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LETTERS TO THE EDITOR

Effect of the Structure of Adamantane-Containing Diesters on the Thermooxidative Stability

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Various derivatives of dicarboxylic acids of the adamantane series are suggested for application as components of drugs, catalysts, polymeric and fuels and lubricating materials or additives to them. Great interest of researchers is explained by liophilicity, high thermal and thermooxidative stability of adamantane and its derivatives [1–7]. However, until now there was no information on the methods allowing to estimate the thermooxidative stability of the adamantane derivatives of various structures and to define the limits of their application.

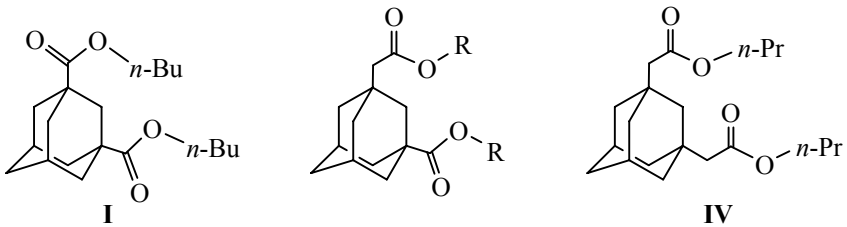
The goal of the present study was to investigate thermooxidative properties of diesters of 1,3-disubstituted dicarboxylic acids of the adamantane series (1,3-adamantane dicarboxylic acid, 3-carboxy-1-adamantylacetic acid, 1,3-adamantyldiacetic acid). In order to examine the effect of the nature of the acidic residues in the adamantane fragment on the thermooxidative stability a series of diesters with short normal alcohol residues C_3–C_4 and the total number of carbon atoms in the molecule of 19–21 was chosen. The esterification was carried out in the presence of *p*-toluenesulfonic acid, the yields of diesters **I–IV** were 71–91% (Scheme 1).

To determine the thermooxidative stability we have used the method of differential scanning calorimetry at high pressure (PDSC), which is widely used for investigation of thermooxidative properties of various oils and their components (CEC L-85-99, ASTM D6186-08, ASTM E2009-08) [8–11].

The results of investigation of thermooxidative stability (the ability to resist oxidation without antioxidative additives) of diesters **I–IV** by ASTM E2009 are shown in the figure as the temperature of the oxidation (extrapolated) onset temperature (OOT).

From these data it is evident that homologous adamantane-containing esters **I–IV**, differing by 1 or 2 methylene bridges between the adamantane backbone and the carboxy group have different

Scheme 1.



R = *p*-Pr (**II**), *p*-Bu (**III**).

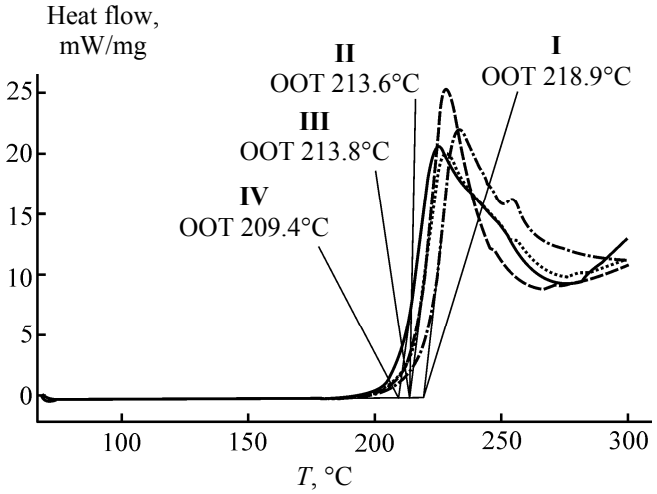
thermooxidative stability. The presence of methylene groups at the bridge-head positions of the adamantane structure decreases the onset oxidative temperature by 4–5°C. Apparently, this is due to a decrease in the steric shielding of the carbonyl carbon atoms of one or two carboxy groups present in the molecules. The length of the normal alcohol residue (esters **II** and **III**) does not seriously affect the value of the temperature of the oxidation onset.

The highest thermooxidative stability among the examined compounds is observed for dibutyl 1,3-adamantanedicarboxylate.

General procedure for the synthesis of compounds I–IV. A mixture of 0.137 mol of the corresponding acid, 0.549 mol of propanol (butanol), and 0.018 mol of *p*-toluenesulfonic acid in 120 mL of toluene was heated at reflux with Dean-Stark trap in the course of 10 h. After separation of the required amount of water the mixture was diluted with 100 mL of toluene, washed with 15% aqueous sodium hydrogen carbonate to pH = 7, then with water, and dried over sodium sulfate. The solvent was removed, the residue was purified by vacuum distillation.

Dibutyl 1,3-adamantanedicarboxylate (I). Yield 88%. bp 160–163°C (0.2 mmHg), n_D^{20} = 1.4799. IR spectrum, ν, cm^{-1}: 1728 (C=O). ^1H NMR spectrum, δ, ppm: 0.87 t (6H, CH_3, J = 7.4 Hz), 1.26–1.36 m (4H, CH_2), 1.50–1.56 m (4H, CH_2), 1.60–1.62 m (4H, CH_2Ad), 1.75–1.83 m (8H, CH_2Ad), 1.95 (2H, CH_2Ad), 2.06–2.09 m (2H, CHAd), 3.99 t (4H, CH_2, J = 6.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.75 (CH_3), 19.19 (CH_2), 27.91 (CH), 30.72 (CH_2), 35.45 (CH_2), 38.02 (CH_2), 39.86 (CH_2), 41.00 (C), 64.17 (CH_2), 176.91(C). Mass spectrum, *m/z* (I_{rel}, %): 336 (5) $[M]^+$, 281 (100), 235 (30), 225 (40), 179 (20), 133 (22). Found, %: C 71.42; H 9.62. $C_{20}H_{32}O_4$. Calculated, %: C 71.39; H 9.59. *M* 336.48

Dipropyl 3-carboxy-1-adamantylacetate (II). Yield 83%. bp 133–138°C (0.05 mmHg), n_D^{20} = 1.4830. IR spectrum, ν, cm^{-1}: 1728 (C=O). ^1H NMR spectrum, δ, ppm: 0.91 t (6H, CH_3, J = 7.4 Hz), 1.56–1.62 m (10H, CH_2Ad), 1.72–1.73 m (4H, CH_2Ad, CH_2), 1.74–1.83 m (2H, CH_2), 2.05–2.07 m (2H, CHAd), 2.09 s (2H, CH_2), 3.96–3.98 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 10.49 (CH_3), 10.61 (CH_3), 22.09 (CH_2), 28.38 (CH), 32.98 (C), 35.67 (CH_2), 38.19 (CH_2), 41.33 (CH_2), 41.51 (C), 43.51 (CH_2), 48.49 (CH_2), 65.79 (CH_2), 171.62 (C), 177.30 (C). Mass spectrum, *m/z* (I_{rel}, %): 322 (2) $[M]^+$, 281 (60), 239 (43), 235 (87), 221 (33), 193 (62), 179 (38), 147 (40), 133 (100), 91 (86), 43 (69). Found, %: C 71.80; H 9.42. $C_{19}H_{30}O_4$. Calculated, %: C 70.74; H 9.38. *M* 322.44.



Thermooxidative stability by ASTM E2009 of esters of 1,3-substituted dicarboxylic acids of adamantane series.

Dibutyl 3-carboxy-1-adamantylacetate (III). Yield 71%. bp 140–148°C (0.026 mmHg), n_D^{20} = 1.4813. IR spectrum, ν, cm^{-1}: 1728 (C=O). ^1H NMR spectrum, δ, ppm: 0.92 t (6H, CH_3, J = 6.9 Hz), 1.34–1.38 m (4H, CH_2Ad), 1.56–1.59 m (10H, CH_2Ad, CH_2), 1.72–1.74 m (2H, CH_2), 1.75–1.81 m (4H, CH_2), 2.07–2.08 m (2H, CH), 2.1 s (2H, CH_2), 4.02–4.04 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 13.79 (CH_3), 13.84 (CH_3), 19.25 (CH_2), 19.30 (CH_2), 28.39 (CH), 30.77 (CH_2), 33.01 (C), 35.67 (CH_2), 38.20 (CH_2), 41.33 (CH_2), 41.58 (C), 43.53 (CH_2), 48.52 (CH_2), 64.04 (CH_2), 64.14 (CH_2), 171.67 (C), 177.35 (C). Mass spectrum, *m/z* (I_{rel}, %): 350 (<1) $[M]^+$, 295 (65), 249 (55), 239 (100), 235 (25), 193 (89), 179 (50), 147 (37), 133 (98), 91 (75), 57 (38). Found, %: C 72.00; H 9.83. $C_{21}H_{34}O_4$. Calculated, %: C 71.96; H 9.78. *M* 350.49.

Dipropyl 1,3-adamantanediacetate (IV). Yield 91%. bp 160–163°C (0.02 mmHg), n_D^{20} = 1.4842. IR spectrum, ν, cm^{-1}: 1730 (C=O). ^1H NMR spectrum, δ, ppm: 0.82 t (6H, CH_3, J = 7.3 Hz), 1.36–1.53 m (16H, CH_2Ad, CH_2), 1.93–1.94 m (2H, CHAd), 1.97 s (4H, CH_2), 3.88 t (4H, CH_2, J = 6.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 10.53 (CH_3), 22.03 (CH_2), 28.85 (CH), 33.35 (C), 35.78 (CH_2), 41.42 (CH_2), 47.21 (CH_2), 48.44 (C), 65.55 (CH_2), 171.55 (C). Mass spectrum, *m/z* (I_{rel}, %): 336 (8) $[M]^+$, 277 (15), 248 (14), 235 (100), 193 (48), 175 (23), 147 (35), 133 (52), 91 (59), 43 (62). Found, %: C 71.42; H 9.63. $C_{20}H_{32}O_4$. Calc, %: C 71.39; H 9.59. *M* 336.48.

^{1}H, ^{13}C NMR spectra were registered on a Jeol JNM ECX-400 (400 MHz) spectrometer in $CDCl_3$. Mass spectra were obtained on a ThermoFinnigan DSQ chromatomass spectrometer with a capillary column BPX-5 30 × 0.32 and the energy of ionizing electrons 70 eV. Elemental analysis was performed on a EuroVector 3000 EA analyzer with L-cystine as a standard. FTIR spectra were taken on a Shimadzu IR Affinity-1 spectrophotometer in thin layer.

Thermooxidative stability of the samples in thin layer was investigated using the method of differential scanning calorimetry at high pressure (PDSC) by ASTM E2009 (method B) in aluminum crucibles in oxygen atmosphere (35 atm) in dynamic regime (from 70 to 300°C with the heating rate 10°C/min) on a DSC 204 HP Phoenix NETZSCH-Gerätebau GmbH instrument (Germany).

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