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Tertiary Acetylenic Alcohols, Ethers, and Esters on the Basis of Isocamphanone, Camphor, Fenchone, Isofenchone, and Adamanthanone

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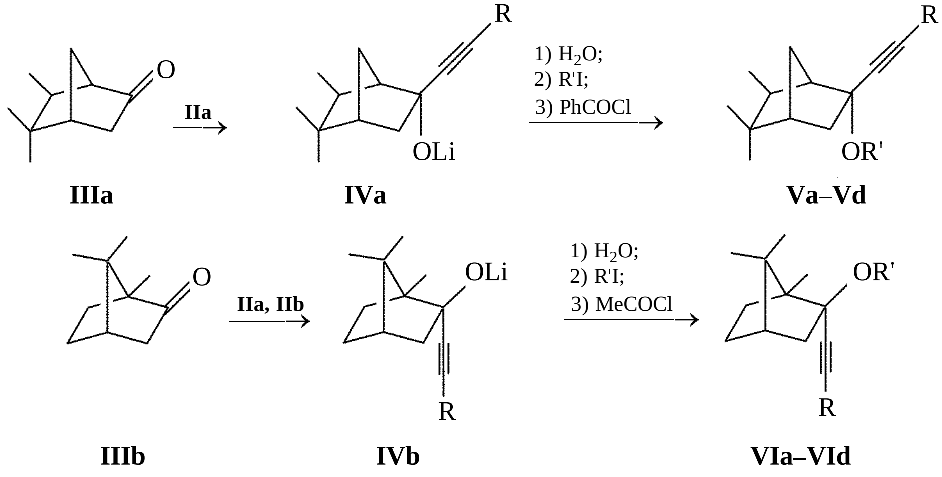
Abstract—Acetylenic lithium alcoholates were synthesized by reactions of 1-hexyne, 1-octyne, and phenylacetylene with butyllithium with subsequent reaction of the resulting acetylides with isocamphanone, (±)-camphor, (+)-fenchone, isofenchone, and adamanthanone. The latter reaction is controlled by steric factors. Lithium alcoholates were used to synthesize the corresponding alcohols, ethers, and esters. Configurational assessment of the products was performed on the basis of quantum-chemical calculations and X-ray diffraction analysis.

We earlier reported [1–4] on the synthesis of tertiary acetylenic alcohols and their derivatives by condensation of lithium peroxy acetylides with terpene and adamantane ketones. These compounds hold interest in terms of their biological, specifically antiviral, activity [5–7].

In the present communication we describe the synthesis of previously unknown tertiary acetylenic alcohols **Va**, **VIa**, **VII**, **VIII**, and **IXa**, methyl ethers **Vb**, **VIb**, and **IXb**, ethyl ethers **Vc** and **VIc**, acetates **VId** and **VIe**, and benzoate **Vd** on the basis of isocamphanone (**IIIa**), (±)-camphor (**IIIb**), (1*S*)-(+)-fenchone (**IIIc**), $[\alpha]_D^{20}$ +57°, racemic isofenchone (**IIId**), and adamanthanone (**IIIe**). The synthesis provides individual isomers of alcohols and ethers and is accomplished without isolation of intermediate lithium acetylides **IIa**–**IIc** and alcoholates **IVa**–**IVe**. The preparative yields of compounds **Va**–**Vd**, **VIa**–**VIe**, **VII**, **VIII**, **IXa**, and **IXb** are 67–80%.

$$\underset{\textbf{Ia–Ic}}{R\!-\!\!\equiv} \xrightarrow{\text{BuLi}} \underset{\textbf{IIa–IIc}}{R\!-\!\!\equiv\!\!-\text{Li}}$$



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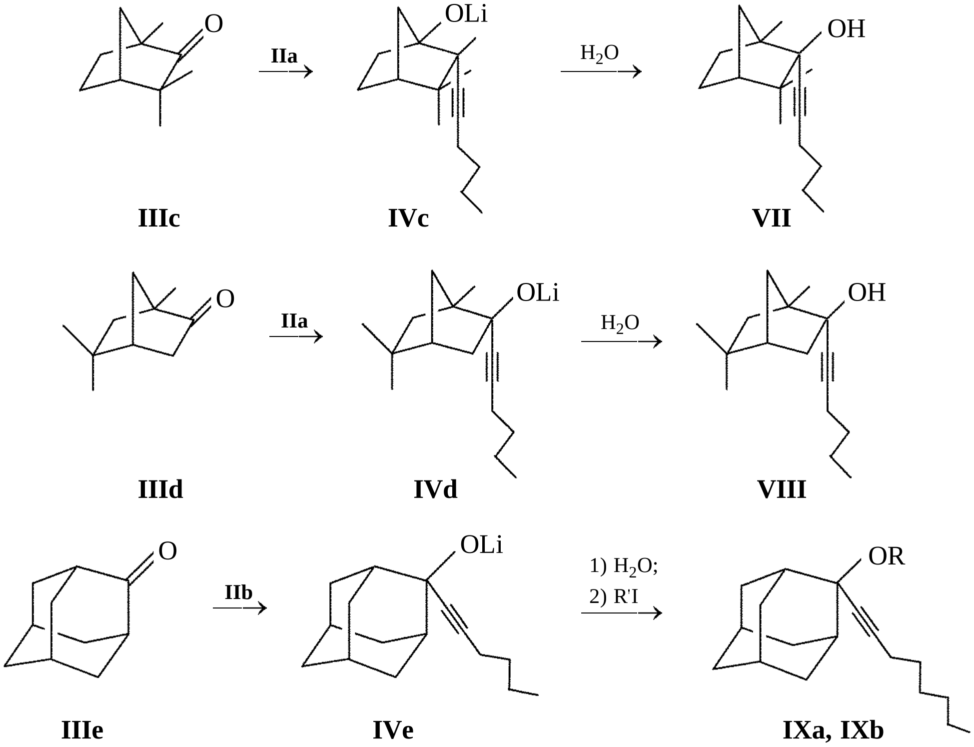


I, II, R = $(CH_2)_3Me$ (**a**), $(CH_2)_5Me$ (**b**), Ph (**c**); **V**, R = $(CH_2)_3Me$, R' = H (**a**), Me (**b**), Et (**c**); R = Ph, R' = PhC(O) (**d**); **VI**, R = $(CH_2)_3Me$, R' = H (**a**), Me (**b**), Et (**c**), MeC(O) (**d**); R = Ph, R' = MeC(O) (**e**); **IX**, R' = H (**a**), Me (**b**).

Table 1. Properties of compounds **Va–Vd, VIa–VIe, VII, VIII, IXa**, and **IXb**

Comp. no.	Yield, %	bp, °C (0.05 mm Hg)	d_{20}^{20}	n_D^{20}	Found, %		Formula	Calculated, %		*M*	
					C	H		C	H	found	calculated
Va	74	86–87	1.0242	1.4905	82.12	11.27	$C_{16}H_{26}O$	81.99	11.18	226.1	234.4
Vb	80	78–79	0.9758	1.4775	82.33	11.44	$C_{17}H_{28}O$	82.20	11.36	238.5	248.4
Vc	69	81–82	0.9591	1.4760	82.51	11.66	$C_{18}H_{30}O$	82.38	11.52	250.0	262.4
Vd	64	95–96[a]	–	–	83.91	7.43	$C_{25}H_{26}O_2$	83.76	7.31	347.1	358.5
VIa	70	84–85	0.9459	1.4900	82.09	11.26	$C_{16}H_{26}O$	81.99	11.18	228.4	234.4
VIb	73	80–81	0.9844	1.4820	82.29	11.43	$C_{17}H_{28}O$	82.20	11.36	236.6	248.4
VIc	67	66–67	0.8927	1.4780	82.53	11.69	$C_{18}H_{30}O$	82.38	11.52	253.6	262.4
VId	71	86–87	0.9925	1.4790	78.44	10.36	$C_{18}H_{28}O_2$	78.21	10.21	267.3	276.4
VIe	67	113–114	1.0404	1.5430	81.34	8.43	$C_{20}H_{24}O_2$	81.04	8.16	288.6	297.4
VII[b]	74	77–78	1.0541	1.4935	82.15	11.37	$C_{16}H_{26}O$	81.99	11.18	220.1	234.4
VIII	81	77–78	0.9754	1.4885	82.21	11.44	$C_{16}H_{26}O$	81.99	11.18	222.6	234.4
IXa	77	118–119	1.1130	1.5025	83.18	10.86	$C_{18}H_{28}O$	83.02	10.84	251.6	260.4
IXb	78	105–106	0.9802	1.5040	83.23	11.10	$C_{10}H_{30}O$	83.15	11.02	264.6	274.4

[a] Melting point, °C. [b] $[\alpha]_D^{20}$ –34°.

The structure of the synthesized compounds was proved by their elemental analyses, molecular weights, and ^1H NMR, IR, and UV spectra. The yields, physicochemical constants, and elemental analyses of compounds **Va**–**Vd**, **VIa**–**VIe**, **VII**, **VIII**, **IXa**, and **IXb** are listed in Table 1, the ^1H NMR spectra, in Table 2, and IR and UV spectra, in Table 3.

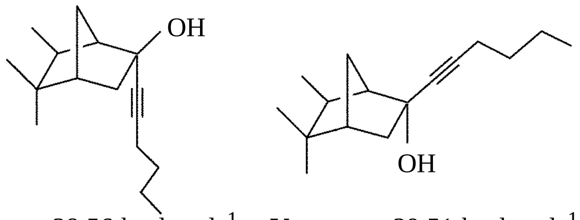
Table 2. ^1H NMR spectra of compounds **Va–Vd, VIa–VIe, VII, VIII, IXa**, and **IXb**

Comp. no.	^1H NMR spectrum, δ, ppm
Va	0.77–1.07 m (12H, 4Me), 1.07–2.12 m [12H, OH, 3CH, $2CH_2$ and $(CH_2)_2$], 2.17 t (2H, $CH_2C\equiv C$)
Vb	0.78–1.03 m (12H, 4Me), 1.03–2.05 m [11H, 3CH, $2CH_2$ and $(CH_2)_2$], 2.22 t (2H, $CH_2C\equiv C$), 3.27 s (3H, MeO)
Vc	0.77–1.05 m (12H, 4Me), 1.19 t (3H, $MeCH_2O$), 1.20–2.05 m [12H, OH, 3CH, $2CH_2$ and $(CH_2)_2$], 2.21 t (2H, $CH_2C\equiv C$), 3.15–3.80 m (2H, CH_2O)
Vd	0.89 d (3H, MeC^6, ^3J 7.0 Hz), 0.91 s (3H, *endo*-C^5Me), 1.03 s (3H, *exo*-C^5Me), 1.60–2.40 m (6H, 2CH and $2CH_2$), 2.75 br.s (1H, HC^1), 7.15–8.12 m (10H, 2Ph)
VIa	0.86 s, 0.88 t, 0.92 s [9H, Me_2C^7 and $Me(CH_2)_3$], 1.05 s (3H, MeC^1), 1.10–2.15 m [12H, OH, CH, $3CH_2$ and $(CH_2)_2$], 2.21 t (2H, $CH_2C\equiv C$)
VIb	0.86 s, 0.90 s, 0.91 t, 0.98 s [12H, Me_2C^7, $Me(CH_2)_3$ and MeC^1], 1.07–2.15 m [11H, CH, $3CH_2$ and $(CH_2)_2$], 2.24 t (2H, $CH_2C\equiv C$), 3.24 s (3H, MeO)
VIc	0.84 s, 0.89 t, 0.90 s, 0.99 s [12H, Me_2C^7, $Me(CH_2)_3$ and MeC^1], 1.00–2.05 m [11H, CH, $3CH_2$ and $(CH_2)_2$], 1.14 t (3H, $MeCH_2O$), 2.22 t (2H, $CH_2C\equiv C$), 3.25–3.75 m (2H, CH_2O)
VId	0.85–1.10 m [12H, Me_2C^7, $Me(CH_2)_3$ and MeC^1], 1.10–2.35 m [11H, CH, $3CH_2$ and $(CH_2)_2$], 2.05 s [3H, MeC(O)], 2.21 t (2H, $CH_2C\equiv C$)
VIe	0.94 s, 1.01 s, 1.06 s (9H, Me_2C^7 and MeC^1), 1.29–2.70 m (7H, CH and $3CH_2$), 2.03 s [3H, MeC(O)], 7.20–7.50 m (5H, Ph)
VII	0.91 t [3H, $Me(CH_2)_3$], 0.96 s (3H, MeC^1), 1.05–2.05 m [12H, OH, CH, CH_2 and $2(CH_2)_2$], 1.11 s (3H, *endo*-C^3Me), 1.17 s (3H, *exo*-C^3Me), 2.23 t (2H, $CH_2C\equiv C$)
VIII	0.85 s (3H, MeC^1), 0.90 t [3H, $Me(CH_2)_3$], 0.93 s (3H, *endo*-C^5Me), 1.12 s (3H, *exo*-C^5Me), 1.10–2.05 m [12H, OH, CH, $3CH_2$ and $(CH_2)_2$], 2.19 t (2H, $CH_2C\equiv C$)
IXa	0.89 t [3H, $Me(CH_2)_5$], 1.12–2.32 m [25H, OH, $(CH_2)_5$ and Ad]
IXb	0.94 t [3H, $Me(CH_2)_5$], 1.07–2.37 m [24H, $(CH_2)_5$ and Ad], 3.38 s (3H, MeO)

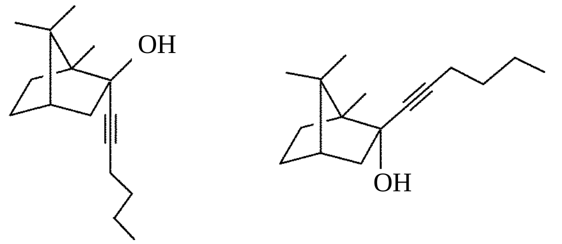
Table 3. IR and UV spectra of compounds **Va–Vd, VIa–VIe, VII, VIII, IXa**, and **IXb**

Comp. no.	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (ε)
Va	3430 (OH); 2960, 2935, 2870 (CH_{Alk}); 2240 ($C\equiv C$); 1470 (CH_2); 1090 (C–O)	204 (150)
Vb	2960, 2935, 2870, 2820 (CH_{Alk}); 2225 ($C\equiv C$); 1470 (CH_2); 1080 (COC)	204 (250), 235 (150)
Vc	2960, 2925, 2870 (CH_{Alk}); 2230 ($C\equiv C$); 1470 (CH_2); 1080 (COC)	204 (450), 238 (600)
Vd	3095, 3060, 3040 (CH_{Ar}), 2990, 2975, 2960, 2930, 2890, 2870 (CH_{Alk}); 2230 ($C\equiv C$); 1730 (C=O); 1600, 1580, 1495 (Ar); 1470 (CH_2); 770, 720, 710, 695 (CH_{Ar})	203 (27000), 242 (26000), 252 (18000)
VIa	3470 (OH); 3020, 2960, 2935, 2870 (CH_{Alk}); 2230 ($C\equiv C$); 1470 (CH_2); 1055 (C–O)	204 (200)
VIb	3020, 2970, 2935, 2870 (CH_{Alk}); 2230 ($C\equiv C$); 1470 (CH_2); 1075 (COC)	204 (250), 234 (150)
VIc	3025, 2965, 2935, 2875 (CH_{Alk}); 2230 ($C\equiv C$); 1470 (CH_2); 1080 (COC)	203 (600), 232 (300)
VId	3020, 2960, 2940, 2875 (CH_{Alk}); 2240 ($C\equiv C$); 1745 (C=O); 1470 (CH_2); 1050 (C–O)	208 (350)
VIe	3080, 3060, 3020 (CH_{Ar}); 2980, 2960, 2930, 2875 (CH_{Alk}); 2230 ($C\equiv C$); 1745 (C=O); 1595, 1480 (Ar); 1470 (CH_2); 1050 (C–O); 755, 690 (CH_{Ar})	207 (21000), 242 (20000), 254 (17000)
VII	3490 (OH); 2965, 2930, 2875 (CH_{Ar}); 2230 ($C\equiv C$); 1470 (CH_2); 1050 (C–O)	204 (200)
VIII	3325 (OH); 2960, 2935, 2875 (CH_{Ar}); 2240 ($C\equiv C$); 1470 (CH_2); 1050 (C–O)	208 (250)
IXa	3420 (OH); 2960, 2935, 2915, 2855 (CH_{Ar}); 2235 ($C\equiv C$); 1470 (CH_2); 1055 (C–O)	206 (600), 285 (150)
IXb	2960, 2940, 2920, 2860, 2825 (CH_{Ar}); 2230 ($C\equiv C$); 1470 (CH_2); 1090 (COC)	203 (600), 235 (300)

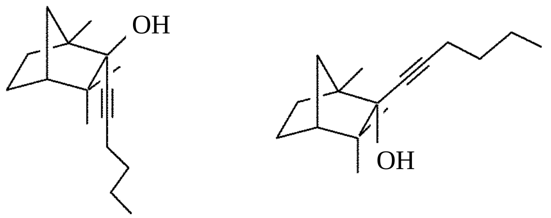
To assess the steric structure of isocamphanone, camphor, fenchone, and isofenchone derivatives **Va**–**Vd**, **VIa**–**VIe**, **VII**, and **VIII**, we performed quantum-chemical calculations of heat of formation (H_f) for all possible isomers of tertiary acetylenic alcohols **Va**, **VIa**, **VII**, and **VIII** by the MNDO–PM3 semiempirical method [8] using the GAMESS program [9]. Full optimization of all bond lengths and bond and dihedral angles was performed. Structures with both *endo* and *exo* positions of the bulky 1-hexynyl group were calculated. The quantum-chemical calculations established that the *endo* configuration of the 1-hexynyl group $Me(CH_2)_3C{\equiv}C$ is preferred over the *exo* configuration by 0.19–1.28 kcal mol^{-1} (compounds **VIa**, **VII**, and **VIII**), whereas isocamphanone derivatives prefer (by 1 kcal mol^{-1}) the *exo* configuration. These results are consistent with the ^{13}C NMR spectra of model compounds [10].



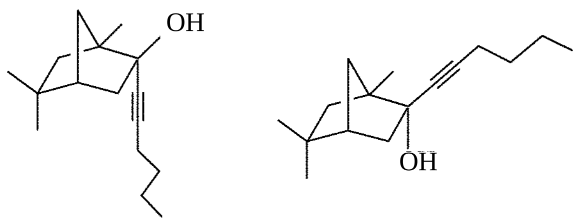
–38.56 kcal mol^{-1} **Va** –39.51 kcal mol^{-1}



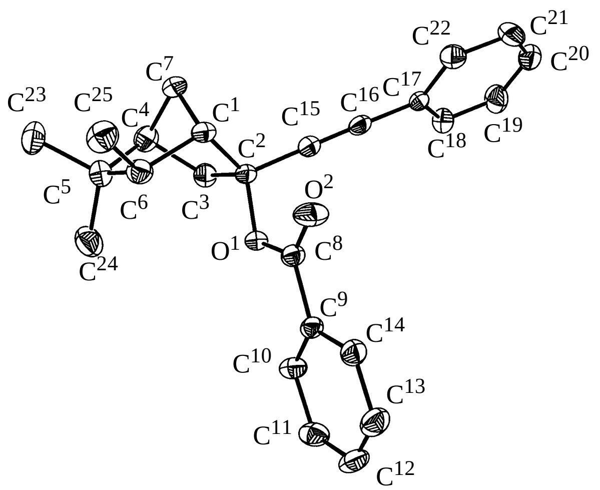
–36.83 kcal mol^{-1} **VIa** –35.66 kcal mol^{-1}



–36.99 kcal mol^{-1} **VII** –36.80 kcal mol^{-1}



–42.59 kcal mol^{-1} **VIII** –41.31 kcal mol^{-1}



Molecular structure of compound **Vd** with 50% probability ellipsoids for anisotropic displacements.

X-Ray diffraction was used to determine the absolute configuration of isocamphanone ester **Vd**. Bicyclo[2.2.1]heptane derivative **Vd** is a diastereomer (see figure). The crystal of **Vd** is a racemate. The relative configurations of the chiral centers are *S* (C^1), *S* (C^2), and *R* (C^6). The bond lengths and angles in the molecule have normal rms values (Tables 4 and 5). Intermolecular distances in the crystal have van der Waals values.

Thus, our study showed that lithium acetylides add to ketones from the least sterically congested side, i.e. this process is controlled by steric factors. When a bridgehead methyl group is present at C^1 (ketones **IIIb**–**IIId**), lithium acetylide attacks the C^2=O bond from the *endo* side to formexoisomers of alcohols **VIa**–**VIe**, **VII**, and **VIII**, whereas when C^1 bears no substituent (ketone **IIIa**), vice versa, the attack occurs from the *exo* side of the molecule to form *endo* isomers of **Va**–**Vd**.

EXPERIMENTAL

The IR spectra of compounds **Va**–**Vc**, **VIa**–**VIe**, **VII**, **VIII**, **IXa**, and **IXb** were measured on a Nikolet Protege-460 Fourier spectrometer in thin films or KBr pellets (**Vd**). The ^{1}H NMR spectra were taken on Tesla BS-567A instrument in CDCl$_3$, internal reference TMS. The UV spectra were obtained on a Specord UV-Vis instrument 1×10^{-2} (**Va**–**Vc**, **VIa**–**VId**, **VII**, **VIII**, **IXa**, **IXb**) or for 1×10^{-4} M (**Vd**, **VIe**) solutions in methanol. The specific rotation

Table 4. Principal bond lengths (*d*, Å) and bond angles (ω, deg) in molecule **Vd**

Bond	*d*	Bond	*d*
$O^1–C^8$	1.349(3)	$C^8–C^9$	1.491(4)
$O^1–C^2$	1.465(3)	$C^9–C^{10}$	1.368(4)
$O^2–C^8$	1.196(3)	$C^9–C^{14}$	1.395(4)
$C^1–C^2$	1.534(4)	$C^{10}–C^{11}$	1.409(4)
$C^1–C^6$	1.551(4)	$C^{11}–C^{12}$	1.370(5)
$C^1–C^7$	1.559(4)	$C^{12}–C^{13}$	1.352(5)
$C^2–C^{15}$	1.470(4)	$C^{13}–C^{14}$	1.366(4)
$C^2–C^3$	1.569(4)	$C^{15}–C^{16}$	1.197(4)
$C^3–C^4$	1.519(4)	$C^{16}–C^{17}$	1.427(4)
$C^4–C^7$	1.505(4)	$C^{17}–C^{22}$	1.388(4)
$C^4–C^5$	1.558(5)	$C^{17}–C^{18}$	1.394(4)
$C^5–C^{24}$	1.534(5)	$C^{18}–C^{19}$	1.376(4)
$C^5–C^{23}$	1.540(5)	$C^{19}–C^{20}$	1.345(5)
$C^5–C^6$	1.558(5)	$C^{20}–C^{21}$	1.370(5)
$C^6–C^{25}$	1.533(4)	$C^{21}–C^{22}$	1.413(5)
Angle	**ω**	**Angle**	**ω**
$C^8O^1C^2$	118.3(2)	$C^{25}C^6C^1$	109.0(3)
$C^2C^1C^6$	109.6(2)	$C^{25}C^6C^5$	116.5(3)
$C^2C^1C^7$	98.5(2)	$C^1C^6C^5$	104.2(2)
$C^6C^1C^7$	101.3(2)	$C^4C^7C^1$	95.3(2)
$O^1C^2C^{15}$	107.4(2)	$O^2C^8O^1$	123.7(3)
$O^1C^2C^1$	115.7(2)	$O^2C^8C^9$	124.0(3)
$C^{15}C^2C^1$	112.2(2)	$O^1C^8C^9$	112.3(2)
$O^1C^2C^3$	106.5(2)	$C^{10}C^9C^{14}$	120.0(3)
$C^{15}C^2C^3$	112.0(2)	$C^{10}C^9C^8$	122.9(2)
$C^1C^2C^3$	103.0(2)	$C^{14}C^9C^8$	117.1(3)
$C^4C^3C^2$	103.4(2)	$C^9C^{10}C^{11}$	119.2(3)
$C^7C^4C^3$	99.2(2)	$C^{12}C^{11}C^{10}$	119.1(3)
$C^7C^4C^5$	102.8(2)	$C^{13}C^{12}C^{11}$	121.7(3)
$C^3C^4C^5$	112.1(3)	$C^{12}C^{13}C^{14}$	119.8(3)
$C^{24}C^5C^{23}$	107.4(3)	$C^{13}C^{14}C^9$	120.3(3)
$C^{24}C^5C^4$	113.3(3)	$C^{16}C^{15}C^2$	178.9(3)
$C^{23}C^5C^4$	107.8(3)	$C^{15}C^{16}C^{17}$	178.9(3)
$C^{24}C^5C^6$	110.8(3)	$C^{22}C^{17}C^{18}$	118.5(3)
$C^{23}C^5C^6$	115.7(3)	$C^{22}C^{17}C^{16}$	121.3(3)
$C^4C^5C^6$	102.0(2)	$C^{18}C^{17}C^{16}$	120.2(3)
$C^{19}C^{18}C^{17}$	121.2(3)	$C^{20}C^{21}C^{22}$	120.0(3)
$C^{20}C^{19}C^{18}$	120.2(3)	$C^{17}C^{22}C^{21}$	119.1(3)
$C^{19}C^{20}C^{21}$	121.0(3)		

of compounds **IIIc** and **VII** was measured on an SM-2 instrument for ~3.5% solutions in methanol. The molecular weights were measured by cryoscopy in benzene. Column chromatography was performed on neutral Al_2O_3 (Brockmann activity grade II). Butyllithium was synthesized by the procedure in [11].

Table 5. Principal torsion angles (τ, deg) in molecule **Vd**

Angle	τ	Angle	τ
$C^8O^1C^2C^{15}$	61.0(3)	$C^5C^4C^7C^1$	55.5(3)
$C^8O^1C^2C^1$	–65.1(3)	$C^2C^1C^7C^4$	58.5(2)
$C^8O^1C^2C^3$	–178.8(2)	$C^6C^1C^7C^4$	–53.6(3)
$C^6C^1C^2O^1$	–44.9(3)	$C^2O^1C^8O^2$	10.5(4)
$C^7C^1C^2O^1$	–150.2(2)	$C^2O^1C^8C^9$	–168.4(2)
$C^6C^1C^2C^{15}$	–168.5(2)	$O^2C^8C^9C^{10}$	–177.7(3)
$C^7C^1C^2C^{15}$	86.2(3)	$O^1C^8C^9C^{10}$	1.2(4)
$C^6C^1C^2C^3$	70.9(3)	$O^2C^8C^9C^{14}$	1.1(4)
$C^7C^1C^2C^3$	–34.5(2)	$O^1C^8C^9C^{14}$	180.0(2)
$O^1C^2C^3C^4$	120.7(2)	$C^{14}C^9C^{10}C^{11}$	0.6(4)
$C^{15}C^2C^3C^4$	–122.1(3)	$C^8C^9C^{10}C^{11}$	178.2(3)
$C^1C^2C^3C^4$	–1.4(3)	$C^9C^{10}C^{11}C^{12}$	0.4(4)
$C^2C^3C^4C^7$	38.4(3)	$C^{10}C^{11}C^{12}C^{13}$	0.2(5)
$C^2C^3C^4C^5$	–69.5(3)	$C^{11}C^{12}C^{13}C^{14}$	–0.6(5)
$C^7C^4C^5C^{24}$	–155.6(3)	$C^{12}C^{13}C^{14}C^9$	0.4(5)
$C^3C^4C^5C^{24}$	–50.0(4)	$C^{10}C^9C^{14}C^{13}$	0.2(4)
$C^7C^4C^5C^{23}$	85.7(3)	$C^8C^9C^{14}C^{13}$	–178.7(3)
$C^3C^4C^5C^{23}$	–168.7(3)	$O^1C^2C^{15}C^{16}$	56(17)
$C^7C^4C^5C^6$	–36.5(3)	$C^1C^2C^{15}C^{16}$	–175(100)
$C^3C^4C^5C^6$	69.1(3)	$C^3C^2C^{15}C^{16}$	–60(17)
$C^2C^1C^6C^{25}$	163.6(2)	$C^2C^{15}C^{16}C^{17}$	10(30)
$C^7C^1C^6C^{25}$	–93.0(3)	$C^{15}C^{16}C^{17}C^{22}$	–172(100)
$C^2C^1C^6C^5$	–71.3(3)	$C^{15}C^{16}C^{17}C^{18}$	7(16)
$C^7C^1C^6C^5$	32.1(3)	$C^{22}C^{17}C^{18}C^{19}$	–0.6(5)
$C^{24}C^5C^6C^{25}$	–117.3(3)	$C^{16}C^{17}C^{18}C^{19}$	179.8(3)
$C^{23}C^5C^6C^{25}$	5.2(4)	$C^{17}C^{18}C^{19}C^{20}$	–0.4(5)
$C^4C^5C^6C^{25}$	121.8(3)	$C^{18}C^{19}C^{20}C^{21}$	0.9(6)
$C^{24}C^5C^6C^1$	122.5(3)	$C^{19}C^{20}C^{21}C^{22}$	–0.5(6)
$C^{23}C^5C^6C^1$	–115.0(3)	$C^{18}C^{17}C^{22}C^{21}$	0.9(4)
$C^4C^5C^6C^1$	1.6(3)	$C^{16}C^{17}C^{22}C^{21}$	–179.4(3)
$C^3C^4C^7C^1$	–59.8(3)	$C^{20}C^{21}C^{22}C^{17}$	0.4(5)

Crystals of compounds **Vd** ($C_{25}H_{26}O_2$, *M* 358.46), monoclinic, space group *P*21/*n*; at 173 K: *a* 10.227(2), *b* 16.136(3), *c* 12.895(3) Å; β 106.04(3)°, *V* 2045.2(7) $Å^3$, *Z* 4, d_{calc} 1.164 mg cm^{-3}, *F*(000) 768, μ 0.072 mm^{-1}.

The unit cell parameters and the intensities of 4643 reflections were measured on a Syntex-$P2_1$ four-circle automated diffractometer (at 173 K, λMoK_α radiation, graphite monochromator, θ/2θ scanning, λ_{max} 27°). The structure was determined by the direct method and refined by full-matrix least squares in the anisotropic appriximation for non-hydrogen atoms. Hydrogen atoms were located geometrically and refined isotropically with fixed positional (rider model) and thermal parameters [$U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 and $U_{iso}(H) = 1.2U_{eq}(C)$ for other groups] (Table 6). Final divergence factors: R_1 0.0764 for

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters U_{eq} (Å$^2 \times 10^3$) in molecule **Vd**

Atom	x	y	z	U_{eq}
O^1	7003(2)	1378(1)	6226(2)	37(1)
O^2	7033(2)	1292(2)	7970(2)	56(1)
C^1	8994(3)	2293(2)	7173(2)	41(1)
C^2	8474(3)	1518(2)	6497(2)	38(1)
C^3	8816(3)	1706(2)	5407(2)	44(1)
C^4	9447(3)	2565(2)	5585(2)	48(1)
C^5	8382(3)	3244(2)	5629(3)	51(1)
C^6	8057(3)	3039(2)	6713(2)	46(1)
C^7	10250(3)	2481(2)	6748(2)	45(1)
C^8	6440(3)	1217(2)	7036(2)	37(1)
C^9	5008(3)	921(2)	6632(2)	36(1)
C^{10}	4366(3)	814(2)	5560(2)	44(1)
C^{11}	3023(3)	510(2)	5252(3)	53(1)
C^{12}	2391(3)	334(2)	6034(3)	55(1)
C^{13}	3021(3)	446(2)	7093(3)	56(1)
C^{14}	4327(3)	737(2)	7403(3)	47(1)
C^{15}	9144(3)	759(2)	7014(2)	40(1)
C^{16}	9678(3)	134(2)	7419(2)	39(1)
C^{17}	10304(3)	–620(2)	7883(2)	36(1)
C^{18}	10299(3)	–1312(2)	7234(3)	48(1)
C^{19}	10901(4)	–2044(2)	7664(3)	60(1)
C^{20}	11517(4)	–2102(2)	8727(3)	61(1)
C^{21}	11542(4)	–1443(3)	9402(3)	67(1)
C^{22}	10923(3)	–686(2)	8983(3)	55(1)
C^{23}	9045(4)	4094(2)	5578(3)	64(1)
C^{24}	7090(4)	3200(3)	4681(3)	71(1)
C^{25}	8315(4)	3731(2)	7560(3)	61(1)

2539 unique with $I > 2\sigma(I)$ and wR_2 0.2319 for 4406 unique reflections. All calculations were performed using the SHELXTL PLUS program package (Version 5.10) [12].

2-*endo*-Hydroxy-2-*exo*-(1-hexynyl)--5,5,6-(Va)-, or (±)-*exo*-hydroxy-2-*endo*-(1-hexynyl)-2-1,7,7-(VIa)-, or (–)-(1*S*)-2-*exo*-hydroxy-2-*endo*-(1-hexynyl)-1,3,3-(VII)-, or 2-*exo*-hydroxy-2-*endo*-(1-hexynyl)-1,5,5-(VIII)-trimethylbicyclo[2.2.1] heptanes and 2-hydroxy-2-(1-octynyl)adamanthane (IXa) *(general procedure).* Bytyllithium, 0.011 mol (hexane solution) was added under argon over the course of 0.5 h to a cold (–40 to –20°C) and vigorously stirred solution of 0.013 mol of alkyne **Ia**–**Ic** in 20 ml of absolute THF. The mixture was stirred for an additional 1 h, and 0.01 mol of ketone **IIIa**–**IIIe** was added to it. The temperature was raised to 20–23°C for 1–2 h, and stirring was continued for 3–4 h, after which the mixture was left to stand for 18 h. The mixture contained 0.01 mol of lithium alcoholate **IV**. It was diluted with 100 ml of water, alcohols **Va**, **VIa**, **VII**, **VIII**, and **IXa** were extracted with hexane, the extract was dried with $CaCl_2$, the solvent was removed, and the product was distilled in a vacuum.

2-*exo*-(1-Hexynyl)-2-*endo*-methoxy-(Vb)-, or -ethoxy-(Vc)-5,5,6-, or 2-*endo*-(1-hexynyl)-2-*exo*-methoxy-(VIb)-, or -ethoxy-(VIc)-(±)-1,7,7-(VIb, VIc)-trimethylbicyclo[2.2.1]heptanes and 2-methoxy-2-(1-octynyl)adamanthane (IXb) *(general procedure).* To a solution of 0.01 mol of lithium alcoholate **IV** we added 0.01 mol of methyl or ethyl iodide and 3 ml of HMPA. The reaction was complete within 18 h at 20–23°C. The reaction mixure was diluted with 100 ml of hexane, the organic layer was washed with 30% NaOH, dried with $CaCl_2$, the solvent was removed, and the product was distilled in a vacuum.

2-*endo*-Benzoyloxy-2-*exo*-(2-phenylethynyl)-5,5,6-trimethylbicyclo[2.2.1]heptane (Vd), (±)-2-*exo*-acetyloxy-2-*endo*-[(1-hexynyl)-(VId)-, or (2-phenylethynyl)-(VIe)]-1,7,7-trimethylbicyclo-[2.2.1]heptanes *(general procedure).* To a solution of 0.01 mol of lithium alcoholate **IV** we added in one portion 0.012 mol of acetyl or benzoyl chloride. The mixture was stirred for 3–4 h and left to stand for 18 h, after which it was diluted with 100 ml of water, and the esters were extracted with hexane, the organic layer was washed with water, saturated aqueous $NaHCO_3$, dried with $CaCl_2$, and the solvent was removed. Benzoate **Vd** was purified by recrystallization with hexane and acetates **VId** and **VIe**, by vacuum distillation.

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