

Novel Strained Alicyclic Hydrocarbons Based on 5-Methylene-2-norbornene

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Received May 14, 2021; revised June 7, 2021; accepted July 21, 2021

Abstract—The paper describes the synthesis of novel strained hydrocarbons based on a diene of the norbornene series, namely 5-methylene-2-norbornene, using catalytic cyclopropanation with diazomethane. The study demonstrated the possibility of selective cyclopropanation solely along the endocyclic double bond. The physicochemical properties of the hydrocarbons were investigated systematically. These hydrocarbons were shown to have an advantageous combination of high density, low freezing point, and high energy density value. The study's findings indicate that the compounds synthesized are promising as a component of high-energy-density fuels for modern jet engines.

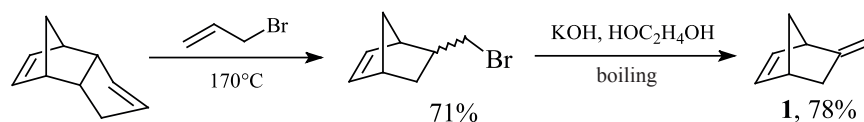
Keywords: high-energy-density fuels, strained hydrocarbons, catalytic cyclopropanation, 5-methylene-2-norbornene

DOI: 10.1134/S0965544121090073

Since the world's first controlled powered flight by the Wright Brothers, aircrafts have been changed dramatically. Modern aerospace vehicles have a limited fuel tank capacity, fly long distances without refueling, and operate at high altitudes at extremely low temperatures. The modernized flying vehicles have accordingly changed the requirements for fuel properties, which have a key influence on an aircraft's flight performance [1–7]. The most important fuel properties are heating value, density, low freezing point, and viscosity. Kerosene of various grades is still the most common aviation fuel. However, aviation kerosene is being gradually replaced by synthetic fuels superior in performance characteristics, specifically a higher density and a higher heating value combined with a lower freezing point. The synthetic fuels consist of alicyclic hydrocarbons, the polycyclic structure of which contributes to the higher density, whereas the strain energy of minor cycles enhances the heating value. Thus, it has become increasingly relevant to develop effective approaches to produce high-energy-density (HED) hydrocarbons, represented both by previously known species and by ones never described before [8–12].

Cyclopropane derivatives have been of interest to researchers for many years due to their unique reactivity. They have been widely used in various fields of organic synthesis and medicinal chemistry. Furthermore, they have served as versatile “building blocks” for the synthesis of large molecules and have proved of significant interest as the base or a component of HED fuels. The introduction of a cyclopropane moiety into a molecule is known to markedly increase its density and volumetric heating value. This, in turn, has a strong influence on an aircraft's engine power. Previously, cyclopropane derivatives with advantageous properties, including density, freezing point, and heating value, were produced from dicyclopentadiene (DCPD) and norbornene [13]. The energy properties of these derivatives were demonstrated to surpass those of JP-10, a commonly used HED fuel based on *exo*-tetrahydrodicyclopentadiene (C₁₀H₁₆). Therefore, it appears relevant to further develop this approach.

Recently, we have described the synthesis and studied the properties of a number of related norbornane-containing hydrocarbons based on 5-vinyl-2-norbornene [14]. Some of these hydrocarbons proved to have significantly better properties than JP-10. With such

Scheme 1. Synthesis of 5-methylene-2-norbornene.

promising results in hand, we have decided to continue research in this area. Accordingly, the presented study describes a method for synthesizing novel strained alicyclic norbornane-type hydrocarbons based on 5-methylene-2-norbornene (MNB) by means of a catalytic cyclopropanation reaction.

MNB is a promising feedstock for the production of synthetic fuels with improved performance. This compound contains two easily-modifiable double bonds with different reactivity. At the same time, the presence of a strained norbornane moiety in MNB will, naturally, improve the heating value of its derivatives. Moreover, MNB is an available compound produced by a Diels–Alder reaction between allyl bromide and cyclopentadiene followed by elimination under basic conditions. MNB has generally been used as a monomer or co-monomer to synthesize various polymers, so research on its transformations has mostly focused on the polymerization aspects [15].

EXPERIMENTAL

All the solvents for this study were purchased from Component-Reaktiv, a Russian company, and were used without pretreatment. The dicyclopentadiene and allyl bromide were purchased from Acros Organics and also used without pretreatment.

NMR spectra were recorded on a Bruker Ascend™ 400 NMR spectrometer. The ^1H signals were assigned on the basis of CDCl_3 residual protons.

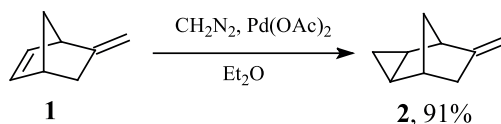
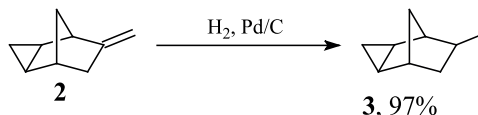
GC/MS analysis was performed using a Thermo Scientific ISQ 7000 chromatography-mass spectrometer equipped with a Thermo TG-SQC 15 m \times 0.25 mm I.D. \times 0.25 μm capillary column with helium as a carrier gas. The operating mode was as follows: injector temperature 300°C; GC thermostat starting temperature 50°C, then a 5-min isotherm and heating to 250°C at a rate of 10 deg/min. The mass spectrometer operating mode was the following: ionization energy 70 eV; ion source temperature 200°C; scanning range 10–700 Da.

The higher heating value of 5-methylene-2-norbornene's cyclopropane derivatives was measured using an IKA C200 calorimeter according to the Russian standard GOST 21261-91 method. The lower heating value was evaluated from the hydrogen weight fraction in pure substance according to GOST 21261-91. The density of the resultant compounds was measured on a VIP-2MR vibration density meter according to GOST R 57037-2016.

Synthesis of Norbornene Derivatives

A mixture of dicyclopentadiene (16 g, 0.12 mol), allyl bromide (35 g, 0.29 mol), and hydroquinone (81 mg, 0.74 mmol) was placed in a 100 mL steel autoclave, heated to 170°C, and held at this temperature for 9 h. 5-Bromomethyl norbornene was isolated from the reaction mixture by vacuum distillation (89–96°C, 20 Torr) with a yield of 71%. The resultant 5-bromomethyl norbornene (32 g, 0.17 mol) and potassium hydroxide (28 g, 0.5 mol) were dissolved under heating in 50 mL of ethylene glycol. The reaction mixture was boiled with a reflux condenser until the complete disappearance of the starting material (under GC control). The target 5-methylene-2-norbornene was isolated from the reaction mixture by vacuum distillation with a yield of 78% (56–58°C, 40 Torr). The MNB spectra agreed with the published data [15] (Scheme 1).

5-Methylene-2-norbornene (1) (5.3 g, 0.05 mol) was dissolved in diethyl ether (15 mL). Then palladium(II) acetate (56 mg, 0.25 mmol, 0.005 eq.) was added, and the solution was cooled to -15°C . An ethereal solution of diazomethane (200 mL), prepared from 18.0 g of *N*-nitroso-*N*-methylurea by the method described in reference [16], was added dropwise to the reaction mixture. The solution was stirred for 2 h at the same temperature, then stirred at room temperature (under GC control) for 24 h. When the reaction was complete, the reaction mixture was filtered through Celite, and the excess solvent was removed in vacuo (Scheme 2).

Scheme 2. Synthesis of monocyclopropanated 5-methylene-2-norbornene.**Scheme 3.** Hydrogenation of monocyclopropanated 2-methylenenorbornane.

Characteristics of resultant monocyclopropanated 2-methylenenorbornane (6-methylenetricyclo[3.2.1.0^{2,4}]octane) (2). Yield 91%, 5.46 g, colorless liquid; ¹H NMR spectrum (400 MHz, CDCl₃): δ, ppm: 0.08–0.15 m (1H), 0.50–0.54 m (1H), 0.77–0.86 m (3H), 1.04–1.06 m (1H), 1.99–2.01 m (3H), 2.10–2.14 m (1H), 2.34–2.37 m (1H), 2.67–2.70 m (1H), 4.61–4.65 m (1H), 4.86–4.89 m (1H). ¹³C NMR spectrum (100 MHz, CDCl₃): δ, ppm: 2.8, 14.3, 15.2, 26.9, 36.1, 38.1, 44.5, 101.9, 155.4. Mass spectrum (EI); *m/z* (*I*, %): 120, [*M*]⁺ (4%); 79, C₆H₇⁺ (100%).

Hydrogenation of Monocyclopropanated 2-Methylenenorbornane

A solution of monocyclopropanated 2-methylenenorbornane (2) (5.4 g, 0.045 mol) in 15 mL of pentane was hydrogenated in the presence of 80 mg of Pd/C (1.5 wt %) at room temperature and a hydrogen pressure of 1 atm. When the reaction was complete, the reaction mixture was filtered through a silica bed, and the excess pentane was removed using a rotary evaporator. The yield of the resultant 6-methylenetricyclo[3.2.1.0^{2,4}]octane (3) was 5.3 g (97%). (Scheme 3).

6-Methylenetricyclo[3.2.1.0^{2,4}]octane (3) is a colorless liquid consisting of a mixture of two isomers. The NMR spectra show the signals of the second isomer in parentheses. ¹H NMR spectrum (400 MHz, CDCl₃): δ, ppm –0.09 to –0.05 m (–0.02–0.00 m) (1H), 0.39–0.42 m (1H), 0.68–0.72 m (0.75–0.81 m) (3H), 0.92–0.99 m (2H), 1.05 (0.91 d (*J*_{HH} = 6.9 Hz]) (*J*_{HH} = 7.0 Hz, 3H), 1.70–1.74 m (1.55–1.58 m) (1H), 1.91–1.95 m (1.62–1.65 m) (1H), 2.06 s (1.89 s) (1H), 2.19 s (1H); ¹³C NMR spectrum (100 MHz, CDCl₃): δ, ppm: 0.8 (2.5), 9.1 (14.86), 14.88 (15.7), 16.8 (21.2), 28.6 (23.3), 36.2 (36.5), 37.1 (36.7),

38.0 (40.0), 40.3 (42.3). Mass spectrum (EI); *m/z* (*I*, %): 122, [*M*]⁺ (2%); 79, C₆H₇⁺ (100%).

RESULTS AND DISCUSSION

The starting 5-methylene-2-norbornene (1) was synthesized in accordance with a relevant two-step method described in published literature. This method involves a Diels–Alder reaction between allyl bromide and cyclopentadiene followed by elimination under basic conditions. As a result, the 5-methylene-2-norbornene (1) was prepared with a good yield of 55% over the two steps.

Knowing that the density and volumetric heating value of hydrocarbons can be enhanced by introducing minor strained cycles (among other techniques), we decided to investigate the catalytic cyclopropanation of 5-methylene-2-norbornene (1) with diazomethane. This reaction, carried out in the presence of palladium(II) acetate, was found to selectively produce monocyclopropanated 2-methylenenorbornane (2) with a nearly quantitative yield. The reaction occurred without the formation of any by-products. Moreover, the reaction involved the norbornene double bond only, whereas the exocyclic double bond remained intact. We believe that the monocyclopropanated product was formed because electron-donating olefins are poor substrates for catalytic cyclopropanation [17].

Given that compound 2 contained a double bond, this compound needed to be hydrogenated because multiple bonds tend to enter into various reactions, thus affecting the stability of such compounds. It turned out that cyclopropanated 2-methylenenorbornane (2) can be selectively hydrogenated in the presence of a Pd/C catalyst at room temperature and under a hydrogen pressure of 1 atm, and that the cyclopropane moiety does not react

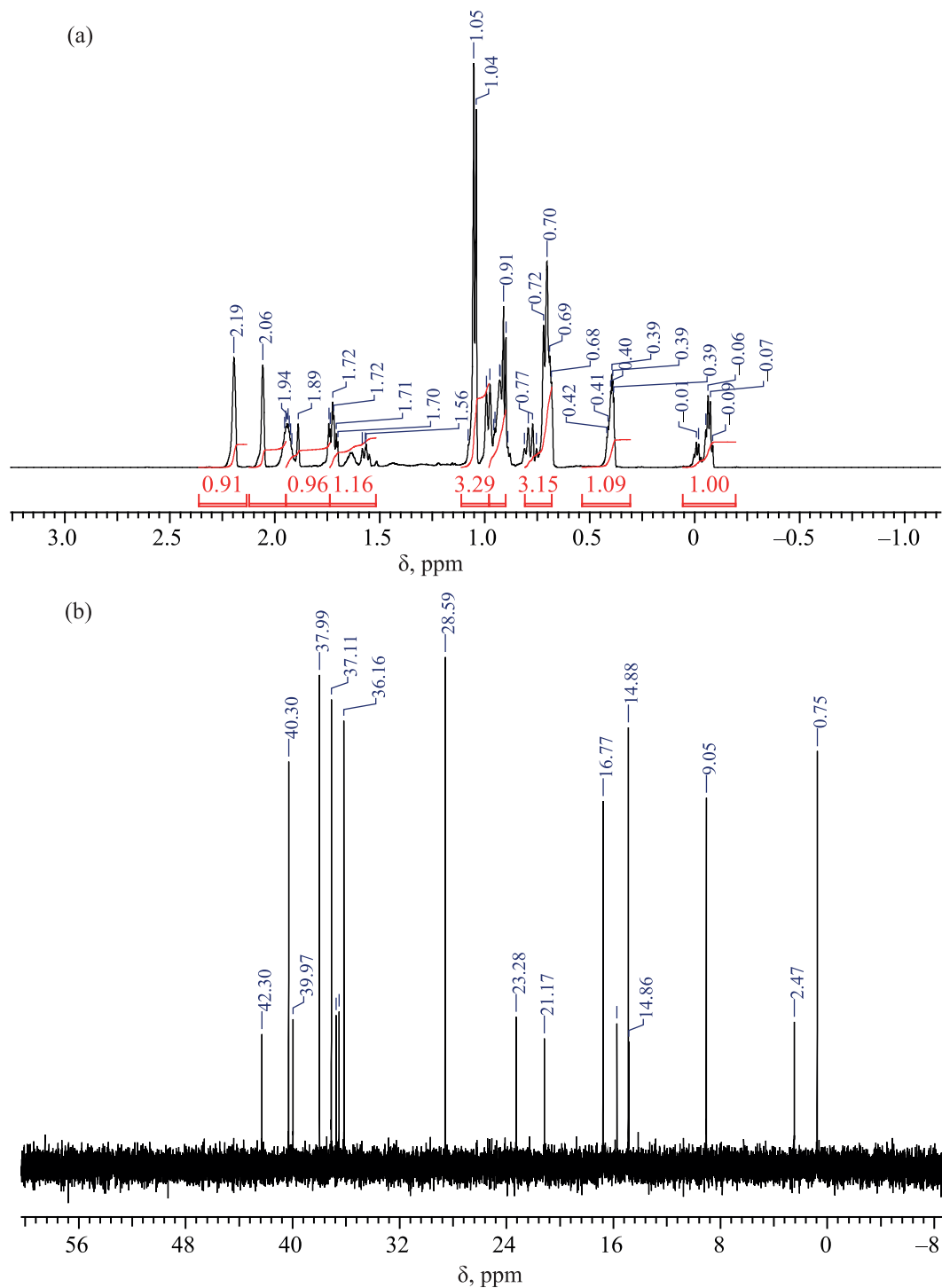
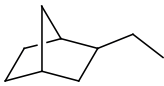

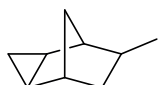
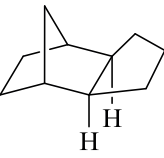


Fig. 1. (a) ^1H and (b) ^{13}C NMR spectra of 6-methyltricyclo[3.2.1.0^{2,4}]octane (**3**) (CDCl_3).

under these conditions. After the hydrogenation, the target product (**3**) was isolated as a mixture of an *endo*-isomer and an *exo*-isomer. The structure of the new compounds was confirmed by ^1H and ^{13}C NMR spectroscopy (Fig. 1).

The synthesized target compounds were examined for compliance with the current aviation fuel standards. The target hydrocarbons appeared as transparent and colorless liquids at room temperature with high boiling point (above 150°C at atmospheric pressure) and low

Table 1. Properties of 5-methylene-2-norbornene derivatives compared to related compounds (2-ethylnorbornane and JP-10)

Compound	Density, g/cm ³ (20°C)	Freezing point, °C	References
	0.8572	< -60	[14]
 2	0.9338	< -60	This study
 3	0.9139	< -60	This study
 (JP-10)	0.9316	< -60	[2]

freezing point (below -60°C). The freezing points and density values for compounds **2** and **3** compared to the properties of related hydrocarbons are summarized in Table 1.

The density of compound **3** was measured in the range of $+10$ to $+60^{\circ}\text{C}$ (Fig. 2). Within this temperature range, the density varied as a linear temperature function. Given the limited performance capabilities of the density meter, an estimated density for -40°C is indicated. The density of the hydrocarbons tested was found to be sufficiently high and comparable to that of JP-10 under similar conditions. In particular, the unsaturated compound **2** exhibited a higher density than the saturated hydrocarbon **3**.

Heating value is another key parameter that influences the usability of the hydrocarbons under study as jet fuels. The heating values of the compounds were measured by a calorimetric bomb. The lower specific energy (kJ/kg , Q_m^L) and lower energy density (kJ/L , Q_v^L) for the hydrocarbons under study are presented in Table 2 in comparison to the properties of related hydrocarbons. The highest value of the specific energy was observed for saturated hydrocarbon **3**, which has a higher H/C ratio. Moreover, the specific energy for compound **3** proved to be significantly higher than that for JP-10.

However, its energy density value was lower because of its lower density (0.914 for **3** vs. 0.931 for JP-10). At the same time, both of the synthesized hydrocarbons demonstrated markedly higher volumetric heating values

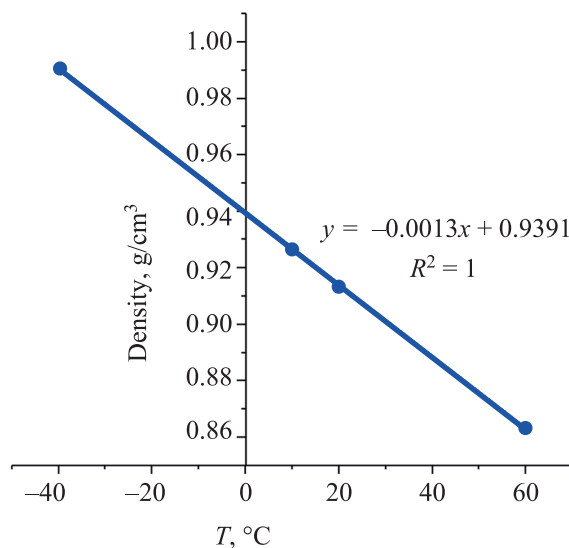
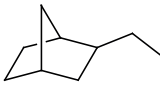
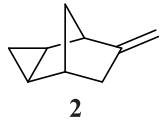
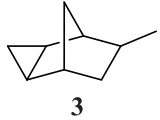
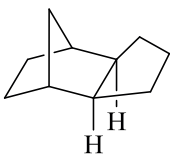
**Fig. 2.** Density of monocyclopropanated 2-methylenenorbornane compound (**3**) as a temperature function.

Table 2. Energy properties of 5-methylene-2-norbornene derivatives compared to related compounds (2-ethylnorbornane and JP-10)

Compound	Empirical formula	H/C ratio	$\Delta H_{\text{vol r}}^0$, kJ/mol	Q_m^L , kJ/rg	Q_v^L , kJ/L	References
	C ₉ H ₁₆	1.78	-239.3±0.2	42470±28	36340±28	[14]
 2	C ₉ H ₁₂	1.33	52.4±0.6	42210±21	39415±22	This study
 3	C ₉ H ₁₄	1.56	-18.2±2.7	42950±14	39250±35	This study
 (JP-10)	C ₁₀ H ₁₆	1.60	-171.0	42100	39400	[2]

compared to 2-ethylnorbornane. This finding confirms the assumption that the presence of a cyclopropane moiety in a hydrocarbon molecule improves its energy properties.

In summary, in this study we were able to prepare two promising novel liquid hydrocarbons with high energy density and low freezing points. These hydrocarbons were synthesized with good yields from commercially available dicyclopentadiene using simple organic reactions such as a Diels–Alder reaction and catalytic cyclopropanation with diazomethane. We systematically investigated the main physicochemical properties of the hydrocarbons prepared, including their densities, freezing points, and heating values. The newly-synthesized strained alicyclic hydrocarbons had low freezing points as well as high density (up to 0.9338 g/cm³) and increased volumetric heating values. Taking into account the low price of starting materials and the simplicity of the synthetic approaches utilized, these hydrocarbons can be considered promising novel candidates to be used as liquid engine fuels for modern aerospace vehicles.

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FUNDING

The study was performed with financial support from the Russian Science Foundation (project no. 20-73-00355).

CONFLICT OF INTEREST

A.L. Maximov, a co-author, is the Chief Editor at the *Neftekhimiya* (Petroleum Chemistry) Journal. The other co-authors declare no conflict of interest requiring disclosure in this article.

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