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Aryl Butyl Acetals as Oxygenate Octane-Enhancing Additives for Motor Fuels

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Abstract—This study is devoted to finding new oxygenate additives improving the quality of motor fuels. Aryl butyl acetals obtained by the addition of phenols to butyl vinyl ethers are used as additives for the first time. The reaction is carried out at room temperature in the presence of catalytic (0.3–0.6 mol %) amounts of CF_3CO_2H and leads to the formation of the desired products in a quantitative yield. The antiknock properties of the synthesized compounds have been investigated. It has been found that synthesized aryl butyl acetals possess quite a high research octane number (RON) (up to 110) and can be promising additives to motor gasoline for increasing knock resistance, thus, the addition of 3 wt % aryl butyl acetal increases the RON of an *n*-heptane–isooctane mixture as model fuel and that of the AI-92-K5 base fuel by 1.0–1.2 and 0.1–0.4 points, respectively. The efficiency of the antiknock additive depends on the structure of the alkoxyl radical in the aryl butyl acetal molecule, thus, the blending ONs of acetals with a branched isobutoxyl radical is higher than the values of linear butoxy derivatives by 3.4–6.7 points. Acetals containing the methyl substituent in the phenoxy radical have higher ON values.

Keywords: aryl butyl acetals, oxygenate additives, antiknock properties, octane number

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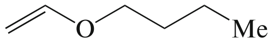
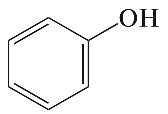
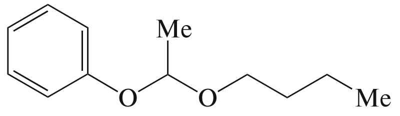
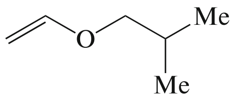
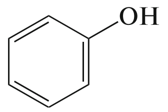
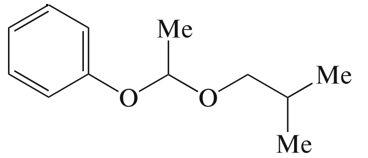
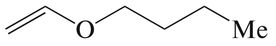
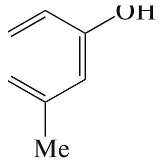
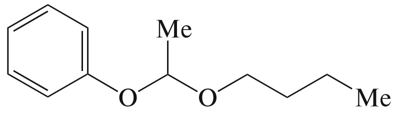
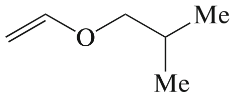
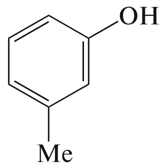
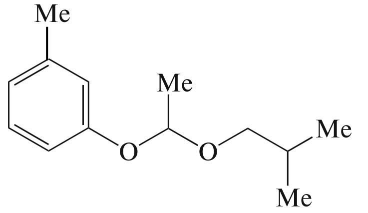
The main global trend of the improvement of the environmental properties and performance of motor fuels is the use of multifunctional additives, mainly oxygenates. The presence of oxygen in the fuel composition makes it possible to reduce hazardous carbon monoxide emissions by 30% and emissions of unburnt hydrocarbons by 15% [1]. In order to increase the antiknock properties, components obtained using secondary methods of processing of petroleum fractions (catalytic cracking, isomerization, and alkylation) are added to gasolines or special high-octane additives are introduced into the fuel.

Alcohols, ethers, and esters, as well as acetals including cyclic acetals (1,3-dioxocyclanes) [2, 3], are the most common among the oxygenates used for increasing the antiknock properties of fuels. The latter are classified with low-hazard chemicals capable of improving the properties of fuels. The technical results of their use as oxygenate additives are an increase in both the phase stability of motor fuels upon contact with water and antiknock rating [4–6]. A decrease in gum formation is noted in the case of combined use of alcohols and cyclic ketals in fuel blends [5, 6], and a synergetic effect of an increase in the ON [7] has been revealed.

In recent years, special attention has been paid to oxygenate additives based on renewable feedstock such as cellulose, waste products of forest and wood processing industries and agriculture, algae, and lignin. The use of such oxygenates expands fuel resources and makes it possible to improve their quality by means of decreasing the toxicity of combustion products [2, 3]. Organic products and liquid fuel ("bio-oil") [8–11] have been obtained during the comprehensive processing of vegetable feedstock. In particular, fast pyrolysis of plant biomass leads to the formation of a mixture of organic oxygen-containing compounds (25–45% O) including carbohydrates, phenols, alcohols, esters, furans, aldehydes, etc. [12]. Many of these components including compounds of the phenol series can also be used as oxygenate additives for both gasoline and diesel fuel [13]. For example, the addition of anisole (methyl phenyl ether) to gasoline (5 wt %) increases the octane number of the fuel by 4 points [14].

We have earlier studied the use of synthetic butyl alcohols of domestic manufacture as the oxygenate additives to motor fuels [15] as well as have found the possibility for the use of aryl vinyl ethers (the modified products of the catalytic lignin destruction) as the additives increasing the antiknock rating of gasolines [16]. The aim of this work is the search for new oxy-

Table 1. Synthesis of alkyl aryl acetals

Vinyl ether	Phenol	Alkyl aryl acetal	Yield of **3**, %
 **1a**	 **2a**	 **3a**	98
 **1b**	 **2a**	 **3b**	99
 **1a**	 **2b**	 **3c**	99
 **1b**	 **2b**	 **3d**	97

gen-containing compounds acceptable as the antiknock additives to motor fuel. To achieve the goal in hand, aryl butyl acetals were synthesized, and their influence on the change in the fuel octane number was assessed.

EXPERIMENTAL

The synthesis methods of aryl butyl acetals with different structures are presented below. The formulae of the initial substances and final reaction products are presented in Table 1 below.

*Synthesis of Aryl Butyl Acetals **3a–3d** (General Procedure)*

0.10–0.18 g (0.3–0.6 mol %) of CF_3CO_2H was added to phenol **2** (0.25 mol), and freshly distilled vinyl ether **1** (0.25 mol) was added dropwise to the obtained mixture over 15–20 min upon vigorous stirring. The reaction was accompanied by an exothermic effect. The maximum temperature of 60–65°C was controlled by the speed of addition of vinyl ether. Upon the completion of the reaction, the acid catalyst was neutralized by 0.1 g of K_2CO_3 during the spontaneous decrease in the temperature to room temperature (~after 30 min), and target aryl butyl acetal **3** was obtained after the removal of the salt.

1-(*n*-Butoxy-1-phenoxy)ethane (3a). Yield 47.55 g (98%). n_D^{24} 1.4805. IR (ν, cm^{-1}): 3065, 3036, 2956, 2935, 2873, 1595, 1491, 1464, 1383, 1349, 1292, 1234, 1171, 1130, 1083, 1030, 971, 924, 813, 754, 694, 611, 510. ^{1}H NMR, δ, ppm: 7.30 m (2H, Ph), 7.02 m (3H, Ph), 5.41 q (1H, J = 5.3 Hz, OCHO), 3.75 and 3.50 m (1H each, OCH_2), 1.58 m (2H, $\underline{CH_2}Et$), 1.52 d (3H, J = 5.3 Hz, $\underline{Me}CH$), 1.38 m (2H, $\underline{CH_2}Me$), 0.92 t (3H, J = 7.3 Hz, Me). ^{13}C NMR, δ_C, ppm: 13.7 ($\underline{Me}CH_2$), 19.2 ($\underline{CH_2}Me$), 20.1 ($\underline{Me}CH$), 31.7 ($\underline{CH_2}Et$), 65.5 (OCH_2), 99.5 (OCHO), 117.3 ($C^{3,5}$), 121.7 (C^4), 129.3 ($C^{2,6}$), 157.0 (C^1). Found, %: C 74.02; H 9.31. Calculated for $C_{12}H_{18}O_2$, %: C 74.19; H 9.34.

1-(Isobutoxy-1-phenoxy)ethane (3b). Yield 47.98 g (99%). n_D^{24} 1.4790. IR (ν, cm^{-1}): 3065, 3036, 2958, 2914, 2875, 1594, 1491, 1385, 1344, 1292, 1235, 1165, 1129, 1084, 1033, 1003, 922, 804, 754, 694, 610, 511. ^{1}H NMR, δ, ppm: 7.30 m (2H, Ph), 7.03 m (3H, Ph), 5.40 q (1H, J = 5.3 Hz, OCHO), 3.50 m and 3.24 dd (2H, J = 9.0, 6.8 Hz, OCH_2), 1.85 m (1H, CH), 1.51

d (3H, J = 5.3 Hz, $\underline{\mathrm{Me}}$CH), 0.89 and 0.91 d (3H each, J = 7.0 Hz, $\underline{\mathrm{Me}}_2$CH). ^{13}C NMR, δ_C, ppm: 19.3 ($\underline{\mathrm{Me}}_2$CH), 20.0 ($\underline{\mathrm{Me}}$CH), 28.4 ($\underline{\mathrm{CH}}Me_2$), 72.3 (OCH$_2$), 99.5 (OCHO), 117.3 (C^{3,5}), 121.7 (C^4), 129.3 (C^{2,6}), 157.0 (C^1). Found, %: C 74.08; H 9.40. Calculated for $C_{12}H_{18}O_2$, %: C 74.19; H 9.34.

1-(*n*-Butoxy)-1-(3-methylphenoxy)ethane (3c). Yield 51.50 g (99%). n_D^{24} 1.4819. IR (ν, cm^{-1}): 3035, 2986, 2955, 2933, 2872, 2735, 1595, 1488, 1456, 1382, 1348, 1283, 1258, 1160, 1126, 1085, 1029, 954, 912, 875, 854, 778, 743, 693, 618, 445. ^{1}H NMR, δ, ppm: 7.17 m (1H, C_6H_4), 6.82 m (3H, C_6H_4), 5.38 q (1H, J = 5.4 Hz, OCHO), 3.74 and 3.49 m (1H each, OCH$_2$), 2.34 s (3H, $\underline{\mathrm{Me}}C_6H_4$), 1.58 m (2H, $\underline{\mathrm{CH_2}}$Et), 1.50 d (3H, J = 5.4 Hz, $\underline{\mathrm{Me}}$CH), 1.38 m (2H, $\underline{\mathrm{CH_2}}$Me), 0.92 t (3H, J = 7.0 Hz, Me). ^{13}C NMR, δ_C, ppm: 13.7 ($\underline{\mathrm{Me}}$), 19.2 ($\underline{\mathrm{CH_2}}$Me), 20.1 ($\underline{\mathrm{Me}}$CH), 21.3 ($\underline{\mathrm{Me}}C_6H_4$), 31.6 (CH$_2$Et), 65.3 (OCH$_2$), 99.4 (OCHO), 114.0 (C^6), 118.0 (C^2), 122.4 (C^4), 129.0 (C^5), 139.2 (C^3), 157.0 (C^1). Found, %: C 75.00; H 9.60. Calculated for $C_{13}H_{20}O_2$, %: C 74.96; H 9.68.

1-(Isobutoxy)-1-(3-methylphenoxy)ethane (3d). Yield 50.43 g (97%). n_D^{24} 1.4794. IR (ν, cm^{-1}): 3036, 2958, 2925, 2874, 2734, 1595, 1486, 1466, 1383, 1351, 1283, 1256, 1157, 1125, 1086, 1035, 1007, 953, 897, 777, 693, 617, 496, 444. ^{1}H NMR, δ, ppm: 7.21 m (1H, C_6H_4), 6.86 m (3H, C_6H_4), 5.41 q (1H, J = 5.3 Hz, OCHO), 3.27 and 3.53 m (1H each, OCH$_2$), 2.36 s (3H, $\underline{\mathrm{Me}}C_6H_4$), 1.89 m (1H, $\underline{\mathrm{CH}}$Me$_2$), 1.53 d (3H, J = 5.3 Hz, $\underline{\mathrm{Me}}$CH), 0.94 and 0.95 d (6H, J = 7.0 Hz, Me$_2$CH). ^{13}C NMR, δ_C, ppm: 19.3 ($\underline{\mathrm{Me}}_2$CH), 20.0 ($\underline{\mathrm{Me}}$CH), 21.3 ($\underline{\mathrm{Me}}C_6H_4$), 28.4 ($\underline{\mathrm{CH}}Me_2$), 72.2 (OCH$_2$), 99.4 (OCHO), 114.1 (C^6), 118.0 (C^2), 122.4 (C^4), 129.0 (C^5), 139.2 (C^3), 157.0 (C^1). Found, %: C 74.80; H 9.73. Calculated for $C_{13}H_{20}O_2$, %: C 74.96; H 9.68.

The RON values were determined on a standard unit with one-cylinder engine according to *GOST* (State Standard) *8226-2015* "Fuel for engines. Research method for determination of octane number". The blending RONs were calculated according to the formula

$$\mathrm{RON_{blend}} = \frac{\mathrm{RON_{base+additive}} - \mathrm{RON_{base}}\omega_{\mathrm{base}}}{\omega_{\mathrm{additive}}},$$

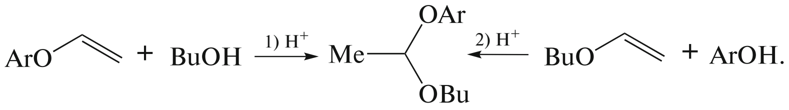
where $\mathrm{RON_{blend}}$ is the blending octane number of the additive, $\mathrm{RON_{base\,+\,additive}}$ is the octane number of the base with the addition of the additive determined by the research method, $\mathrm{RON_{base}}$ is the octane number of the base, ω_{base} is the weight fraction of the base (0.97), and $\omega_{\mathrm{additive}}$ is the weight fraction of the additive (0.03).

The IR spectra of the synthesized compounds were recorded in a thin film on a Bruker JFS-25 spectrometer in a region of 400–4000 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker-DPX-400 instrument with the operating frequencies of 400.13 and 100.62 MHz, respectively; the solvent was CDCl$_3$. The chemical shifts of ^{1}H and ^{13}C NMR were recorded relative to CDCl$_3$ as the internal standard (δ 7.27 and 77.0 ppm, respectively). The elemental analysis was performed on a Flash EA 1112 Series analyzer.

RESULTS AND DISCUSSION

The atom-efficient reaction of electrophilic addition of OH reagents to vinyl ethers [17] deserves special attention among the known methods of preparation of acetals. This technique is universal. By varying substituents in vinyl ether and protogenic reagent, various and often hardly accessible by other methods symmetrical and unsymmetrical acetaldehyde acetals can be obtained.

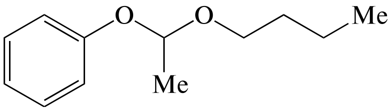
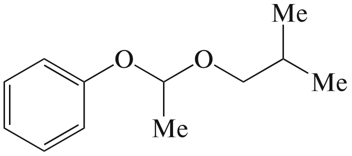
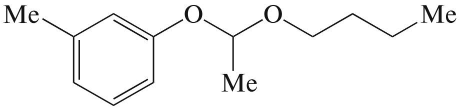
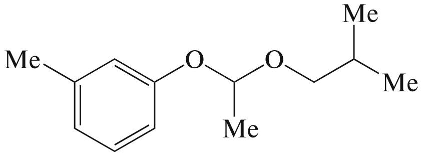
Aryl butyl acetals required for the study can be obtained either from butyl alcohols and aryl vinyl ethers (reaction 1) or from butyl vinyl ethers and phenols (reaction 2).



Reaction 1 requires harsh conditions because of the decreased electron density of the double bond of aryl vinyl ethers. The experiments showed that *n*-BuOH does not add to vinyl *m*-cresyl ether in the presence of a catalyst, 0.5 mol % CF$_3$CO$_2$H (60°C, 4 h). The formation of acetal **3c** was not detected in the ^{1}H NMR spectrum even in trace amounts. Harsher reaction conditions (10 mol % CF$_3$CO$_2$H, 60°C, 8 h) lead to side processes such as disproportionation of unsymmetrical acetal **3c** and telomerization of aryl vinyl ether, which eventually decreases the yield of the target product. As a result of this, the samples of acetals **3** for their investigation as additives to motor fuels were prepared according to reaction 2, namely, from butyl vinyl ethers **1a** and **1b** and phenols **2a** and **b**.

The most universal preparation method of alkyl vinyl (in particular, butyl vinyl) ethers is the addition reaction of alcohols to acetylene in the presence of basic catalysts which gained scientific and industrial development in the 1930s–1970s [18–20]. With the

Table 2. Blending research octane numbers of acetals **3** (3 wt %) in the model fuel blend*

Additive	RON	Gain in RON	Blending RON
None	70.0	–	70.0
 **3a**	71.0	1.0	103.3
 **3b**	71.1	1.1	106.7
 **3c**	71.0	1.0	103.3
 **3d**	71.2	1.2	110.0

* The ON values were obtained using the results of three measurements.

discovery of a new principle of increasing the reactivity of nucleophilic reagents by means of the use of catalytic media consisting of a strong base and a polar nonhydroxylic complexing solvent by Academician B.A. Trofimov, it turned out to be possible to intensify the classical base-catalyzed reactions of acetylene and to perform them at moderate temperatures and reduced (down to atmospheric) pressures [21, 22].

Butyl vinyl ethers react with phenols much more readily and selectively. Under standard conditions (room temperature, equimolar ratio of the reactants, and 0.3–0.6 mol % CF_3CO_2H), *n*-butyl vinyl ether (**1a**) and isobutyl vinyl ether (**1b**) interact with phenol (**2a**) and *m*-cresol (**2b**) to form corresponding aryl butyl acetals **3a**–**3d** in quantitative yield (Table 1).

The reaction progress was monitored via IR spectroscopy by the disappearance of the absorption bands of the OH group of phenols **2** (in a region of 3400 cm^{-1}) and the vinyloxy group of ethers **1** (3119, 1639, 1612, and 1204 cm^{-1}) in the reaction mixtures. The presence of just one quartet of the protons of the methine group ($\delta \sim 5.4$ ppm) and a doublet of the methyl group ($\delta \sim 1.5$ ppm) of the acetal moiety in the ^1H NMR spectra gives evidence for the absence of disproportionation of adducts **3** under the synthesis conditions.

Synthesized alkyl aryl acetals **3a**–**3d** are colorless thin liquids with a pleasant odor, they are highly soluble in hydrocarbons and form homogenous solutions with gasoline. The density of these compounds (0.95–0.97 g/cm^3) slightly depends on the structure of the alkyl and aryl parts and is close to the density of aryl vinyl ethers. The boiling point is 250–270°C, and it is higher than that of the corresponding aryl vinyl ethers. It is expected that 15.3–16.5% oxygen (21.6% in butyl alcohols) will promote a decrease in the concentration of oxides and harmful substances in the exhaust fumes.

The influence of synthesized acetals **3a**–**3d** on the change in the ON was evaluated using an *n*-heptane–isooctane model system at a ratio of 3 : 7 (ON 70) and unleaded gasoline of the AI-92-K5 brand (Angarsk Petrochemical Company) taken as a base fuel. This brand of gasoline is the most common in Russia [23].

The tests on a standard unit showed that the introduction of acetals **3a**–**3d** (3.0 wt %) into the model

Table 3. Blending research octane numbers of acetals **3** (3 wt %) in base gasoline AI-92-K5*

Additive	RON	Growth in RON	Blending RON
None	90.3	–	–
3a	90.4	0.1	93.3
3b	90.5	0.2	96.7
3c	90.4	0.1	93.3
3d	90.6	0.3	100.0

* The ON values were obtained using the results of three measurements.

fuel blend provided a gain in the RON by 1.0–1.2 points (Table 2).

All the acetals possess quite high blending RONs of 103.3–110.0, which are close to the RON of ethanol by value. The latter possess good operating and ecological characteristics; however, its widespread application is limited by the absence of phase stability and high excise taxes on alcohol-containing products [23]. Methyl *tert*-butyl ether that is widely used in Russia in the production of high-octane gasolines has the RON of 118; however, it is currently prohibited for use in many countries due to the toxicity and environmental hazard [24].

The antiknock properties of the additives under study (with respect to the rate of increase in the RON) decrease in the following series: **3d** > **3b** > **3a** = **3c**.

Like for the majority of antiknock agents of different classes, the efficiency of the additions of acetals **3a**–**3d** to a gasoline with a high RON (90.3) is lower when compared to a low-octane base blend, thus, the gain in the RON was 0.1–0.3 points in the case of addition of 3 wt % (Table 3).

In the production of motor gasolines by compounding various components, the determining role belongs to the blending octane numbers that differ from the weighted sum of the octane numbers of the individual components [25]. The blending RONs of the synthesized acetals **3a**–**3d** are 93.3–100.0.

The trends in the RON gain depending on the structure of the additive in the model fuel blend are preserved in the gasoline as well. The efficiency of the antiknock additive depends on the alkoxyl radical, thus, the blending ONs of acetals **3b** and **3d** with the branched isobutoxyl radical is higher than those of linear butoxy derivatives **3a** and **3c** by 3.4–6.7 points. As it was expected, acetals containing a methyl substituent in the phenoxy radical have higher values of the ON [26]. For butoxy derivatives, the antiknock rating slightly depends on the structure of the aromatic radical.

In summary, the studied oxygenates, the adducts of butyl vinyl ethers and phenols, possess quite high RONs (up to 110) and hold promise as motor gasoline additives increasing the knock resistance and improving the performance characteristics.

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CONFLICT OF INTEREST

The authors declare no conflict of interest to be disclosed in this paper.

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