. It is significant that compounds with a desired viscosity value depending on the task for particular equipment or application area can be prepared by varying the number and nature of substituents, with the thermo-oxidative stability and environmental safety of the oils remaining at a high level. Moreover, the thermo-oxidative properties of such compounds have good prospects for optimization.

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