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# Stereoselective *exo*-Addition to Norbornenes of Acetic Acid Generated from Vinyl Acetate in the Presence of Rhodium Complexes

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**Abstract**—Rhodium complexes catalyzed decomposition of vinyl acetate with liberation of acetic acid and subsequent stereoselective *exo*-addition of the latter to norbornene and its derivatives under mild conditions.

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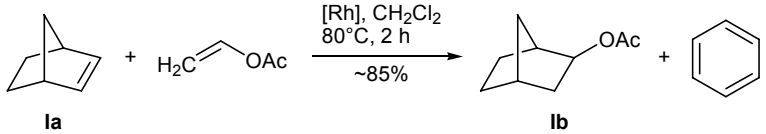
We previously found that Wilkinson's complex $Rh(PPh_3)_3Cl$ promotes decomposition of vinyl acetate with formation of acetic acid, acetylene, benzene, and ethylidene diacetate [1]. Taking into account that ethylidene diacetate is the product of addition of acetic acid at the double bond of vinyl acetate, in the present work we made an attempt to use the ability of vinyl acetate to generate acetic acid to effect mild hydroacetoxylation of norbornene and its derivatives.

Norbornene (**Ia**) was selected as substrate due to its specific place among cyclic olefins. High reactivity in electrophilic addition processes and the ability to undergo rearrangements in various media make norbornene and its derivatives indispensable subjects for chemical and physicochemical studies. Increased interest in norbornene derivatives is also related to their structural similarity to numerous naturally occurring compounds of the terpene series and their increased synthetic accessibility as a result of improvement of procedures for Diels–Alder reactions.

Esters derived from norbornene were synthesized previously via addition of monocarboxylic acids, including acetic acid, to norbornene in the presence of sulfuric acid [2, 3], boron trifluoride–ether complex [4], or *p*-toluenesulfonic acid [5] as catalyst. These reactions were successful with the use of 1.5–4-fold excess of acetic acid under fairly severe conditions (90–140°C), which promoted formation of the corresponding ester as a mixture of *exo* and *endo* isomers.

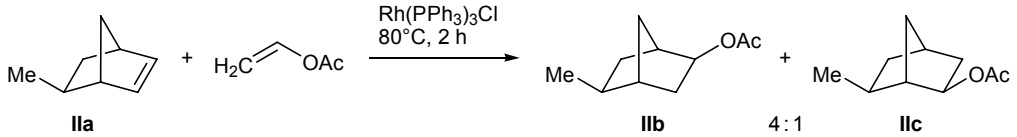
We found that vinyl acetate can be used as synthetic equivalent of acetic acid in the above reaction. The reaction of vinyl acetate with norbornene on heating to 80°C (2 h) in the presence of rhodium catalysts, such as $Rh(PPh_3)_3Cl$, $[Rh(CO)_2Cl]_2$, and $[Rh(C_7H_8)Cl]_2$, gave bicyclo[2.2.1]hept-*exo*-2-yl acetate (**Ib**) in 85% yield (Scheme 1). Analysis of the reaction mixture by gas–liquid chromatography (after 1 h) showed that vinyl acetate undergoes complicated transformations leading to the formation of acetic acid, ethylidene diacetate (20–25%), and benzene and that the concentration of acetic acid at each moment does not exceed 3–5%; therefore, the given reaction conditions may be regarded as "mild." Preliminary activation of rhodium catalyst by heating in methylene chloride or chloroform for 2–3 h at 200°C is necessary, while the reaction of vinyl acetate with norbornene occurred at 80–120°C in 1–6 h, the molar ratio [Rh]–norbornene–vinyl acetate being 1 : 100 : 120. The addition of acetic

**Scheme 1.**

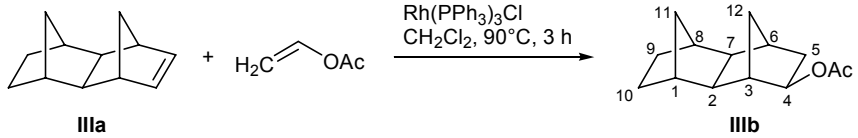



**Ia** **Ib**

**Scheme 2.**




**Scheme 3.**

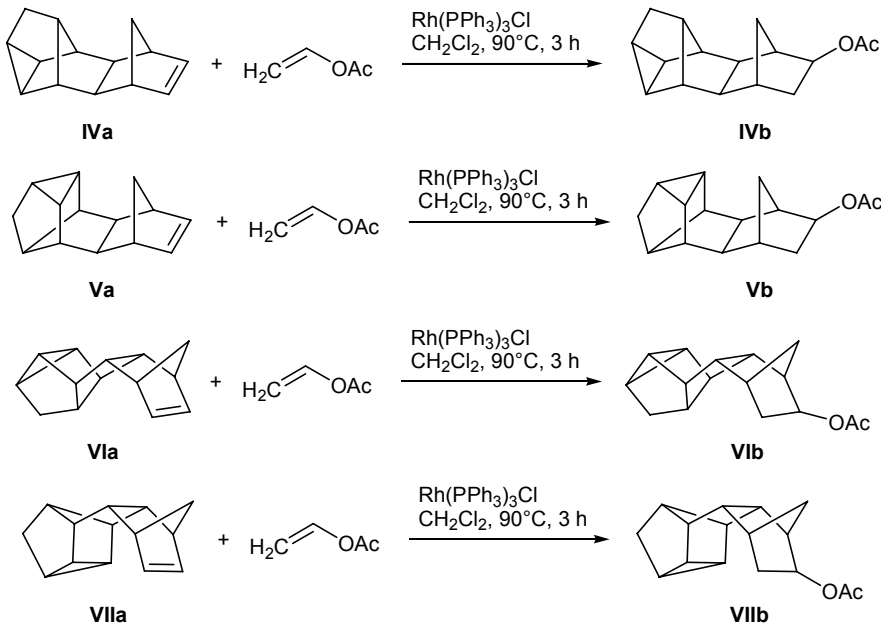



acid to vinyl acetate was stereoselective, and the product was *exo*-acetoxy derivative **Ib** whose structure was unambiguously confirmed by the NMR data. The $^{13}C$ NMR spectrum of **Ib** contained signals at $\delta_C$ 41.68 ($C^1$), 77.50 ($C^2$), 39.70 ($C^3$), 35.52 ($C^4$), 28.33 ($C^5$), 24.40 ($C^6$), 35.37 ($C^7$), and 170.9 ppm (C=O) (cf. [6]). No signals assignable to the corresponding *endo* isomer were observed {$\delta_C$ 40.7 ($C^1$), 75.6 ($C^2$), 37.3 ($C^3$), 37.0 ($C^4$), 29.7 ($C^5$), 21.3 ($C^6$), 37.6 ($C^7$) [7]}.

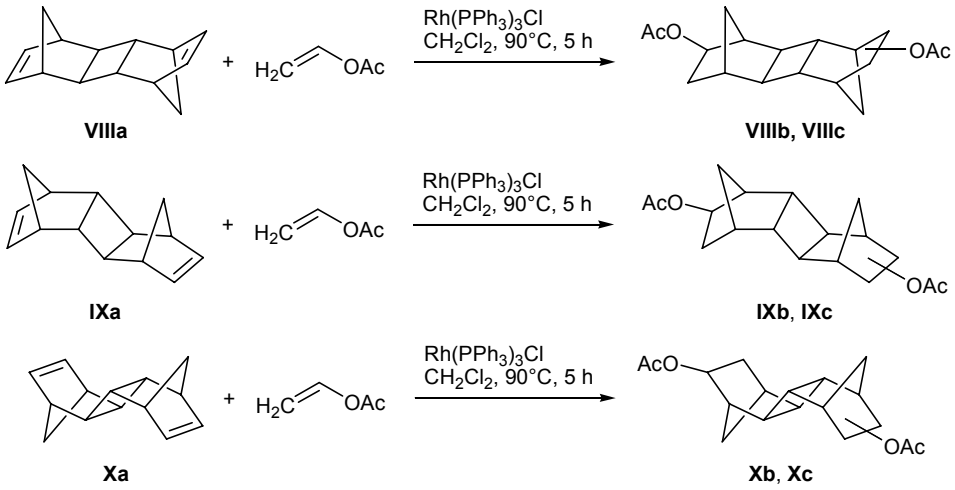
Analogous reaction of *exo*-5-methylnorbornene **IIa** with vinyl acetate in the presence of $Rh(PPh_3)_3Cl$ resulted in the formation of two regioisomeric acetoxy(methyl)norbornanes **IIb** and **IIc** at a ratio of 4 : 1 (overall yield 80%; Scheme 2). The chemical shifts of the methyl carbon atoms in the $^{13}C$ NMR spectra of **IIb** and **IIc**, $\delta_C$ 22.05 and 21.66 ppm, respectively, indicated that the original *exo* orientation of the methyl group remained unchanged. The *exo* orientation of the acetoxy group in both isomers followed from the chemical shifts of $C^2$, $\delta_C$ 76.45 and 77.35 ppm for compounds **IIb** and **IIc**, respectively. In addition, signals from the bridging $C^7$ atom in the spectra of **IIb** and **IIc** appeared in a strong field ($\delta_C$ 31.05 and 32.17 ppm), in support of the *exo* orientation of the substituent [7].

Norbornene derivatives with a complex structure readily reacted with vinyl acetate under analogous conditions. *exo*,*exo*-Tetracyclo[6.2.1.1.$^{3,6}$.0$^{2,7}$]dodec-4-ene (**IIIa**) reacted with vinyl acetate in the presence of Wilkinson's catalyst preliminarily activated with $CH_2Cl_2$ at 200°C (2 h) to give 71% of *exo*,*exo*-tetracyclo[6.2.1.0$^{2,7}$1.$^{3,6}$]dodec-*exo*-4-yl acetate (**IIIb**) (Scheme 3). The assignment of signals in the $^{13}C$ NMR spectrum of **IIIb** was not difficult, taking into account high molecular symmetry. The upfield shift of the $C^{12}$ signal ($\delta_C$ 32.82 ppm) and downfield of the $C^4$ signal

**Scheme 4.**



**Scheme 5.**

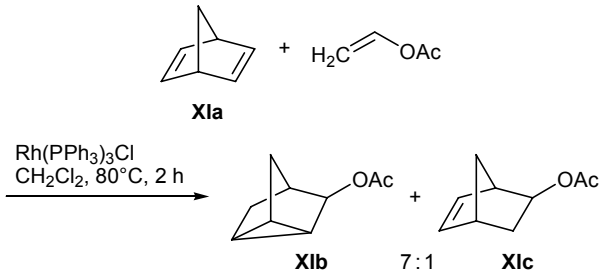



($\delta_C$ 76.98 ppm) indicated *exo* orientation of the acetoxy group. The $C^4$ atom in the corresponding *endo* isomer resonates in a stronger field ($\delta_C$ 70.95 ppm) [8].

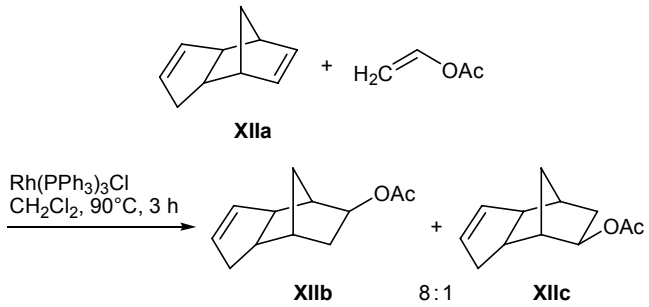
Hexacyclic norbornadiene dimers **IVa**–**VIIa** having two potential reaction centers, double bond and cyclopropane ring, reacted with vinyl acetate only at the norbornene double bond, while the three-membered ring remained intact (Scheme 4). The yields of acetates **IVb**–**VIIb** were 60–78%. Unlike hexacyclic norbornadiene dimers **IVa**–**VIIa**, pentacyclic dimers **VIIIa**–**Xa** containing two equivalent norbornene fragments took up acetic acid at both double bonds provided that 4 equiv of vinyl acetate was used (Scheme 5). The reactions with pentacyclic compounds **VIIIa**–**Xa** in each case gave both possible regioisomers in approximately equal amounts; both acetoxy groups in both isomers had *exo* orientation.

In the reaction of a "pseudoconjugated" diene, norbornadiene with vinyl acetate in the presence of $Rh(PPh_3)_3Cl$ we obtained two products, 3-acetoxynortricyclane (**XIb**, 72%) and bicyclo[2.2.1]hept-5-en-*exo*-2-yl acetate (**XIc**, 10%) (Scheme 6). The structure of the latter was confirmed by the presence of characteristic signals from $sp^2$-carbon atoms [$\delta_C$ 129.68 ($C^5$), 134.70 ppm ($C^6$)], bridging carbon atom ($C^7$, $\delta_C$ 30.76 ppm), and $C^2$ ($\delta_C$ 76.75 ppm) in the $^{13}C$ NMR spectrum. Unusual behavior of *endo*-dicyclopentadiene (**XIIa**) in the examined reaction should be noted. This compound reacted with vinyl acetate exclusively at the double bond in the norbornene fragment to give two regioisomeric products, *endo*-tricyclo[$5.2.1.0^{2,6}$]dec-3(4)-ene-*exo*-8-yl acetates **XIIb** and **XIIc** at a ratio of 8 : 1 (Scheme 7). The $^1H$ NMR spectrum of isomer mixture **XIIb**/**XIIc** contained a signal at δ 4.65 ppm due to *endo*-oriented proton on $C^8$; this suggests *exo* orientation of the acetoxy group [6, 7]. The double bond in the five-membered ring of **XIIa** remains intact even under severe conditions (130°C, 10 h).

**Scheme 6.**




**Scheme 7.**




The structure of the isolated products was confirmed by spectral data, as well as by comparing with authentic samples and published data [6–9].

## EXPERIMENTAL

The reaction mixtures and products were analyzed by GLC on a Khrom-5 chromatograph equipped with flame ionization detectors and 1.2 m × 3-mm and 3 m ×

3-mm columns; stationary phase 5% of SE-30 on Chromaton N-AW-HMDS (0.125–0.160 mm); carrier gas helium, flow rate 50 ml/min; oven temperature programming from 50 to 220°C. The IR spectra were recorded in the range from 550 to 3600 $cm^{-1}$ on a Specord 75IR spectrometer from samples prepared as KBr pellets or dispersed in mineral oil. The $^1H$ and $^{13}C$ NMR spectra were measured on a JEOL FX 90Q instrument at 90 and 22.5 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT-112S GC–MS system, ion source temperature 220°C. The elemental compositions were determined on a Carlo Erba 1106 analyzer.

**Reactions of norbornenes Ia–XIIa with vinyl acetate in the presence of rhodium catalyst.** A 17-ml stainless steel high-pressure microreactor was charged under argon with 0.1 mmol of $Rh(PPh_3)_3Cl$ in 3 ml of methylene chloride or chloroform. The reactor was hermetically sealed and heated for 2–3 h at 200°C. After cooling, the reactor was opened, 10 mmol of compound **Ia**–**XIIa** and 12 mmol (in the reactions with **Ia**–**VIIa**) or 24 mmol (in the reactions with **VIIIa**–**XIIa**) of vinyl acetate were added under argon. The reactor was hermetically sealed, and the mixture was heated under continuous stirring for 2–5 h at 80–100°C (depending on the substrate structure). The reactor was then cooled to room temperature and opened, the mixture was filtered through a layer of $Al_2O_3$, the sorbent was additionally washed with hexane–diethyl ether (1 : 1), the solvent was distilled off under reduced pressure, and the residue was distilled under reduced pressure or separated by column chromatography on $Al_2O_3$.

**Bicyclo[2.2.1]hept-e*xo*-2-yl acetate (Ib).** Yield 85%, bp 60°C (8 Pa); published data [6]: bp 64–66°C (10 Pa). IR spectrum, ν, $cm^{-1}$: 1740 (C=O), 1200 (C–O–C). $^1H$ NMR spectrum, δ, ppm: 4.75 s (2-H), 2.45 s (2H, 1-H, 4-H), 2.18 d ($CH_3$), 1.30–1.90 m (4H, 3-H, 5-H, 6-H, 7-H). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 41.68 ($C^1$), 77.50 ($C^2$), 39.70 ($C^3$), 35.52 ($C^4$), 28.33 ($C^5$), 24.40 ($C^6$), 35.37 ($C^7$), 170.91 ($C^8$), 20.94 ($C^9$). Found, %: C 69.88; H 9.05. $C_9H_{14}O_2$. Calculated, %: C 70.10; H 9.15.

***exo*-5-Methylbicyclo[2.2.1]hept-e*xo*-2-yl acetate (IIb).** Yield 65%, bp 80°C (10 Pa); published data [5]: bp 105–106°C (30 Pa). $^1H$ NMR spectrum, δ, ppm: 4.70 (2-H), 2.47 s (2H, 1-H, 4-H), 2.20 d ($CH_3$), 1.26–1.90 m (4H, 3-H, 5-H, 6-H, 7-H), 1.19 d ($CH_3$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 42.40 ($C^1$), 76.45 ($C^2$), 39.64 ($C^3$), 42.22 ($C^4$), 35.64 ($C^5$), 34.45 ($C^6$), 31.05 ($C^7$), 169.70 ($C^8$), 21.32 ($C^9$), 22.25 ($C^{10}$). Found, %: C 71.25; H 9.48. $C_{10}H_{16}O_2$. Calculated, %: C 71.39; H 9.59.

***exo*-6-Methylbicyclo[2.2.1]hept-e*xo*-2-yl acetate (IIc).** Yield 15%. $^1H$ NMR spectrum, δ, ppm: 5.17 s (2-H), 2.45 (2H, 1-H, 4-H), 2.20 d ($CH_3$), 1.30–1.85 m (4H, 3-H, 5-H, 6-H, 7-H), 1.25 d ($CH_3$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 44.14 ($C^1$), 74.35 ($C^2$), 40.75 ($C^3$), 36.77 ($C^4$), 34.52 ($C^5$), 33.81 ($C^6$), 37.17 ($C^7$), 169.95 ($C^8$), 20.77 ($C^9$), 21.66 ($C^{10}$).

***exo*,*exo*-Tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-*exo*-4-yl acetate (IIIb).** Yield 71%, bp 90°C (3 Pa). IR spectrum: ν 1740–1745 $cm^{-1}$ (C=O). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 40.63 ($C^1$, $C^8$), 53.90 ($C^2$), 41.29 ($C^3$), 76.98 ($C^4$), 39.72 ($C^5$), 39.76 ($C^6$), 53.90 ($C^7$), 31.98 ($C^9$, $C^{10}$), 35.47 ($C^{11}$), 32.82 ($C^{12}$), 170.91 ($C^{13}$), 20.77 ($C^{14}$). Found, %: C 76.27; H 9.20. $C_{14}H_{20}O_2$. Calculated, %: C 76.32; H 9.15.

***exo*,*exo*-Hexacyclo[9.2.1.0$^{2,10}$.0$^{3,8}$.0$^{4,6}$.0$^{5,9}$]tetradec-*exo*-12-yl acetate (IVb).** Yield 78%. IR spectrum ν, $cm^{-1}$: 1740 (C=O), 1190–1195 (C–O–C). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 11.59 ($C^6$), 16.68 ($C^4$, $C^5$), 20.92 ($C^{16}$), 33.45 ($C^7$), 36.82 ($C^{14}$), 38.39 ($C^8$), 39.72 ($C^{13}$), 39.79 ($C^1$), 41.29 ($C^{11}$), 46.25 ($C^3$, $C^9$), 52.55 ($C^2$, $C^{10}$), 76.98 ($C^{12}$), 168.80 ($C^{15}$). Found, %: C 78.32; H 8.15. $C_{16}H_{20}O_2$. Calculated, %: C 78.65; H 8.25.

***exo*,*endo*-Hexacyclo[9.2.1.0$^{2,10}$.0$^{3,8}$.0$^{4,6}$.0$^{5,9}$]tetradec-*exo*-12-yl acetate (Vb).** Yield 78%. $^{13}C$ NMR spectrum, $\delta_C$, ppm: 12.66 ($C^4$, $C^5$), 16.95 ($C^6$), 20.89 ($C^{16}$), 28.09 ($C^7$), 34.63 ($C^{14}$), 39.48 ($C^1$), 40.64 ($C^{11}$), 42.90 ($C^{13}$), 43.73 ($C^8$), 47.25 ($C^3$, $C^9$), 49.15 ($C^2$, $C^{10}$), 77.45 ($C^{12}$), 165.70 ($C^{15}$). Found, %: C 78.45; H 8.19. $C_{16}H_{20}O_2$. Calculated, %: C 78.65; H 8.25.

***endo*,*exo*-Hexacyclo[9.2.1.0$^{2,10}$.0$^{3,8}$.0$^{4,6}$.0$^{5,9}$]tetradec-*exo*-12-yl acetate (VIb).** Yield 64%. $^{13}C$ NMR spectrum, $\delta_C$, ppm: 13.70 ($C^6$), 18.20 ($C^4$, $C^5$), 20.58 ($C^{16}$), 32.17 ($C^{14}$), 33.46 ($C^7$), 37.62 ($C^8$), 40.29 ($C^1$), 40.42 ($C^{11}$), 42.82 ($C^3$, $C^9$), 43.12 ($C^{13}$), 49.20 ($C^2$, $C^{10}$), 76.98 ($C^{12}$), 165.80 ($C^{15}$). Found, %: C 78.35; H 8.19. $C_{16}H_{20}O_2$. Calculated, %: C 78.65; H 8.25.

***endo*,*endo*-Hexacyclo[9.2.1.0$^{2,10}$.0$^{3,8}$.0$^{4,6}$.0$^{5,9}$]tetradec-*exo*-12-yl acetate (VIIb).** Yield 60%. $^{13}C$ NMR spectrum, $\delta_C$, ppm: 12.66 ($C^4$, $C^5$), 13.88 ($C^6$), 20.89 ($C^{16}$), 27.44 ($C^7$), 32.80 ($C^{13}$), 34.89 ($C^{14}$), 40.64 ($C^{11}$), 41.26 ($C^1$), 46.03 ($C^3$, $C^9$), 47.64 ($C^2$, $C^{10}$), 50.02 ($C^8$), 76.98 ($C^{12}$), 162.80 ($C^{15}$). Found, %: C 78.42; H 8.21. $C_{16}H_{20}O_2$. Calculated, %: C 78.65; H 8.25.

***exo*,*trans*,*exo*-Pentacyclo[8.2.1.1$^{4,7}$.0$^{2,9}$.0$^{3,8}$]tetradecane-*exo*-5(6),*exo*-11-diyl diacetate (VIIIb/VIIIc).** Yield 53% (**VIIIb**), 12% (**VIIIc**). $^{13}C$ NMR spectrum, $\delta_C$, ppm: **VIIIb**: 35.96 ($C^{13}$, $C^{14}$), 21.32 ($C^{16}$, $C^{18}$),

39.55 ($C^1$, $C^7$), 40.63 ($C^4$, $C^{10}$), 41.96 ($C^6$, $C^{12}$), 44.15 ($C^3$, $C^8$), 44.21 ($C^2$, $C^9$), 75.66 ($C^5$, $C^{11}$), 170.91 ($C^{15}$, $C^{17}$); **VIIIc**: 21.32 ($C^{16}$, $C^{18}$), 35.96 ($C^{14}$), 39.55 ($C^1$, $C^4$), 35.96 ($C^{13}$), 40.63 ($C^7$, $C^{10}$), 41.96 ($C^5$, $C^{12}$), 44.15 ($C^3$, $C^8$), 44.21 ($C^2$, $C^9$), 75.66 ($C^6$, $C^{11}$), 170.91 ($C^{15}$, $C^{17}$). Found, %: C 70.92; H 7.68. $C_{18}H_{24}O_4$. Calculated, %: C 71.02; H 7.95.

***endo*,*trans*,*exo*-Pentacyclo[8.2.1.1$^{4,7}$.0$^{2,9}$.0$^{3,8}$]tetradecane-*exo*-5(6),*exo*-11-diyl diacetate (IXb/IXc).** Yield 58% (**IXb**), 10% (**IXc**). $^{13}$C NMR spectrum, $\delta_C$, ppm: **IXb**: 20.77 ($C^{18}$), 21.29 ($C^{16}$), 33.42 ($C^{14}$), 39.62 ($C^6$, $C^{12}$), 40.09 ($C^1$, $C^7$), 41.26 ($C^{13}$), 41.39 ($C^3$, $C^8$), 42.69 ($C^2$, $C^9$), 43.95 ($C^4$, $C^{10}$), 76.88 ($C^5$, $C^{11}$), 169.95 ($C^{17}$), 170.85 ($C^{15}$); **IXc**: 20.93 ($C^{16}$), 21.29 ($C^{18}$), 33.42 ($C^{14}$), 39.62 ($C^5$, $C^{12}$), 40.09 ($C^1$, $C^4$), 41.26 ($C^{13}$), 41.39 ($C^3$, $C^8$), 42.69 ($C^2$, $C^9$), 43.95 ($C^7$, $C^{10}$), 76.88 ($C^6$, $C^{11}$), 169.95 ($C^{15}$), 170.85 ($C^{17}$). Found, %: C 70.69; H 7.78. $C_{18}H_{24}O_4$. Calculated, %: C 71.02; H 7.95.

***endo*,*trans*,*endo*-Pentacyclo[8.2.1.1$^{4,7}$.0$^{2,9}$.0$^{3,8}$]-tetradecane-*exo*-5(6),*exo*-11-diyl diacetate (Xb/Xc).** Yield 41% (**Xb**), 9% (**Xc**). $^{13}$C NMR spectrum, $\delta_C$, ppm: **Xb**: 20.77 ($C^{18}$), 21.29 ($C^{16}$), 39.72 ($C^6$, $C^{12}$), 40.18 ($C^1$, $C^7$), 43.00 ($C^{13}$, $C^{14}$), 43.79 ($C^2$, $C^3$), 43.79 ($C^8$, $C^9$), 43.95 ($C^4$, $C^{10}$), 76.85 ($C^5$, $C^{11}$), 169.99 ($C^{17}$), 170.85 ($C^{15}$); **Xc**: 21.29 ($C^{16}$, $C^{18}$), 37.52 ($C^7$), 37.96 ($C^{14}$), 39.62 ($C^5$), 39.72 ($C^{12}$), 40.18 ($C^1$, $C^4$), 43.00 ($C^{13}$), 43.79 ($C^2$, $C^3$), 43.79 ($C^9$), 43.95 ($C^{10}$), 44.15 ($C^8$), 74.35 ($C^6$), 76.85 ($C^{11}$), 170.85 ($C^{15}$), 170.85 ($C^{17}$). Found, %: C 70.93; H 7.84. $C_{18}H_{24}O_4$. Calculated, %: C 71.02; H 7.95.

**Tricyclo[2.2.1.0$^{2,6}$]hept-*exo*-3-yl acetate (XIb).** Yield 72%, bp 65–66°C (10 Pa). $^{13}$C NMR spectrum, $\delta_C$, ppm: 11.74 ($C^6$), 13.21 ($C^1$), 14.24 ($C^2$), 20.79 ($C^9$), 30.73 ($C^5$), 30.76 ($C^7$), 33.90 ($C^4$), 52.55 ($C^{10}$), 80.74 ($C^3$), 169.51 ($C^8$). Found, %: C 70.92; H 7.69. $C_9H_{12}O_2$. Calculated, %: C 71.02; H 7.95.

**Bicyclo[2.2.1]hept-5-en-*exo*-2-yl acetate (XIc).** Yield 10%, bp 63–64°C (8 Pa). IR spectrum, ν, cm$^{-1}$: 1740 (C=O), 1380 ($CH_3$), 1200–1250 (C–O–C), 910, 730, 700 (C=C). $^{13}$C NMR spectrum, $\delta_C$, ppm: 18.01 ($C^9$), 26.51 ($C^7$), 35.48 ($C^6$), 39.72 ($C^4$), 41.44 ($C^1$), 76.75 ($C^5$), 129.68 ($C^2$), 134.70 ($C^3$), 166.89 ($C^8$). Found, %: C 70.85; H 7.79. $C_9H_{12}O_2$. Calculated, %: C 71.02; H 7.95.

**e*ndo*-Tricyclo[5.2.1.0$^{2,6}$]dec-3(4)-en-*exo*-8-yl acetate (XIIb/XIIc).** Yield 75%, bp 95°C (2 Pa). IR spectrum, ν, cm$^{-1}$: 1740 (C=O), 1380 ($CH_3$), 1200–1250 (C–O–C). $^{13}$C NMR spectrum, $\delta_C$, ppm: **XIIb**: 20.90 ($C^{12}$), 34.22 ($C^{10}$), 34.76 ($C^5$), 35.93 ($C^7$), 37.19 ($C^8$), 38.22 ($C^1$), 40.50 ($C^6$), 42.81 ($C^2$), 74.22 ($C^9$), 125.82 ($C^3$), 131.53 ($C^4$), 166.36 ($C^{11}$); **XIIc**: 20.85 ($C^{12}$), 36.05 ($C^5$), 39.62 ($C^9$), 40.09 ($C^7$), 41.32 ($C^6$), 41.26 ($C^{10}$), 43.95 ($C^1$), 54.80 ($C^2$), 74.48 ($C^8$), 131.80 ($C^4$), 132.61 ($C^3$), 166.58 ($C^{11}$). Found, %: C 74.25; H 7.99. $C_{12}H_{16}O_2$. Calculated, %: C 74.97; H 8.39.

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