Synthesis of Derivatives of Alkylamino Alkyloxy Propanol Structures by *N*-alkylation, Acylation, and Nitration. Application as Fuel Additives

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ABSTRACT: Polyfunctional compounds were prepared by alkylation, acylation, and nitration of hydroxyl and amine functions of the following alkanolamine ether structures: (di)alkylamino alkyloxy propanol, hydroxy alkyloxy (di)alkylamino propanol, and their dimer compounds. The resulting compounds were characterized by conventional spectroscopic methods, and complete nuclear magnetic resonance data are given. These reactions extented the application of these propanic compounds to use as multipurpose fuel additives. In particular, they enhance phase stability and improve the cetane number in ethanol–diesel fuel blends.
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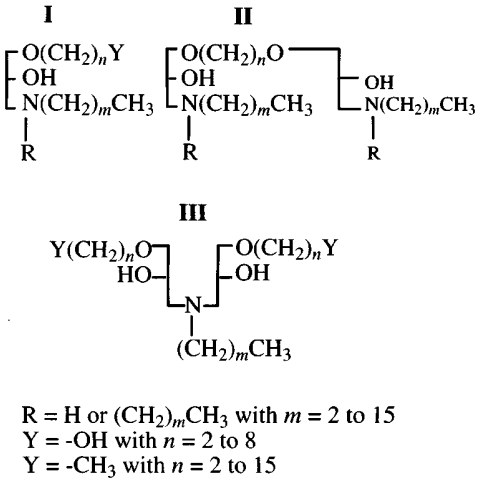
KEY WORDS: Alkyloxy alkylamino propanol derivatives, acylation, ethanol–diesel fuel-additive blends, fuel additive, ignition improvement, *N*-alkylation, nitration, polyfunctional compounds, surface-active agent, viscosity.

Triglyceride derivatives, such as phospholipids or acyloxy/aryloxy propanolamines, have been employed in a variety of biological application (1–4). In the present experiments, we developed other types of polyfunctional propanic compounds for application as fuel additives.

In a previous study (5), we described the synthesis of the following three basic alkanolamine ether structures, the alkyloxy alkylamino propanols (**I**) and the two dimer structures (**II** and **III**). These compounds present several active sites on the basic propanic skeleton (Scheme 1).

In the present work, these materials were modified by chemical alteration of the –OH and –NH sites by *N*-alkylation, *O*-acylation, *N*-acylation, *O*-nitration, or *N*-nitration. These novel compounds were prepared in quantitative yield by a method that could be scaled up for cost-effective production. Of significance for use as fuel additives, the C/N and N/O ratios of the derivatives could be altered, and hydrocarbon chains could be added at will by the present method.



R = H or $(CH_2)_mCH_3$ with m = 2 to 15
Y = -OH with n = 2 to 8
Y = $-CH_3$ with n = 2 to 15

SCHEME 1

A number of ethers, esters, phenols, or nitrated compounds have been mentioned as specific fuel additives (6), although most of them are not suitable for fuels that contain ethanol. They often have a reduced efficiency in the presence of ethanol (peroxides, alkyl nitrates) or they are not miscible in blends with ethanol (polyethylene glycol dinitrates). Furthermore, some pro-cetane compounds require careful handling or can only be synthesized by onorous methods (7).

The present compounds exhibited good compatibility with ethanol–diesel fuel blends. Owing to multiple actions of these derivatives, the resulting ternary blend presented good qualities to be used in compression ignition engines (8,9).

EXPERIMENTAL PROCEDURES

Materials. Alkanoyl chlorides (99%) and 3,5-di-*tert*-butyl-4-hydroxy benzyl chloride (>98%) were purchased from Lancaster (Strasbourg, France). Hydrochloric acid (36%), methyl iodide (99%), triethylamine (99%), and fuming nitric acid (>99.5%) were purchased from Fluka (St. Quentin Fallavier, France). Organic solvents (purum for synthesis) were supplied

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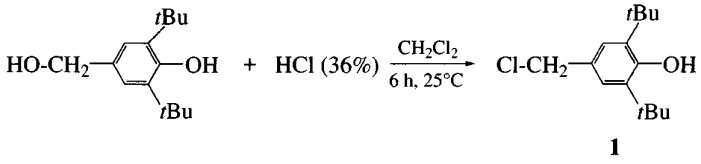

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SCHEME 2

by SDS (Solvants, Documentation, Synthèses; Bordeaux, France). The reagents were used without further purification.

Analyses. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on an ARX400 Bruker (Wissenbourg, France) spectrometer (400,134 MHz), in $CDCl_3$ solvent. Signal positions (δ values) were measured relative to the signal for $CHCl_3$ (δ 7.24). ^{13}C NMR $\{^{1}H\}$ spectra were recorded on a AC200 Bruker spectrometer (50,323 MHz) with $CDCl_3$ solvent. The resonance positions were measured relative to the $CDCl_3$ signal (δ 77.0). ^{15}N NMR $\{^{1}H\}$ spectra were recorded on a AM300 Bruker spectrometer (30,424 MHz). Signal positions (δ values) were measured relative to the liquid ammonia signal. IR spectra were recorded on a 1600 FT-IR Perkin-Elmer spectrophotometer (Norwalk, CT) with liquid films between KBr plates. Ultraviolet (UV) spectra were recorded in the 190–400 nm region in solution (petroleum ether) with a Vectra ES/12 Hewlett-Packard spectrophotometer (Palo Alto, CA). Mass spectra were recorded on a HP5989 Hewlett-Packard instrument with a chemical-ionization detector. High-performance liquid chromatography (HPLC) chromatograms were obtained with a UV detector (λ = 254 nm) by using a Kromasil (Phase Separations; Pessac, France) silica column (hexane–dichloromethane: 1:1) for **3**–**8**, or a C_{18} Nucleosil (Phase Separations) column (acetonitrile) for **1** and **2**. A 70–230-mesh silica gel was used for column chromatography. Satisfactory microanalyses were obtained for all compounds (Carlo Erba elemental analyzer; Rueil Malmaison, France).

Viscosities were measured with a Carri-Med CSL 100 (Rheo, Champlan, France) controlled-stress rheometer with a cone-plate geometry. Most of the properties were tested according to standard methods (10):

NF M07-035 = ASTM D613-84 = ISO 5165. (Ref. 10) Determination of autoignition characteristics: compared to *n*-cetane and heptamethylnonane.

NF M07-042 = EN 116 (Ref. 10). Determination of low flow temperature: The fuel blend is made to pass through a standard filtering device under decreasing temperature.

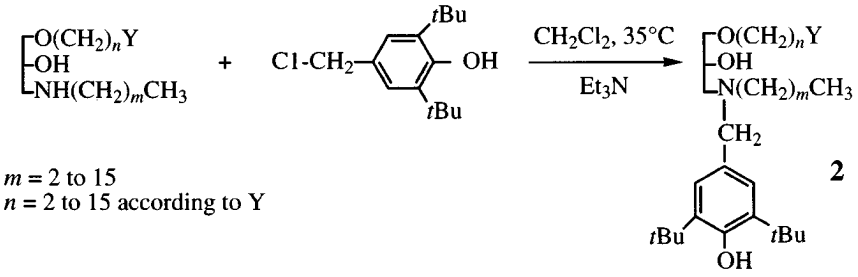
NF M07-047 = ASTM D 2274/70 (Ref. 10). Stability of diesel fuel: The fuel remains under oxygen bubbling for 16 h at 95°C. The amount of insoluble materials formed is weighed.

N-ALKYLATION REACTION BY ALKYL CHLORIDE

This step consisted in linking a specific antioxidative group to the basic structures. A direct condensation between two alcohol functions or between alcohol and amine functions was prevented by steric hindrance of the functional sites. The benzyl alcohol function was first chlorinated under the following conditions (Scheme 2).

The benzyl chloride **1** was then condensed with the alkyloxy propanolamine structures (**I** or **II**) to give the desired *N*-alkylation product (Scheme 3).

Preparation of reactional intermediate: 3,5-di-tert-*butyl-4-hydroxy benzyl chloride* (**1**). Concentrated HCl (36%) (10 mL) was added to a solution of 3,5-di-*tert*-butyl-4-hydroxy benzylic alcohol (10 g, 0.0423 mol) in CH_2Cl_2 (100 mL). The solution was stirred at room temperature for 6 h. Several extractions were carried out with 100 mL water until pH was neutral. The organic phase was dried with $MgSO_4$ before removing solvent to obtain 10.5 g of an orange oil (97%): $C_{15}H_{23}OCl$ (M = 254.85 g/mol). Infrared (IR) (neat, cm^{-1}): 3637 (ν_{OH} phenol), 1250–1166 ($\nu_{C\text{-}O}$ phenol), 3070 (ν_{CH} aromatic ring), 1481, 1470 ($\nu_{C=C}$ tetrasubstituted aromatic), 885 (CH out of plane bending for tetrasubstituted aromatic), 785 (C-Cl), 2873 (ν_{CH} CH_2), 1435 (δ_{CH} CH_2). ^{1}H NMR δ (ppm): 1.45 (*s*, 18 H, CH_3 of *t*Bu); 4.6 (*s*, 2 H, CH_2-Cl); 5.3 (*s*, 1 H, OH); 7.2 (*s*, 2 H, CH aromatic). ^{13}C NMR δ (ppm) (Scheme



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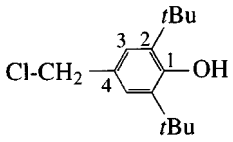
SCHEME 3



SCHEME 4

4): 30.3 (CH_3 of *t*Bu); 34.4 [$C(CH_3)_3$]; 47.7 (CH_2-Cl); 125.6 (C_3); 128.3 (C_4); 136.3 (C_2); 154.1 (C_1), attributed by comparison with calculated values (11).

Synthesis of N-*(3,5-di*-tert-*butyl-4-hydroxy) benzyl,*N-*(2-hydroxy-3-octyloxy propyl) octylamine* (**2**). A solution of 1-octylamino-3-octyloxy-2-propanol (10 g, 0.032 mol) and triethylamine (5 mL, 0.036 mol) in dichloromethane (50 mL) was stirred at 40°C. A solution of 3,5-di-*tert*-butyl-4-hydroxy benzyl chloride (8.2 g, 0.032 mol) in diethyl ether (60 mL) was gradually added for 2 h. The medium was then stirred for 4 h. Several extractions were carried out with water (2 × 70 mL), then with HCl (pH = 5), and finally with water. The organic phase was dried ($MgSO_4$) before removing solvent to obtain 15.5 g of an orange oil. The product was further purified on a Florisil magnesium silicate (SDS) chromatography column eluted with Et_2O. The product was characterized as follows: $C_{34}H_{63}O_3N$ (M = 533.87 g/mol); n_D^{20} = 1.49080; UV-vis: λ_{max} = 242 and 270 nm ($\pi \rightarrow \pi^*$). IR (neat, cm^{-1}): 3430 (ν_{OH} alcohol), 3645 (ν_{OH} phenol), 1250 and 1155 ($\nu_{C\text{-}O}$ phenol), 3070 (ν_{CH} aromatic ring), 1481 and 1470 ($\nu_{C=C}$ tetrasubstituted aromatic), 1135 and 1119 (CH in-plane bending for tetrasubstituted aromatic), 885 (CH out-of-plane bending for tetrasubstituted aromatic), 2925 to 2855 (ν_{CH} CH_2, CH_3), 1455 (δ_{CH} CH_2, CH_3). ^1H NMR δ (ppm): 0.90 (*m*, 6 H, CH_3); 1.2 (*m*, 20 H, CH_2); 1.35 (*s*, 18 H, CH_3 of *t*Bu); 1.45 (*m*, 4 H, CH_2 β from O and N); 2.5 (*m*, 4 H, CH_2-N); 3.4 (5 H; *d*, CHAr, *J* = 13.3 Hz; *t*, O-CH_2, *J* = 6.9 Hz; 2 AB, CH_2-O, J_{AB} = 9.9 Hz); 3.65 (*d*, 1 H, CHAr, *J* = 13.3 Hz); 3.8 (*m*, X part of ABX, 1 H, CH); 5.1 (*s*, 1 H, Ar-OH); 7 (*s*, 2 H, CH aromatic). Two-dimensional NMR (Cosy ^1H-^1H) confirmed that the doublet at 3.65 ppm belongs to the AM system, corresponding to the methylene diastereotopic protons Ar-CH_2-N. ^{13}C NMR δ (ppm): 14.1 (CH_3); 30.4 (CH_3 *t*Bu); 22.6 to 34.3 (CH_2); 54.0, 56.7, 58.6 (CH_2-N); 66.6 (CH); 71.6, 73.4 (CH_2-O); 125.5 (H-C aromatic); 129.5 (C *t*Bu); 135.7 (H_2C-C aromatic); 152.8 (HO-C aromatic).

ACYLATION REACTIONS ON ALCOHOL AND AMINE GROUPS

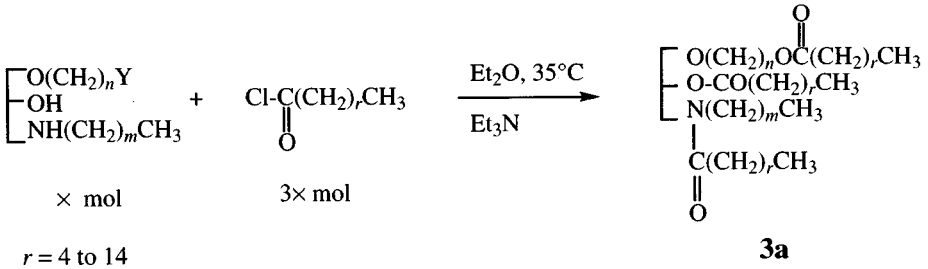
The most appropriate reagent to prepare ester derivatives was found to be an acid chloride. Acid anhydrides of fatty acids are not available, and carboxylic acids are not efficient enough to react with these derivatives without employing expensive catalysts.

Esterification of hydroxy functions of similar compounds with acetyl chloride has been described (12–14). We have shown that both amino and alcohol sites can be modified with a fatty acid chloride in an appropriate solvent. Under such conditions, amide and ester functions were produced in the same reaction. Triethylamine favored the reaction the hydrochloric acid produced is trapped (Scheme 5).

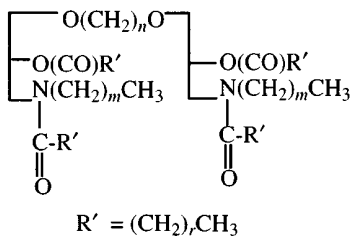
As suggested above, the different –OH and –NH– groups of structures **I**, **II**, or **III** were readily acylated. For example, the dimer structure **4** harbors four acylated sites (Scheme 6).

A tertiary amino function in the initial structure conferred the same role as triethylamine, while for the derivatives with an amide function, NMR revealed two configurational isomers that correspond to the forms shown in Scheme 7. Split signals in proton and ^{13}C NMR were observed.

Synthesis of N-*octyl,* N-*(3-octyloxy-2-octanoyloxy) propyl octanamide* (**3b**). A solution of octanoyl chloride (185 mL, 1.07 mol:light excess) in diethyl ether (100 mL) was gradually added to a solution of 1-octylamino-3-octyloxy-2-propanol (158 g, 0.5 mol) and triethylamine (140 mL, 1.0 mol) in diethyl ether (200 mL). The medium was then stirred for 5 h under reflux (35°C). The solution was first washed with water, then several times with sat. aq. $NaHCO_3$, and finally with water. Removal of solvent led to a yellow oil (250 g, 90%): $C_{35}H_{69}O_4N$ (M = 567.93 g/mol), n_D^{20} = 1.45667. UV-vis: λ_{max} = 224 nm ($n \rightarrow \pi^*$). IR (neat, cm^{-1}): 1739 ($\nu_{C=O}$ ester), 1108 ($\nu_{C\text{-}O}$ ester), 1620 and 1653 ($\nu_{C=O}$ amide, 2 conformers), 1166 ($\nu_{C\text{-}N}$), 1078 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2955 to 2855 (ν_{CH} CH_2, CH_3), 1467 (δ_{CH} CH_2, CH_3). ^1H NMR δ (ppm): 0.85 (*m*, 12 H, CH_3); 1.25 (*m*, 36 H, CH_2); 1.6 (*m*, 8 H, CH_2 β from O, N and C=O); 2.3 [*m*, 4 H, $CH_2C(O)N$, $CH_2C(O)O$]; 3.3 [*m*, 4 H, C(O)-N-CH_2, CH_2-O]; 3.6 (AB, 2 H, CH–CH_2–N–C=O, J_{AB} = 13.5 Hz); 5.0, 5.15 (*m*, 0.5 H + 0.5 H, CH, 2 isomers). ^{13}C NMR δ (ppm): splitting of peaks due to two configurational isomers; 14.0, 14.1 (CH_3); 22.6 to 31.7 (CH_2); 34.3 (CH_2–C=O); 46.3, 46.4, 47.5, 48.7 (2



SCHEME 5



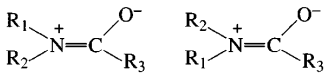
4a

SCHEME 6

CH_2–N); 71.2, 71.5 (*C*H–OCO); 69.1, 70.3, 71.5, 71.6 (2 CH_2–O); 172.9, 173.2 (O=C–N); 173.9, 174.1 (O=C–O). The same procedure was employed to prepare the other acylated derivatives, but different amounts of octanoyl chloride and triethylamine were used. The yields were comparable.

Synthesis of 1-dibutylamino-3-(6-octanoyloxy hexyloxy)-2-octanoyloxy propane (**3c**). Octanoyl chloride (185 mL, 1.07 mol), 152 g (0.5 mol) of 1-dibutylamino-3-(6-hydroxy hexyloxy)-2-propanol (**I**), 140 mL (1 mol) of triethylamine: $C_{33}H_{65}O_5N$ (M = 555.87 g/mol), n_D^{20} = 1.45566. UV-vis: λ_{max} = 226 nm ($n \rightarrow \pi^*$). IR (neat, cm^{-1}): 1737 ($\nu_{C=O}$ ester), 1108, 1050 ($\nu_{a\ C\text{-}O\text{-}C}$ ether, $\nu_{C\text{-}O}$ ester), 2930 to 2858 (ν_{CH} CH_2, CH_3), 1465 (δ_{CH} CH_2, CH_3). ^{1}H NMR δ (ppm): 0.8 (*m*, 12 H, CH_3); 1.2 (*m*, 24 H, CH_2); 1.5 (*m*, 12 H, CH_2 β from O, N and C=O); 2.2 (*m*, 4 H, CH_2–C=O); 2.4 (*td*, 4 H, CH_2–N); 2.6 (2 AB, 2 H, CH–CH_2–N, J_{AB} = 13.6 Hz); 3.4 (*m*, 4 H, CH_2–O); 4 [*t*, 2 H, CH_2–O–C(O), *J* = 6.6 Hz]; 5.1 (*m*, 1 H, CH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 20.5 to 31.7 (CH_2); 34.5, 35.3 [*C*H_2C(O)O]; 54.2 (CH_2–N); 54.5 [N(CH_2)$_2$]; 64.2 [CH_2–O–C(O)]; 70.6, 71.2 (CH_2–O); 71.0 (CH); 173.3, 173.5, 173.9 (C=O).

*Synthesis of di-[3-(*N*-octyl octamido)-2-octanoyloxy propyloxy] hexamethylene* (**4a**).Octanoyl chloride (370 mL, 2.15 mol), 245 g (0.5 mol) of di[(2-hydroxy-3-octylamino) propyloxy] hexamethylene (**II**), 280 mL (2 mol) of triethylamine: $C_{60}H_{116}O_8N_2$ (M = 992.16 g/mol), n_D^{20} = 1.45967. UV-vis: λ_{max} = 222 nm ($n \rightarrow \pi^*$). IR (neat, cm^{-1}): 1738 ($\nu_{C=O}$ ester), 1110 ($\nu_{C\text{-}O}$ ester), 1650 ($\nu_{C=O}$ amide), 1080 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2955 to 2855 (ν_{CH} CH_2, CH_3), 1421 and 1465 (δ_{CH} CH_2, CH_3). ^{1}H NMR δ (ppm): 0.85 (*m*, 18 H, CH_3); 1.25 (*m*, 56 H, CH_2); 1.5 (*m*, 16 H, CH_2 β from O, N and C=O); 2.3 [*t*, 8 H, CH_2–C(O)O, CH_2–C(O)N]; 3.3 [*m*, 16 H, CH_2–N–C(O), CH_2–O]; 5.1 (*m*, 2 H, CH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 22.6 to 33.0 (CH_2); 34.3, 34.5 [*C*H_2C(O)O, *C*H_2C(O)N]; 46.1, 48.8 (CH_2–N); 70.4, 71.7 (CH_2–O); 71.1 (CH); 173.2, 173.9 (C=O ester, amide).



SCHEME 7

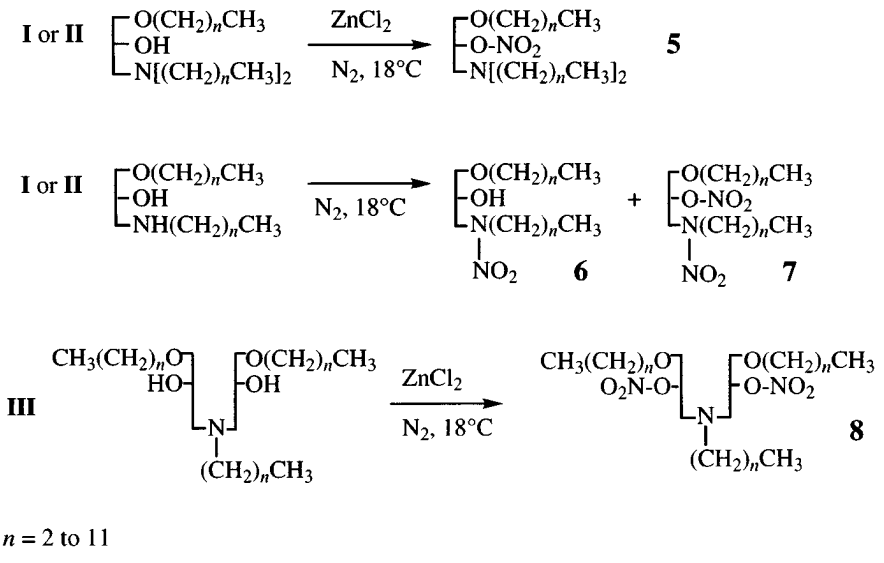
NITRATION OF ALCOHOL AND AMINO FUNCTIONS

In novel nitration methods, generally, nitrated tetrafluoroborate salts (15,16) or transfer nitration agents (17,18) are used. Satisfactory results were not obtained with such methods, and we therefore employed a conventional nitration method with acid mixture. The nitration products were obtained in the absence of water or solvent in the medium. These experimental conditions afforded products of high purity without using an elaborated nitration agent. The same procedure was applied to the different alkanolamine ethers and led to the nitrate **5**, the nitramines **6** and **7** or the dinitrate product **8** (Scheme 8).

A Lewis acid, such as zinc chloride, improved the quality of the final compound by a better control of the exothermicity of the reaction. These reagents enhanced nitration of hydroxyl sites according to the mechanism decribed by Chute and coworkers (19,20). Amino sites were nitrated in the absence of metal salts to prevent quaternization of the amine function. Proportions of products **6** and **7** depended on the amount of reagent, although they could be separated by crystallization of the dinitrate **7** from pentane.

Synthesis of 1-dibutylamino-2-nitrato-3-octyloxy propane (**5**). Fuming nitric acid (5 mL) was added dropwise for 10 min to the stirred mixture of 1-dibutylamino-3-octyloxy-2-propanol (10 g, 0.032 mol) and $ZnCl_2$ (2.2 g, 0.016 mol), followed by dropwise addition of acetic anhydride (5 mL). The medium was stirred for 45 min at 18°C under nitrogen and then diluted in diethyl ether (50 mL). The mixture was neutralized by several extractions with water and then with sat. aq. $NaHCO_3$ until neutral pH of the aq. phase. The organic phase was dried with $MgSO_4$ before removing solvent. The crude product was purified on a silica chromatography column (eluted with Et_2O) to obtain 10.5 g of an orange oil (90%). The product was kept in solution (Et_2O) in the absence of light: $C_{19}H_{40}O_4N_2$ (M = 360.52 g/mol), n_D^{20} = 1.46470; UV-vis: λ_{max} = 226 nm ($n \rightarrow \pi^*$). IR (neat, cm^{-1}): 1635 ($\nu_{a\ NO_2}$), 1275 ($\nu_{s\ NO_2}$), 1123 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 1030 ($\nu_{C\text{-}O}$ alcohol), 2950 to 2810 (ν_{CH} CH_2, CH_3), 1465 (δ_{CH} CH_2, CH_3). ^{1}H NMR δ (ppm): 0.85 (*m*, 9 H, CH_3); 1.25 (*m*, 14 H, CH_2); 2.4 (*t*, 4 H, N–CH_2, *J* = 6.2 Hz); 2.6 (*d*, 2 H, CH_2–N, *J* = 6.0 Hz); 3.3 (AA′ part of AA′XX′ system, 2 H, O–CH_2); 3.6 (2 *dd*(AMX), 2 H, CH–CH_2–O, J_{AM} = 0.66 Hz, J_{AX} = 3.8 Hz, J_{MX} = 5.9 Hz); 5.2 (*m*, 1 H, CH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 20.5 to 31.6 (CH_2); 53.3 (CH_2–N); 54.6 [N(CH_2)$_2$]; 69.1, 71.6 (CH_2–O); 81.4 (CH–NO_2). MS (*m/z*): 361 (M + 1); 316 [361 − 46 (NO_2^+)]; 190 [316 − 126 ($C_8H_{16}N^+$)]; 176 [190 − 14 (CH_2^+)]; 130 [176 − 46 ($C_2H_5OH^+$)].

N-*(2-hydroxy-3-octyloxy propyl),* N-*octyl nitramine* (**6**) *and* N-*(2-nitrato-3-octyloxy propyl),* N-*octyl nitramine* (**7**). Fuming nitric acid (25 mL) was added dropwise for 15 min to 1-octylamino-3-octyloxy-2-propanol (80 g, 0.25 mol) under stirring, followed by dropwise addition of acetic anhydride (23 mL). The medium was stirred for 3 h at 18°C under nitrogen and was then diluted in diethyl ether (100 mL). The mixture was neutralized by several extractions with water and then with sat. aq. $NaHCO_3$. The organic phase was dried



SCHEME 8

($MgSO_4$) before removing solvent. Compound **8** was crystallized from pentane to give a white solid (40 g), while 60 g of **7** were obtained as an orange oil. The product was kept in solution (Et_2O) in the absence of light: (**6**) $C_{19}H_{39}O_6N_3$ (M = 405.52 g/mol). IR (neat, cm^{-1}): 1050 ($\nu_{C\text{-}O}$ alcohol), 1663 ($\nu_{a\ NO_2}$), 1291 ($\nu_{s\ N\text{-}NO_2}$), 1120 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2955 to 2855 (ν_{CH} CH_2, CH_3), 1398 (δ_{CH} CH_2, CH_3). ^1H NMR δ (ppm): 0.85 (*t*, 6 H, CH_3); 1.25 (*m*, 20 H, CH_2); 1.5 (*m*, 2 H, CH_2 β from N); 1.65 (*m*, 2 H, CH_2 β from O); 3.4 (*m*, 6 H, CH_2–O, CH_2–N); 3.6 (*d*, 2 H, CH_2–O); 5.5 (*m*, 1 H, CH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 22.6 to 31.8 (CH_2); 49.2, 46.6 (CH_2–N); 78.1 (CH); 72.2, 66.8 (CH_2–O). (**7**) $C_{19}H_{40}O_4N_2$ (M = 360.52 g/mol), n_D^{20} = 1.46570. UV-vis : λ_{max} = 260 nm ($n \rightarrow \pi^*$). IR (neat, cm^{-1}): 3166 (ν_{OH}), 1050 ($\nu_{C\text{-}O}$ alcohol), 1635 ($\nu_{a\ NO_2}$), 1275 ($\nu_{s\ NO_2}$), 1120 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2955 to 2855 (ν_{CH} CH_2, CH_3), 1463 (δ_{CH} CH_2, CH_3). ^1H NMR δ (ppm): 0.85 (*t*, 6 H, CH_3); 1.25 (*m*, 20 H, CH_2); 1.5 (*m*, 2 H, CH_2 β from N); 1.65 (*m*, 2 H, CH_2 β from O); 3.4 (XX′ part of AA′XX′ + doublet, 4 H, CH_2–O); 3.6 to 3.9 (*m*, 4 H, CH_2–N); 4.1 (*m*, 1 H, CH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 22.6 to 31.8 (CH_2); 53.2, 54.4 (CH_2–N); 66.2 (CH); 71.8, 72.2 (CH_2–O). ^{15}N NMR δ (ppm): 354.5 (NO_2); 183.3 (*N*–NO_2); MS (*m/z*): 379 [M + 18 (NH_4^+)]; 361 (M + 1); 316 [361 − 46 (NO_2^+)]; 298 [361 − 63 (HNO_3^+)]; 190 [316 − 126 ($C_8H_{16}N^+$)].

N,N-*di-(2-nitrato-3-octyloxy propyl) octylamine* (**8**). Fuming nitric acid (8 mL) was added dropwise for 10 min to a stirred mixture of *N,N*-di-(2-hydroxy-3-octyloxy propyl) octylamine (15 g, 0.03 mol) and $ZnCl_2$ (2 g, 0.015 mol), followed by dropwise addition of acetic anhydride (7 mL). The medium was stirred for 1 h at 18°C under nitrogen and was then diluted in diethyl ether (50 mL). The mixture was neutralized by several extractions with water, then with sat. aq. $NaHCO_3$. The organic phase was dried ($MgSO_4$) before removing solvent to give 16 g of an orange oil (90%). The product was kept in solution (Et_2O) in the absence of light. $C_{30}H_{61}O_8N_3$ (M = 591.81 g/mol), n_D^{20} = 1.46068. UV-vis: λ_{max} = 250 nm ($n \rightarrow \pi^*$). IR (neat, cm^{-1}): 1633 ($\nu_{a\ NO_2}$), 1275 ($\nu_{s\ NO_2}$), 1128 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 1044 ($\nu_{C\text{-}O}$ alcohol), 2925 to 2855 (ν_{CH} CH_2, CH_3), 1465 (δ_{CH} CH_2, CH_3). ^1H NMR δ (ppm): 0.85 (*t*, 9 H, CH_3); 1.25 (*m*, 32 H, CH_2); 1.5 (*m*, 4 H, CH_2 β from O); 2.7 (XX′ part of AA′XX′ system, 2 H, N–CH_2); 3.4 (*m*, 4 H, CH–CH_2–N); 3.5 (*m*, 8 H, CH_2–O); 5.1 (*m*, 2 H, CH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 22.7 to 31.6 (CH_2); 53.8, 54.0, 55.5 (CH_2–N); 69.1, 71.9 (CH_2–O); 80.9, 81.0 (CH–NO_2). ^{15}N NMR δ (ppm): 380.2 (O–NO_2); 195.9 (R_2N–C_8H_{17}). MS (*m/z*): 592 (M + 1); 379 [316 + 63 (HNO_3^+)]; 361 [379 − 18 (H_2O^+)]; 190 [316 − 126 ($C_8H_{16}N^+$)].

RESULTS AND DISCUSSION

Physicochemical properties. The compounds were tested in diesel fuel containing 15 vol% ethanol, at a proportion of 2 wt% in the blend. Additive **I** was sometimes combined with another additive, in the same formulation, at proportions of 2 × 1%. The synthesized compounds improved the characteristics of ethanol-diesel fuel blends. Firstly, the emulsifying power of the compounds improved the stability of the blend. The results listed in Table 1 show that the additives retarded the onset of turbidity due to phase separation. The performance of the tested molecules was compared to that of a conventional cetane improver (Octel CI-0801; Octel Company, London, England).

The nitrate derivatives **5**–**8** were good cetane improvers (Table 2). The resulting blends thus possess satisfactory self-ignition characteristics. The dinitrated derivatives **7** and **8** appeared to be the most efficient.

Despite the hindered phenolic group in compound **2**, derivatives **2** and **I** had similar antioxidative activity. A mixture of compounds **I** and **6** also afforded resistance to oxidation,

TABLE 1
Stability of 15% Ethanol Blends with 2% Additive, Tested Under Influence of a Progressive Increase in Hydration

10-mL samples Compounds with $n = 7$, $m = 7$, $r = 6$	Duration of phase stability
Blend without additive	1 h
Octel CI[a]	1 h 30
2	4 h
3b	4 h
3c	2 h
4a	4 h 30
5	3 h
6	4 h
I + **6**	6 h

[a]Octel CI is the commercial name for 2-ethyl hexyl nitrate.

although the nitrated compounds tend to be susceptible to oxidation (Table 3). Moreover, the ability to lower the cold-flow temperature in the blend was improved for molecules that possessed good emulsifying power, such as **3b**, **4a**, or **6** (Tables 1 and 4).

The derivatives also behaved as potential lubricants by improving the viscosity of the blend. The additives stabilized the viscosity around 2 mPa · s when the temperature reached 50°C (Fig. 1). Two types of behavior were observed. Compounds such as the ester derivatives induced a 40% gain in viscosity at 50°C (curve b), while the other compounds (**6** or **8**) led to a greater gain in viscosity, between 65 and 80% (curves c and d). The thermal decomposition line shape of the latter compounds indicated a polycondensation, which could favor formation of a lubricating film.

In fact, we noted that the combination of structure **I** with a nitrate derivative generated good polyfunctional activity (Tables 1–4).

Engines tests. Compared with conventional diesel fuel, the blended fuel presented the same engine efficiency (8,9). With 10% ethanol and 2% additives, the ignition delay of a diesel fuel was preserved. With 20% ethanol and 2% additives, the oxides of nitrogen emissions were reduced between 5 and 10%, depending on the load point. The smoke also decreased between 30 and 60%. At cold start, the engine presented better behavior when the blend was augmented with 2% additives.

TABLE 2
Cetane Number Determination (CFR engine) for 15% Ethanol Diesel Fuel Blends with 2% Additive

Addition components ($n = 7$)	Cetane number (NF M07-035)
Without additive	41.0
5	46.5
6	44.5
7	49.5
8	47.5
I + **7**	47.0

TABLE 3
Antioxidative Activity (NF M07-047) for the Blends, Standard Hydrocarbon Base + 2% Additive

Addition components R = H or ≠ H	Insoluble substances generated under accelerated oxidation conditions (mg/mL)
Without additive	8
I	1–1.5
2	1
6 + **I**	2–2.5

TABLE 4
Low-Temperature Flow (LTF) Determination for 15% Ethanol Blends with 2% Additive

Addition components ($n = 7$, $m = 7$, $r = 6$)	LTF (°C) (NF M07-042)
Without additive	–12
2	–16
3b	–18
3c	–14
4a	–18
6	–19
6 + **I**	–18

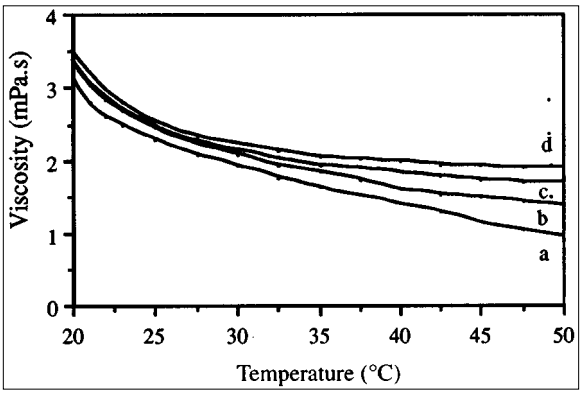


FIG. 1. Effect of additives on the viscosity curve as a function of temperature. a) Diesel fuel + 15% ethanol = B; b) B + 2% addtive (**2** to **5**); c) B + 2% additive (**III** or **8**); d) B + 2% additive **6**.

Finally, the production cost for these synthetic procedures was modest (8). The multifunctional activity of the compounds makes them particularly attractive, especially because only low proportions are required. A ternary fuel blend, such as diesel fuel–ethanol additive, may thus have potential as an alternative to diesel fuel (21).

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