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Synthesis of New 1-Adamantanecarboxylic Acid Derivatives

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Abstract—Reactions of 1-adamantanecarbonyl chloride with functionally substituted alcohols, phenols, amines, thiols, and ketone oximes gave hitherto unknown 1-adamantanecarboxylic acid esters, amides, and thio esters, including those containing a peroxide group.

Continuously increasing number of studies on the synthesis and properties of adamantane derivatives is explained by the high biological activity of these compounds [1, 2]. Adamantane derivatives exhibit antiviral, curare-like, myorelaxing, anti-choline esterase, psychostimulating, neurotropic, and local anaesthetic activity [1]. Such efficient drugs as Midantan, Memantine, Gludantan, Amantadine, and Adapromin have been developed on the basis of compounds containing an adamantane fragment [3]. In the recent years, considerable efforts were made to develop methods of synthesis of adamantane derivatives having pharmacophoric fragments with a view to reveal new biologically active substances [4–22].

The goal of the present work was to synthesize new 1-adamantanecarboxylic acid esters, thio esters, and amides. As initial compounds we selected functionally substituted alcohols and phenols **Ia**–**Xa**, amines **XXIa**–**XXVIIIa**, thiols **XXIXa**–**XXXIb**, and ketone oximes **XXXIIa**–**XXXIVa**. The corresponding esters **Ib**–**Xb**, amides **XXIb**–**XXVIIIb**, thio esters **XXIXb**–**XXXIb**, and ketone oxime esters **XXXIIb**–**XXXIVb** were synthesized by heating of 1-adamantanecarbonyl chloride (**XXXV**) with compounds **Ia**–**XXXIVa** in boiling dry benzene in the presence of pyridine. The yields of products **Ib**–**XXXIVb** were 70–95%.

The structure of 1-adamantanecarboxylic acid derivatives **Ib**–**XXXIVb** was confirmed by their elemental compositions, molecular weights, and IR, UV, and ^{1}H NMR spectra. The purity of the products was 98±1%.

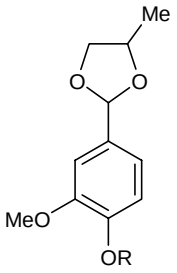
EXPERIMENTAL

The IR spectra were obtained on a Protege-460 Fourier spectrometer from samples prepared as KBr pellets (compounds **Ib**, **IVb**–**IXb**, **XXIb**–**XXIXb**, **XXXIIb**, and **XXXIVb**) or thin films (neat; **IIb**, **IIIb**, **Xb**–**XXb**, **XXXb**, **XXXIb**, **XXXIIIb**). The ^{1}H NMR spectra were recorded on a Tesla 587A spectrometer (100 MHz) from solutions in $CDCl_3$; the chemical shifts were measured in the δ scale relative to octamethyltrisiloxane (OMTS) as internal reference. The UV spectra were obtained on a Specord UV spectrophotometer from 1×10^{-3} M solutions in 1-butanol. The molecular weights were determined by cryoscopy in benzene. Neutral aluminum oxide L 40/250 μm (Brockman activity grade II) was used for column chromatography. Peroxy-containing alcohols **XIIa**–**XXa** were synthesized by the procedure described in [23]; 1-adamantanecarbonyl chloride (**XXXV**) was prepared by treatment of 1-adamantanecarboxylic acid with thionyl chloride in benzene as described in [24].

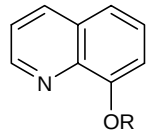
1-Adamantanecarboxylic acid derivatives Ib–**XXXIVb (***general procedure***).** Compound **Ia**–**XXXIVa**, 10 mmol, was dissolved in 130 ml of dry benzene, and approximately 30 ml of the solvent was distilled off to remove water (as azeotrope) adsorbed by the initial compound. The solution was cooled, and 2 g (10 mmol) of 1-adamantanecarbonyl chloride (**XXXV**) and 1.2 g (15 mmol) of anhydrous pyridine were added in one portion. The mixture was heated for 8 h under reflux and cooled, the precipitate of pyridine hydrochloride was filtered off, and the filtrate was

Ia, **Ib**

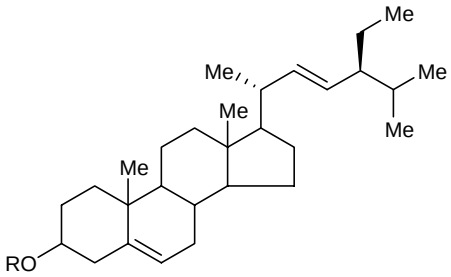
IIa, **IIb**



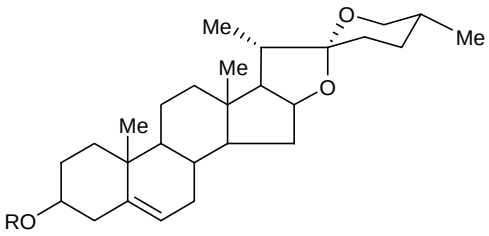
IIIa, **IIIb**



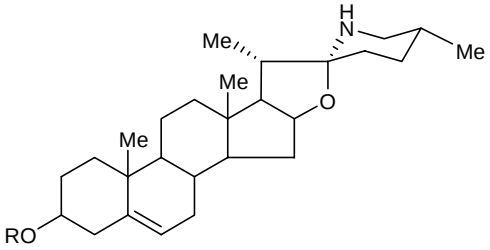
IVa, **IVb**



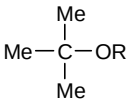
Va, **Vb**

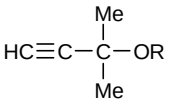


VIa, **VIb**



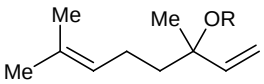
VIIa, **VIIb**



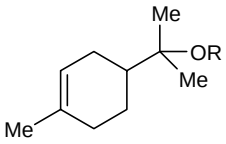


VIIIa, **VIIIb**

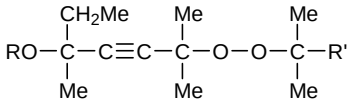
IXa, **IXb**



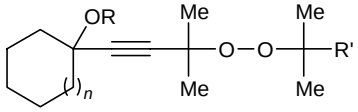
Xa, **Xb**



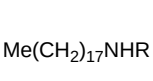
XIa, **XIb**



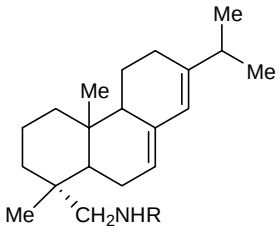
XII–**XIV**



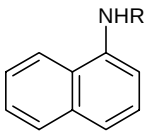
XV–**XX**



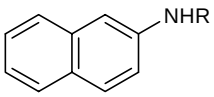
XXIa, **XXIb**



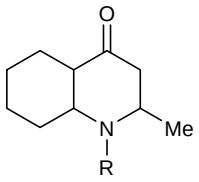
XXIIa, **XXIIb**



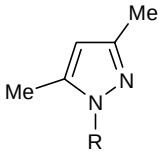
XIIIa, **XXIIIb**



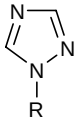
XXIVa, **XXIVb**



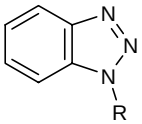
XXVa, **XXVb**



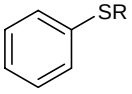
XXVIa, **XXVIb**



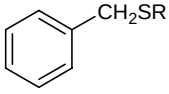
XXVIIa, **XXVIIb**



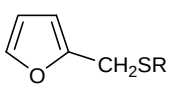
XXVIIIa, **XXVIIIb**



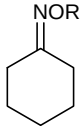
XXIXa, **XXIXb**



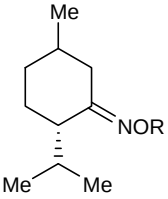
XXXa, **XXXb**



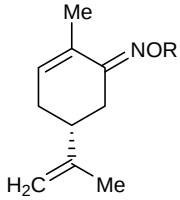
XXXIa, **XXXIb**



XXXIIa, **XXXIIb**



XXXIIIa, **XXXIIIb**



XXXIVa, **XXXIVb**

I–**XXXIV**, R = H (**a**), 1-AdCO (**b**); **XII**, R' = Me; **XIII**, R' = Et; **XIV**, R' = Pr; **XV**, R' = Me, *n* = 1; **XVI**, R' = Pr, *n* = 1; **XVII**, R' = Me, *n* = 2; **XVIII**, R' = Et, *n* = 2; **XIX**, R' = Pr, *n* = 2; **XX**, R' = Et, *n* = 7.

washed with water (3×50 ml) and a 5% aqueous solution of sodium hydrogen carbonate (3×50 ml), and dried over calcium chloride. The drying agent was filtered off, and the filtrate was evaporated. Compounds **Ib**, **IVb**–**IXb**, **XXIb**–**XXIXb**, **XXXIIb**, and **XXXIVb** were purified by low-temperature crystallization, and **IIb**, **IIIb**, **Xb**–**XXb**, **XXXb**, **XXXIb**, and **XXXIIIb**, by column chromatography on aluminum oxide using hexane as eluent. The waste solvents (benzene and hexane) were reused after distillation over lithium aluminum hydride.

1-Heptadecyl 1-adamantanecarboxylate (Ib). Yield 3.81 g (91%), mp 26–27°C (from 96% ethanol). IR spectrum, ν, cm^{-1}: 2950, 2917, 2850 (CH_{aliph}); 1726 (C=O); 1473, 1452 (CH_2); 1240, 1084 (C–O). UV spectrum, λ_{max}, nm (ε): 207 (150), 218 (200). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, Me, ^3J = 6.0 Hz), 1.15–2.15 m [30H, $(CH_2)_{15}$], 1.60–2.10 m (15H, $C_{10}H_{15}$), 4.04 t (2H, CH_2O, ^3J = 6.2 Hz). Found, %: C 80.46; H 12.22. *M* 409.7. $C_{28}H_{50}O_2$. Calculated, %: C 80.32; H 12.04. *M* 418.7.

2-Oxopropyl 1-adamantanecarboxylate (IIb). Yield 1.87 g (79%), d_4^{20} = 0.9877, n_D^{20} = 1.5035. IR spectrum, cm^{-1}: 3000, 2940, 2907, 2852 (CH_{aliph}); 1728 (C=O); 1452, 1418 (CH_2); 1236, 1177, 1088 (C–O). UV spectrum, λ_{max}, nm (ε): 208 (200), 255 (100). ^{1}H NMR spectrum, δ, ppm: 1.60–2.10 m (15H, $C_{10}H_{15}$), 2.15 s (3H, Me), 4.61 s (2H, CH_2). Found, %: C 71.28; H 8.63. *M* 230.4. $C_{14}H_{20}O_3$. Calculated, %: C 71.16; H 8.53. *M* 236.3.

2-Methoxy-4-(4-methyl-1,3-dioxolan-2-yl)phenyl 1-adamantanecarboxylate (IIIb). Yield 2.68 g (72%), d_4^{20} = 1.1123, n_D^{20} = 1.5395. IR spectrum, ν, cm^{-1}: 3070, 3025 (CH_{arom}), 2970, 2935, 2906, 2852 (CH_{aliph}); 1751 (C=O); 1603, 1509, 1453 ($C=C_{arom}$); 1455, 1423 (CH_2); 1277, 1215, 1200, 1180, 1161, 1119, 1102, 1070, 1050, 1040, 1009, 978 (C–O); 850, 820, 780, 735, 675 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 207 (9000), 220 (10000), 260 (4000), 277 (2000), 305 (1000). ^{1}H NMR spectrum, δ, ppm: 1.20–1.45 m (1H, C**H**Me), 1.60–2.20 m (15H, $C_{10}H_{15}$), 3.35–4.55 m (2H, CH_2), 3.83 s (3H, MeO), 5.78 s (1H, C**H**Ar), 6.80–7.55 m (3H, C_6H_3). Found, %: C 71.11; H 7.67. *M* 363.0. $C_{22}H_{28}O_5$. Calculated, %: C 70.95; H 7.58. *M* 372.5.

8-Quinolyl 1-adamantanecarboxylate (IVb). Yield 2.49 g (81%), mp 135–136°C (from benzene, hexane). IR spectrum, ν, cm^{-1}: 3100, 3060, 3050, 3040, 3010 (CH_{arom}); 2930, 2910, 2902, 2850 (CH_{aliph}); 1745 (C=O); 1650, 1625, 1590, 1570, 1498, 1430, 1390, 1360, 1310 (Ar); 1465, 1451 (CH_2), 1210, 1180, 1161, 1085 (C–O); 835, 810, 803, 783, 765, 753, 723, 705 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (15000), 227 (18000), 231 (18000), 280 (3000), 313 (2000). ^{1}H NMR spectrum, δ, ppm: 1.55–2.35 m (15H, $C_{10}H_{15}$), 7.00–8.95 m (6H, C_9H_6N). Found, %: C 78.22; H 7.03; N 4.23. *M* 296.9. $C_{20}H_{21}NO_2$. Calculated, %: C 78.15; H 6.89; N 4.56. *M* 307.4.

(24*S*)-Stigmasta-5,22-dien-3β-yl 1-adamantanecarboxylate (Vb). Yield 4.60 g (80%), mp 196–197°C (from 96% ethanol). IR spectrum, ν, cm^{-1}: 3030 (=CH); 2975, 2960, 2933, 2906, 2895, 2853, 2825 (CH_{aliph}); 1726 (C=O); 1670, 1640 (C=C); 1458 (CH_2); 1237, 1081 (C–O). UV spectrum, λ_{max}, nm (ε): 203 (9000). ^{1}H NMR spectrum, δ, ppm: 0.71 s (3H, 18-Me), 0.73–1.10 m (12H, 21-Me, 24-CH_2**Me**, 26-Me, 27-Me), 1.04 s (3H, 19-Me), 1.10–2.45 m (25H), 1.67–2.15 m (15H, $C_{10}H_{15}$), 4.30–4.95 m (1H, 3-H), 4.97–5.45 m (3H, 6-H, 22-H, 23-H). Found, %: C 83.71; H 11.02. *M* 559.2. $C_{40}H_{62}O_2$. Calculated, %: C 83.57; H 10.87. *M* 574.9.

(25*R*)-Spirost-5-en-3β-yl 1-adamantanecarboxylate (VIb). Yield 4.67 g (81%), mp 206–207°C (from 96% ethanol). IR spectrum, ν, cm^{-1}: 3030 (=CH); 2990, 2938, 2930, 2906, 2875, 2850 (CH_{aliph}); 1726 (C=O); 1660 (C=C); 1475, 1456 (CH_2); 1271, 1239, 1184, 1106, 1082, 1065, 1052, 1008, 899 (C–O). UV spectrum, λ_{max}, nm (ε): 204 (4000). ^{1}H NMR spectrum, δ, ppm: 0.80 s (3H, 18-Me), 1.05 s (3H, 19-Me), 0.70–1.15 m (6H, 2Me), 1.15–2.40 m (24H), 1.60–2.10 m (15H, $C_{10}H_{15}$), 3.15–4.75 m (4H, 3-H, 16-H, CH_2O), 5.25–5.45 m (1H, 6-H). Found, %: C 79.27; H 9.91. *M* 552.3. $C_{38}H_{56}O_4$. Calculated, %: C 79.12; H 9.78. *M* 576.9.

(25*R*)-Solasod-5-en-3β-yl 1-adamantanecarboxylate (VIIb). Yield 4.49 g (78%), mp 129–130°C (from 96% ethanol). IR spectrum, ν, cm^{-1}: 3284 (NH); 3030 (=CH); 2929, 2907, 2851 (CH_{aliph}); 1726 (C=O); 1656 (C=C); 1453 (CH_2); 1268, 1236, 1103, 1184, 1077 (C–O). UV spectrum, λ_{max}, nm (ε): 204 (4000). ^{1}H NMR spectrum, δ, ppm: 0.83 s (3H, 18-Me), 1.04 s (3H, 19-Me), 0.85–1.10 m (6H, 2Me), 1.10–2.85 m (26H), 1.60–2.05 m (15H, $C_{10}H_{15}$), 3.20–4.85 m (2H, 3-H, 16-H), 5.25–5.45 m (1H, 6-H). Found, %: C 79.34; H 10.11; N 2.21. *M* 553.6. $C_{38}H_{57}NO_3$. Calculated, %: C 79.26; H 9.98; N 2.43. *M* 575.9.

***tert*-Butyl 1-adamantanecarboxylate (VIIIb).** Yield 1.84 g (78%), mp 38–39°C (from hexane). IR spectrum, ν, cm^{-1}: 3003, 2975, 2920, 2852, 2815 (CH_{aliph}); 1711 (C=O); 1478, 1454 (CH_2); 1265, 1166,

1104, 1080 (C–O). UV spectrum, λ_{max}, nm (ε): 206 (250), 217 (200). ^{1}H NMR spectrum, δ, ppm: 1.43 s (9H, Me_3C), 1.65–2.15 m (15H, $C_{10}H_{15}$). Found, %: C 76.41; H 10.34. *M* 220.8. $C_{15}H_{24}O_2$. Calculated, %: C 76.23; H 10.23. *M* 236.4.

1,1-Dimethyl-2-propynyl 1-adamantanecarboxylate (IXb). Yield 2.29 g (93%), mp 73–74°C (from hexane). IR spectrum, ν, cm^{-1}: 3265 (≡CH); 2994, 2940, 2925, 2904, 2878 (CH_{aliph}); 2115 (C≡C); 1727 (C=O); 1474, 1452 (CH_2); 1271, 1246, 1138, 1107, 1077 (C–O). UV spectrum, λ_{max}, nm (ε): 206 (200), 222 (150). ^{1}H NMR spectrum, δ, ppm: 1.66 s (6H, Me_2C), 1.65–2.15 m (15H, $C_{10}H_{15}$), 2.50 m (1H, C≡C). Found, %: C 78.23; H 9.08. *M* 227.7. $C_{16}H_{22}O_2$. Calculated, %: C 78.01; H 9.00. *M* 246.3.

1,5-Dimethyl-1-vinyl-4-hexenyl 1-adamantanecarboxylate (Xb). Yield 2.75 g (87%), d_4^{20} = 0.9415, n_D^{20} = 1.4970. IR spectrum, ν, cm^{-1}: 3088 (=CH); 2969, 2940, 2907, 2852 (CH_{aliph}); 1726 (C=O); 1680, 1644 (C=C); 1453 (CH_2); 1269, 1236, 1103, 1077 (C–O). UV spectrum, λ_{max}, nm (ε): 204 (10 000), 212 (8000). ^{1}H NMR spectrum, δ, ppm: 1.52 s (6H, **Me**$_2$C=), 1.61 s (3H, 1-Me), 1.60–2.20 m (19H, C^2H_2, C^3H_2, $C_{10}H_{15}$), 4.90–6.20 m (4H, $=CH_2$, CH=, 4-H). Found, %: C 79.96; H 10.25. *M* 307.2. $C_{21}H_{32}O_2$. Calculated, %: C 79.70; H 10.19. *M* 316.5.

Dimethyl(4-methyl-3-cyclohexenyl)methyl 1-adamantanecarboxylate (XIb). Yield 2.82 g (89%), d_4^{20} = 1.0426, n_D^{20} = 1.5070. IR spectrum, ν, cm^{-1}: 3050 (=CH); 3002, 2975, 2955, 2935, 2906, 2851 (CH_{aliph}); 1722 (C=O); 1679 (C=C); 1427 (CH_2); 1268, 1242, 1133, 1103, 1078 (C–O). UV spectrum, λ_{max}, nm (ε): 204 (4000). ^{1}H NMR spectrum, δ, ppm: 1.43 d (6H, Me_2C, ^4J = 2.1 Hz), 1.66 s (3H, Me), 1.55–2.75 m [7H, CH, CH_2, $(CH_2)_2$], 1.65–2.15 m (15H, $C_{10}H_{15}$), 5.40 br.s (1H, =CH). Found, %: C 80.03; H 10.32. *M* 308.4. $C_{21}H_{32}O_2$. Calculated, %: C 79.70; H 10.19. *M* 316.5.

4-*tert*-Butyldioxy-1-ethyl-1,4-dimethyl-2-pentynyl 1-adamantanecarboxylate (XIIb). Yield 2.81 g (72%), d_4^{20} = 1.0435, n_D^{20} = 1.4750. IR spectrum, ν, cm^{-1}: 2979, 2933, 2908, 2853 (CH_{aliph}); 1736 (C=O); 1454 (CH_2); 1235, 1159, 1102, 1073 (C–O); 870 (O–O). UV spectrum, λ_{max}, nm (ε): 205 (200), 222 (150). ^{1}H NMR spectrum, δ, ppm: 1.02 t (3H, **Me**CH_2, ^3J = 7.1 Hz), 1.25 s (9H, Me_3C), 1.46 s (6H, Me_2C), 1.56 q (2H, CH_2, ^3J = 7.1 Hz), 1.62 s (3H, MeCC≡C), 1.65–2.15 m (15H, $C_{10}H_{15}$). Found, %: C 74.02; H 10.01. *M* 379.6. $C_{24}H_{38}O_4$. Calculated, %: C 73.81; H 9.81. *M* 390.6.

1-Ethyl-1,4-dimethyl-4-*tert*-pentyldioxy-2-pentynyl 1-adamantanecarboxylate (XIIIb). Yield 3.03 g (75%), d_4^{20} = 1.0118, n_D^{20} = 1.4740. IR spectrum, ν, cm^{-1}: 2978, 2934, 2908, 2853 (CH_{aliph}); 1736 (C=O); 1454 (CH_2); 1235, 1158, 1102, 1073 (C–O); 870 (O–O). UV spectrum, λ_{max}, nm (ε): 205 (200), 221 (150). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, **Me**CH_2Me_2C, ^3J = 7.1 Hz), 1.02 t (3H, **Me**$CH_2CC{\equiv}C$, ^3J = 7.1 Hz), 1.21 s (6H, Me_2COO), 1.36–1.58 m (4H, $2CH_2$), 1.45 s (6H, Me_2C), 1.62 s (3H, MeCC≡C), 1.70–2.10 m (15H, $C_{10}H_{15}$). Found, %: C 74.41; H 10.08. *M* 392.8. $C_{25}H_{40}O_4$. Calculated, %: C 74.22; H 9.96. *M* 404.6.

1-Ethyl-1,4-dimethyl-4-(1,1-dimethylbutyl)-2-pentynyl 1-adamantanecarboxylate (XIVb). Yield 3.26 g (78%), d_4^{20} = 0.9398, n_D^{20} = 1.4740. IR spectrum, ν, cm^{-1}: 2980, 2955, 2935, 2908, 2855 (CH_{aliph}); 1736 (C=O); 1454 (CH_2), 1235, 1158, 1102, 1073 (C–O), 863 (O–O). UV spectrum, λ_{max}, (ε): 206 (200), 222 (150). ^{1}H NMR spectrum, δ, ppm: 0.91 t [3H, **Me**$(CH_2)_2$, ^3J = 6.4 Hz], 1.02 t (3H, **Me**$CH_2CC{\equiv}C$, ^3J = 7.1 Hz), 1.22 s (6H, Me_2COO), 1.30–1.55 m [6H, CH_2, $(CH_2)_2$], 1.45 s (6H, Me_2C), 1.62 s (3H, MeCC≡C), 1.65–2.15 m (15H, $C_{10}H_{15}$). Found, %: C 74.70; H 10.24. *M* 407.3. $C_{26}H_{42}O_4$. Calculated, %: C 74.60; H 10.11. *M* 418.6.

1-(3-*tert*-Butyldioxy-3-methyl-1-butynyl)cyclohexyl 1-adamantanecarboxylate (XVb). Yield 3.04 g (73%), d_4^{20} = 1.0107, n_D^{20} = 1.4895. IR spectrum, ν, cm^{-1}: 2981, 2934, 2908, 2854 (CH_{aliph}); 1735 (C=O); 1453 (CH_2); 1230, 1186, 1158, 1103, 1072 (C–O); 875 (O–O). UV spectrum, λ_{max}, nm (ε): 205 (200), 221 (150). ^{1}H NMR spectrum, δ, ppm: 1.25 s (9H, Me_3C), 1.46 s (6H, Me_2C), 1.37–2.40 m [25H, $(CH_2)_5$, $C_{10}H_{15}$]. Found, %: C 75.14; H 9.83. *M* 404.9. $C_{26}H_{40}O_4$. Calculated, %: C 74.96; H 9.68. *M* 416.6.

1-[3-Methyl-3-(1,1-dimethylbutyldioxy)-1-butynyl]cyclohexyl 1-adamantanecarboxylate (XVIb). Yield 3.16 g (71%), d_4^{20} = 1.0109, n_D^{20} = 1.4900. IR spectrum, ν, cm^{-1}: 2982, 2955, 2933, 2908, 2853 (CH_{aliph}); 1735 (C=O); 1453 (CH_2); 1229, 1183, 1156, 1103, 1071 (C–O); 874 (O–O). UV spectrum, λ_{max}, nm (ε): 206 (200), 222 (150). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, Me, ^3J = 6.5 Hz), 1.22 s (6H, Me_2COO), 1.35–1.55 m [4H, $(CH_2)_2$], 1.48 s (6H, Me_2C), 1.65–2.05 m [25H, $(CH_2)_5$, $C_{10}H_{15}$]. Found, %: C 75.91; H 10.14. *M* 423.5. $C_{28}H_{44}O_4$. Calculated, %: C 75.63; H 9.97. *M* 444.7.

1-(3-*tert*-Butyldioxy-3-methyl-1-butynyl)cycloheptyl 1-adamantanecarboxylate (XVIIb). Yield

3.10 g (72%), d_4^{20} = 1.0416, n_D^{20} = 1.920. IR spectrum, ν, cm^{-1}: 2980, 2955, 2935, 2907, 2853 (CH_{aliph}); 1735 (C=O); 1453 (CH_2); 1234, 1181, 1156, 1103, 1073 (C–O); 870 (O–O). UV spectrum, λ_{max}, nm (ε): 205 (200), 222 (150). ^{1}H NMR spectrum, δ, ppm: 1.25 s (9H, Me_3C), 1.46 s (6H, Me_2C), 1.40–2.30 m [27H, $(CH_2)_6$, $C_{10}H_{15}$]. Found, %: C 75.62; H 10.00. *M* 414.2. $C_{27}H_{42}O_4$. Calculated, %: C 75.31; H 9.83. *M* 430.6.

1-(3-Methyl-3-*tert*-pentyldioxy-1-butynyl)cycloheptyl 1-adamantanecarboxylate (XVIIIb). Yield 3.25 g (73%), d_4^{20} = 1.0085, n_D^{20} = 1.4925. IR spectrum, ν, cm^{-1}: 2982, 2935, 2908, 2854 (CH_{aliph}); 1734 (C=O); 1454 (CH_2); 1233, 1182, 1157, 1103, 1072 (C–O); 872 (O–O). UV spectrum, λ_{max}, nm (ε): 205 (200), 223 (150). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, Me, ^3J = 6.8 Hz), 1.21 s (6H, Me_2COO), 1.45 s (6H, Me_2C), 1.42–2.24 m [29H, CH_2, $(CH_2)_6$, $C_{10}H_{15}$]. Found, %: C 75.88; H 10.20. *M* 422.7. $C_{28}H_{44}O_4$. Calculated, %: C 75.63; H 9.97. *M* 444.7.

1-[3-Methyl-3-(1,1-dimethylbutyldioxy)-1-butynyl]cycloheptyl 1-adamantanecarboxylate (XIXb). Yield 3.49 g (76%), d_4^{20} = 1.0210, n_D^{20} = 1.4930. IR spectrum, ν, cm^{-1}: 2983, 2945, 2920, 2851 (CH_{aliph}); 1735 (C=O); 1453 (CH_2); 1235, 1183, 1158, 1103, 1073 (C–O); 871 (O–O). UV spectrum, λ_{max}, nm (ε): 204 (200), 223 (150). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, Me, ^3J = 6.4 Hz), 1.22 s (6H, Me_2COO), 1.35–1.55 m [4H, $(CH_2)_2$], 1.45 s (6H, Me_2C), 1.55–2.05 m, [27H, $(CH_2)_6$, $C_{10}H_{15}$]. Found, %: C 76.12; H 10.27. *M* 430.4. $C_{29}H_{46}O_4$. Calculated, %: C 75.94; H 10.11. *M* 458.7.

1-(3-Methyl-3-*tert*-pentyldioxy-1-butynyl)cyclododecyl 1-adamantanecarboxylate (XXb). Yield 3.60 g (70%), d_4^{20} = 0.9906, n_D^{20} = 1.5065. IR spectrum, ν, cm^{-1}: 2970, 2925, 2851 (CH_{aliph}); 1732 (C=O); 1470, 1454 (CH_2); 1235, 1182, 1155, 1103, 1073 (C–O); 870 (O–O). UV spectrum, λ_{max}, nm (ε): 206 (200), 222 (150). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, Me, ^3J = 6.9 Hz), 1.20 s (6H, Me_2COO), 1.48 s (6H, Me_2C), 1.00–2.55 m [39H, CH_2, $(CH_2)_{11}$, $C_{10}H_{15}$]. Found, %: C 77.23; H 10.64. *M* 490.7. $C_{33}H_{54}O_4$. Calculated, %: C 77.00; H 10.57. *M* 514.8.

***N*-Octadecyl 1-adamantanecarboxamide (XXIb).** Yield 3.93 g (91%), mp 68–69°C (from 96% ethanol). IR spectrum, ν, cm^{-1}: 3308 (NH); 2955, 2916, 2850 (CH_{aliph}); 1632, 1543 (C=O); 1473 (CH_2). UV spectrum, λ_{max}, nm (ε): 210 (1200). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, Me, ^3J = 6.4 Hz), 1.10–1.50 m [32H, $(CH_2)_{16}$], 1.60–2.10 m (15H, $C_{10}H_{15}$), 3.23 q (2H, CH_2N, ^3J = 6.4 Hz), 5.52 br.s (1H, NH). Found, %: C 80.93; H 12.48; N 2.97. *M* 411.5. $C_{29}H_{53}NO$. Calculated, %: C 80.68; H 12.37; N 3.24. *M* 431.7.

***N*-(Abieta-7,13-dien-18-yl)-1-adamantanecarboxamide (XXIIb).** Yield 3.64 g (81%), mp 212–213°C (from hexane). IR spectrum, ν, cm^{-1}: 3378 (NH); 3030 (=CH); 2975, 2952, 2935, 2902, 2847 (CH_{aliph}); 1630, 1522 (C=O); 1450 (CH_2). UV spectrum, λ_{max}, nm (ε): 204 (10000), 235 (19000), 243 (19000), 250 (13000). ^{1}H NMR spectrum, δ, ppm: 0.82 s (3H, 12-Me), 0.83 d (6H, Me_2C, ^3J = 2.2 Hz), 0.93 s (3H, 1-Me), 1.00–2.10 m (15H), 1.60–1.90 m (15H, $C_{10}H_{15}$), 3.70–4.00 m (2H, CH_2N), 5.40–5.70 m (3H, NH, =CH). Found, %: C 83.03; H 10.70; N 2.88. *M* 422.5. $C_{31}H_{47}NO$. Calculated, %: C 82.79; H 10.53; N 3.11. *M* 449.7.

N-(1-Naphthyl)-1-adamantanecarboxamide (XXIIIb). Yield 2.78 g (91%), mp 263–264°C (from benzene). IR spectrum, ν, cm^{-1}: 3284 (NH); 3095, 3051, 3005 (CH_{arom}); 2901, 2846 (CH_{aliph}); 1641, 1520 (C=O); 1596, 1500 (C=C_{arom}); 1449 (CH_2); 790, 773, 768 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 223 (54000), 290 (6000). ^{1}H NMR spectrum, δ, ppm: 1.60–2.25 m (15H, $C_{10}H_{15}$), 7.20–7.95 m (8H, NH, $C_{10}H_7$). Found, %: C 82.71; H 7.72; N 4.33. *M* 291.3. $C_{21}H_{23}NO$. Calculated, %: C 82.59; H 7.59; N 4.59. *M* 305.4.

***N*-(2-Naphthyl)-1-adamantanecarboxamide (XXIVb).** Yield 2.84 g (93%), mp 182–183°C (from benzene). IR spectrum, ν, cm^{-1}: 3303 (NH); 3095, 3055, 3030 (CH_{arom}); 2900, 2849 (CH_{aliph}); 1651, 1542 (C=O); 1600, 1583, 1500 (C=C_{arom}); 1470, 1449, 1430 (CH_2); 811, 748, 680 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 222 (31000), 242 (57000), 251 (46000), 270 (11000), 290 (12000), 296 (11000). ^{1}H NMR spectrum, δ, ppm: 1.75–2.30 m (15H, $C_{10}H_{15}$), 7.25–8.30 m (8H, NH, $C_{10}H_7$). Found, %: C 82.74; H 7.70; N 4.30. *M* 292.9. $C_{21}H_{23}NO$. Calculated, %: C 82.59; H 7.59; N 4.59. *M* 305.4.

1-(1-Adamantylcarbonyl)-2-methylperhydroquinolin-4-one (XXVb). Yield 2.54 g (77%), mp 165–166°C (from hexane). IR spectrum, ν, cm^{-1}: 2927, 2905, 2850 (CH_{aliph}); 1716, 1606 (C=O); 1454 (CH_2). UV spectrum, λ_{max}, nm (ε): 211 (4000). ^{1}H NMR spectrum, δ, ppm: 1.00–2.90 m [11H, 3CH, $(CH_2)_4$], 1.63 d (3H, Me, ^3J = 7.4 Hz), 1.65–2.15 m (15H, $C_{10}H_{15}$), 3.70–4.05 m and 4.65–5.10 m [2H, $CH_2C(O)$]. Found, %: C 76.72; H 9.61; N 4.04. *M* 318.3. $C_{21}H_{31}NO_2$. Calculated, %: C 76.55; H 9.48; N 4.25. *M* 329.5.

1-Adamantylcarbonyl-3,5-dimethyl-1*H*-pyrazole (XXVIb). Yield 2.45 g (95%), mp 105–106°C (from hexane). IR spectrum, ν, cm^{-1}: 3165, 3135, 3110 (CH_{arom}); 2970, 2935, 2905, 2850 (CH_{aliph}); 1710, 1584 (C=O); 1479, 1454, 1413, 1373, 1330, 1306 (Ar); 926, 805, 762, 724, 673 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 202 (4000), 242 (15000). ^{1}H NMR spectrum, δ, ppm: 1.65–2.40 m (15H, $C_{10}H_{15}$), 2.23 s (3H, Me), 2.49 s (3H, Me), 5.85 s (1H, =CH). Found, %: C 74.66; H 8.69; N 10.70. *M* 243.2. $C_{16}H_{22}N_2O$. Calculated, %: C 74.38; H 8.58; N 10.84. *M* 258.4.

1-Adamantantylcarbonyl-1*H*-1,2,4-triazole (XXVIIb). Yield 1.76 g (76%), mp 126–127°C (from hexane). IR spectrum, ν, cm^{-1}: 3141, 3118 (CH_{arom}); 2971, 2908, 2862, 2848 (CH_{aliph}); 1733, 1523 (C=O); 1453, 1392, 1360, 1343, 1275, 1215 (Ar); 922, 903, 828, 805, 767, 720, 676, 668, 625 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 222 (9000). ^{1}H NMR spectrum, δ, ppm: 1.75–2.35 m (15H, $C_{10}H_{15}$), 8.01 s (1H, =CH), 8.89 s (1H, =CH). Found, %: C 67.80; H 7.53; N 17.88. *M* 219.5. $C_{13}H_{17}N_3O$. Calculated, %: C 67.51; H 7.41; N 18.17. *M* 231.3.

1-Adamantylcarbonyl-1*H*-1,2,3-benzotriazole (XXVIIIb). Yield 2.25 g (80%), mp 126–127°C (from benzene, hexane). IR spectrum, ν, cm^{-1}: 3125, 3090, 3055, 3030 (CH_{arom}); 2970, 2950, 2911, 2852 (CH_{aliph}); 1719 (C=O); 1605, 1595, 1485, 1449, 1345, 1309, 1282 (Ar); 927, 825, 804, 772, 750, 680, 640 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (10000), 220 (19000), 257 (9000), 298 (5000). ^{1}H NMR spectrum, δ, ppm: 1.75–2.55 m (15H, $C_{10}H_{15}$), 7.25–8.35 m (4H, C_6H_4). Found, %: C 72.84; H 7.02; N 14.61. *M* 263.9. $C_{17}H_{19}N_3O$. Calculated, %: C 72.57; H 6.81; N 14.93. *M* 281.4.

***S*-Phenyl 1-adamantanecarbothioate (XXIXb).** Yield 2.45 g (90%), mp 54–55°C (from hexane). IR spectrum, ν, cm^{-1}: 3075, 3055, 3005 (CH_{arom}); 2980, 2906, 2850 (CH_{aliph}); 1693 (C=O); 1580, 1475, 1450, 1439 (Ar); 916, 793, 753, 742, 705, 685, 674 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 208 (21000), 218 (15000), 234 (9000). ^{1}H NMR spectrum, δ, ppm: 1.70–2.15 m (15H, $C_{10}H_{15}$), 7.38 s (5H, C_6H_5). Found, %: C 75.18; H 7.44; S 11.53. *M* 261.8. $C_{17}H_{20}OS$. Calculated, %: C 74.96; H 7.40; S 11.71. *M* 272.4.

***S*-Benzyl 1-adamantanecarbothioate (XXXb).** Yield 2.29 g (80%), d_4^{20} = 1.1987, n_D^{20} = 1.5825. IR spectrum, ν, cm^{-1}: 3090, 3062, 3028 (CH_{arom}); 2940, 2906, 2850 (CH_{aliph}); 1672 (C=O); 1602, 1495, 1452 (C=C_{arom}); 927, 823, 798, 764, 699, 677 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 207 (7000), 212 (8000), 218 (7000), 232 (4000). ^{1}H NMR spectrum, δ, ppm: 1.65–2.15 m (15H, $C_{10}H_{15}$), 4.07 s (2H, CH_2), 7.26 s (5H, C_6H_5). Found, %: C 75.71; H 7.92; S 10.94. *M* 272.1. $C_{18}H_{22}OS$. Calculated, %: C 75.48; H 7.74; S 11.19. *M* 286.4.

***S*-Furfuryl 1-adamantanecarbothioate (XXXIb).** Yield 2.18 g (79%), d_4^{20} = 1.0708, n_D^{20} = 1.5525. IR spectrum, ν, cm^{-1}: 3147, 3118 (CH_{arom}); 2930, 2906, 2851 (CH_{aliph}); 1676 (C=O); 1595, 1502, 1452 (C=C_{arom}); 885, 822, 798, 764, 736, 677, 598 (CH_{Ar}). UV spectrum, λ_{max}, nm (ε): 225 (13000). ^{1}H NMR spectrum, δ, ppm: 1.60–2.25 m (15H, $C_{10}H_{15}$), 4.09 s (2H, CH_2), 5.90–6.40 m and 7.20–7.45 m (3H, C_4H_3O). Found, %: C 69.64; H 7.38; S 11.27. *M* 261.0. $C_{16}H_{20}O_2S$. Calculated, %: C 69.53; H 7.29; S 11.60. *M* 276.4.

Cyclohexanone *O*-(1-adamantylcarbonyl)oxime (XXXIIb). Yield 2.23 g (81%), mp 65–66°C (from hexane). IR spectrum, ν, cm^{-1}: 2932, 2905, 2851 (CH_{aliph}); 1747 (C=O); 1640 (C=N); 1451 (CH_2); 1293, 1056 (C–O); 867 (N–O). UV spectrum, λ_{max}, nm (ε): 208 (4000). ^{1}H NMR spectrum, δ, ppm: 1.55–2.15 m [21H, $(CH_2)_3$, $C_{10}H_{15}$), 2.25–2.67 m (4H, $2CH_2$). Found, %: C 74.33; H 9.21; N 4.87. *M* 261.4. $C_{17}H_{25}NO_2$. Calculated, %: C 74.14; H 9.15; N 5.09. *M* 275.4.

***trans-p*-Menthan-3-one *O*-(1-adamantylcarbonyl)-oxime (XXXIIIb).** Yield 2.62 g (79%), d_4^{20} = 1.0009, n_D^{20} = 1.5170. IR spectrum, ν, cm^{-1}: 2955, 2935, 2907, 2820, 2852 (CH_{aliph}); 1752 (C=O); 1629 (C=N); 1453 (CH_2); 1207, 1056 (C–O); 875 (N–O). UV spectrum, λ_{max}, nm (ε): 208 (4000). ^{1}H NMR spectrum, δ, ppm: 0.80–1.00 m (9H, 3Me), 1.00–3.00 m (8H), 1.65–2.10 m (15H, $C_{10}H_{15}$). Found, %: C 76.21; H 10.23; N 4.06. *M* 320.8. $C_{21}H_{33}NO_2$. Calculated, %: C 76.09; H 10.03; N 4.23. *M* 331.5.

***trans-p*-Mentha-1(6),8-dien-2-one *O*-(1-adamantylcarbonyl)oxime (XXXIVb).** Yield 2.69 g (82%), mp 78–79°C (from hexane). IR spectrum, ν, cm^{-1}: 3080, 3030 (=CH); 2960, 2926, 2903, 2851 (CH_{aliph}); 1747 (C=O); 1644, 1582 (C=C, C=N); 1452, 1440 (CH_2); 1205, 1180, 1054 (C–O); 895 (N–O). UV spectrum, λ_{max}, nm (ε): 206 (8000), 242 (16000). ^{1}H NMR spectrum, δ, ppm: 1.60–3.25 m (26H), 4.70–4.85 m (2H, $=CH_2$), 6.10–6.35 m (1H, =CH). Found, %: C 77.18; H 9.12; N 3.99. *M* 320.6. $C_{21}H_{29}NO_2$. Calculated, %: C 77.03; H 8.93; N 4.28. *M* 327.5.

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