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Unusual pathway of the tantalum-catalyzed carboalumination reaction of alkenes with triethylaluminum

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Abstract

Carboalumination of 1-alkenes (1-hexene, 1-octene, 1-decene) with Et₃Al in the presence of catalytic amounts of TaCl₅ results in a mixture of 2-(R-substituted)- and 3-(R-substituted)-*n*-butylaluminates (1:1 ratio) in total yields of 75–85%. The TaCl₅-catalyzed reaction of bicyclo[2.2.1]hept-2-ene, *endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, and *(exo/endo)-5-*methylbicyclo[2.1.1]hept-2-ene with Et₃Al leads to the formation of diethyl[2-*exo-*(2'-norbornylethyl)]aluminates in high yields. DFT calculations confirm the thermodynamic preference of the final *exo* product. The multistep reaction mechanisms for the formation of the resultant organoaluminates through tantalacyclopentanes as key intermediates are also discussed.

Keywords: 1-Alkenes; Norbornenes; Organoaluminates; Catalysis; Tantalum complexes; Tantalacyclopentanes; Carboalumination; DFT calculations.

The carboalumination reaction is widely used as an efficient procedure for the construction of the metal–carbon and carbon–carbon bonds giving rise to new types of higher organoaluminum compounds (OACs). The catalytic systems for this reaction based upon titanium and zirconium compounds or complexes are recognized to be the most active and well studied (Scheme 1).¹

Scheme 1. Carboalumination of 1-alkenes in the presence of Ti and Zr catalysts.

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However, there is practically no data in the literature regarding the catalytic behavior of Ta complexes and compounds in the reaction between OACs and unsaturated hydrocarbons, though Ta and Nb complexes are reported to catalyze dimerization, codimerization, and oligomerization of 1-alkenes,² as well as metathesis³ and polymerization of ethylene.⁴

In this paper, we report the first use of $TaCl_5$ as a catalyst for the carboalumination of linear alkenes and norbornenes with Et_3Al .

Our preliminary experiments showed that $TaCl_5$ catalyzed the reaction between 1-alkenes and Et₃Al. But, in this case, the major products differed from those obtained with Ti and Zr complexes as shown in Scheme 1. We continued our investigations by studying the Ta-catalyzed carboalumination reaction of 1-alkenes with Et₃Al (see *Supporting Information*). 1-Hexene, 1octene and 1-decene were selected as the starting reactants.

The model reaction of 1-octene with Et_3Al (1:1 ratio) in the presence of 5 mol% of the TaCl₅ catalyst (1-octene:[Ta] = 100:5) in hexane at r.t. for seven hours resulted mainly in a mixture of two OACs, **1b** and **2b**, in 75% yield relative to the starting 1-octene. Together with the carboalumination products, **1b** (classic) and **2b** (with an unusual structure), small amounts of the hydroalumination products **3b** (10–15%) derived initial 1-octene, were also detected in the reaction mixture (Scheme 2) (see *Supporting Information*).

Scheme 2. The Ta-catalyzed carboalumination of 1-alkenes.

The structures of the synthesized compounds **4**, **5**, **6a**, **6c**, **8**, and **11** were confirmed by recording IR, ¹H and ¹³C NMR spectra, mass measurements and elemental analysis of their derivatives generated upon deuterolysis and oxidation with molecular oxygen.⁵

The only hydrolysis product, **4b** (3-methylnonane)^{5b} was obtained upon treatment of **1b** and **2b** with dilute hydrochloric acid (8%), while their deuterolysis led to two monodeuterated hydrocarbons, **6b** and **7b** (1:1 ratio). The yield and molar ratio of the resulting regioisomers were determined by calculating their GLC peak area ratios (see *Supporting Information*).

Oxidation of these reaction products with anhydrous oxygen afforded regioisomeric alcohols **9b** and **10b**, in which the hydroxyl groups were attached to different carbon atoms (see *Supporting Information*).

The observations described above confirmed unambiguously the structures of the reaction products **1b** and **2b** as 2-(R-substituted)- and 3-(R-substituted)-*n*-butylaluminates.

To gain a more detailed insight into this unusual tantalum-catalyzed alkene carboalumination with Et_3Al , we have studied the influence of the solvent, the temperature, the molar ratio of reactants, the ligand environment of tantalum, the concentration of the catalyst as well as the duration of the reaction on the yield and composition of the OACs **1b** and **2b** in the model reaction with 1-octene (Table 1).

Table 1. The effect of the molar ratio of reactants, the solvent, the ligand environment of tantalum, and the concentration of the catalyst on the yield and composition of the carboalumination products of 1-octene.

Reaction conditions: concentration of $Et_3Al \ 2 \ mmol/mL$, $[Ta]:[L] = 1:1, \ 20 \ ^{\circ}C, \ 7 \ h$.

As seen in Table 1, the carboalumination reaction of 1-octene with Et_3Al in the presence of TaCl₅ occurred in hydrocarbon solvents such as hexane, benzene, and toluene (entries 1–4, 6, and 7) over 7 hours to afford the OACs **1b** and **2b** (1:1 ratio) in good yields. In dichloroethane (entry 5), this reaction produced predominantly the classic carboalumination product **1b** (2:1). It should be noted that we could not obtain the desired result when ethereal solvents such as the diethyl ether, tetrahydrofuran or methyl *tert*-butyl ether were employed.

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The search for an efficient catalytic system revealed that the binary $TaCl_5-P(OPr^{i})_3$ (1:1) catalytic system produced the highest yield of the unusual carboalumination product **2b** (Table 1, entry 9). Our experiments also showed that ligand-modified Ta catalysts (Table 1, entries 8, 11, 12, and 13) reduced the total yield of the carboalumination products but, at the same time, favored predominant formation of the OAC **1b**. As can be seen from Table 1, the above reaction did not produce **1b** and **2b** when a bidentate ligand (entry 10), or a two-fold excess of other ligands (L/Ta = 2) listed in the Table were used in the carboalumination.

The temperature also played an important role in the reaction of 1-alkenes with Et_3Al , significantly influencing the product yield and the **1b**:**2b** ratio. Thus, at elevated temperature (60 °C), the yield of **2b** decreased (**1b**:**2b** = 70:30), while over five hours the total yield of **1b** and **2b** reached 78%. At a lower temperature (~0 °C), the total yield did not exceed 20% at a molar ratio of **1b**:**2b** = 4:5.

Taking into account our own experimental findings, as well as published data on the synthesis and transformations of substituted tantalacyclopentanes,^{3,6} we can suggest possible routes for the simultaneous formation of OACs 1 and 2 via the carboalumination reaction (Scheme 3).

Scheme 3. The catalytic cycle for the TaCl₅-catalyzed carboalumination reaction of 1-alkenes with Et_3Al .

In accordance with Scheme 3, the reaction between $TaCl_5$ and Et_3Al afforded unstable diethyl tantalum complex 12, which eliminates an ethane molecule to produce the alkene complex 13 as a result of β -hydride transfer. The latter transforms into complex 14 containing molecules of ethylene and the initial 1-alkene in the coordination sphere. Intramolecular oxidative cyclization of complex 14 afforded labile β -alkyl-substituted tantalacyclopentane 15, of which further reaction with excess Et_3Al may proceed along two possible parallel routes.

The first route involves the formation of a bimetallic complex via transmetallation of **15** with Et_3Al at the C1–Ta bond. The subsequent conversion of **16** leads to the OAC **1** as a result of β -hydride transfer. The second route can be realized through the stepwise transmetallation reaction of intermediate **15** with Et_3Al at the C4–Ta bond to give bimetallic complex **17**, followed by its transformation into the unusual carboalumination product **2** after β -hydride transfer.

As shown in all our experiments the hydroalumination products of the original 1-alkene were also detected in the reaction mixture. This can be explained by the fact that the tantalum alkyl derivatives are easily converted into hydrides,⁷ which can serve as promoters for the hydrometallation process.

1-Hexene and 1-decene also reacted with Et_3Al giving rise to the OACs **1a** and **2a**, as well as **1c** and **2c**, respectively. We found that these reactions proceeded in a similar way. They retain all the regularities described above for 1-octene, resulting in deuterated **6a**, **6c**, **7a**, and **7c**, as well as the oxidation products **9a**, **9c** and **10a**, **10c**, respectively (see *Supporting Information*). In all these experiments, the carboalumination reaction was also accompanied by small amounts of hydroalumination products **3** (10–15%).

For more detailed investigations of the carboalumination reaction and its regio- and stereoselectivity in order to synthesize new classes of organoaluminum compounds, we have studied the reaction of norbornenes with Et₃Al under the reaction conditions described above (5 mol% TaCl₅, hexane, 20 °C). Bicyclo[2.2.1]hept-2-ene (norbornene), *endo*-tricyclo[5.2.1.0^{2.6}]deca-3,8-diene (*endo*-dicyclopentadiene) and *exo-endo*-5-methylbicyclo[2.2.1]hept-2-ene (*exo/endo* = 2:1) were selected for this study. The structures of the resulting organoaluminates were deduced from 1D and 2D NMR,⁸ and IR spectra and chromatography-mass spectrometry data of their hydrolysis, deuterolysis, and oxidation products.

Our experiments revealed that norbornene reacted with an equimolar amount of Et_3Al in the presence of 5 mol% TaCl₅ as the catalyst (hexane, 20 °C, 6 h) giving rise, exclusively, to an

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organoaluminate compound (*exo*-adduct) **18** (85% yield) as the product of an unusual carboalumination pathway of the reaction (Scheme 4).

Scheme 4. The TaCl₅-catalyzed carboalumination reaction of norbornene with triethylaluminum

The chemical structure of adduct **18** was elucidated by standard chemical transformations. Thus, hydrolysis of **18** with dilute hydrochloric acid (~5% aq. HCl) gave 2-*exo*-ethylbicyclo[2.2.1]heptane (**19**),⁹ whereas deuterolysis of the reaction mixture led to *exo*-monodeuteroethylnorbornane (**20**). Oxidation of **18** resulted in the appropriate alcohol **21** (see *Supporting Information*). The yields of the end products were estimated from the GLC peak areas of their hydrolysis and deuterolysis products.

To clarify the influence of the norbornene structure on the pathway and stereochemistry of the carboalumination reaction we studied *endo*-dicyclopentadiene and *exo-endo*-5-methylbicyclo[2.2.1]hept-2-ene in the reaction with Et_3Al under the optimized conditions.

Dicyclopentadiene took part in the reaction with Et_3A1 to give a mixture of two regioisomeric organoaluminates 22 and 23, which differed from one another in the position of the aluminum-containing substituent relative to the double bond (Scheme 5). The total yield of 22 and 23 (1:1 ratio) reached 88%.

Scheme 5. The reaction of dicyclopentadiene with triethylaluminum in the presence of TaCl₅.

Deuterolysis of **22** and **23** resulted in a mixture of *exo*-8-(1-deuteroethyl)-*endo*-tricyclo[$5.2.1.0^{2.6}$]-dec-3-ene (**24**) and *exo*-9-(1-deuteroethyl)-*endo*-tricyclo[$5.2.1.0^{2.6}$]-dec-3-ene (**25**), respectively.¹⁰ The formation of only **24** and **25** from four possible dicyclopentene isomers was clearly confirmed by the ¹³C NMR assignments (see *Supporting Information*).

The reaction between *exo-endo*-5-methylbicyclo[2.2.1]-hept-2-ene and Et_3Al in the presence of TaCl₅ as the catalyst under the above reaction conditions resulted in a more complex product mixture (Scheme 6).

Scheme 6. The reaction of *exo-endo-5*-methylbicyclo[2.2.1]-hept-2-enes with triethylaluminum in the presence of TaCl₅.

Deuterolysis of the reaction mixture (compounds 26-29), in this case, led to methyl(deuteroethyl)norbornanes 30, 31, 32, and 33 [(30+31):(32+33) = 2:1] in a total yield of 86%.¹¹

According to the ¹³C NMR spectral data, products **30**, **31**, **32**, and **33** differed from each other in the positions of their monodeuteroethyl substituents relative to the methyl substituent, and were epimers of each other at the C2 position (see *Supporting Information*).

Based on our current and earlier experimental data, and taking into account the published data dealing with the synthesis, application and transformations of tantalum complexes,^{2,6} we suggest possible pathways for the reaction under discussion.

The catalytic cycle of the $TaCl_5$ -catalyzed reaction involving norbornenes and Et_3Al is represented by the example of bicyclo[2.2.1]hept-2-ene (Scheme 7).

In accordance with the Scheme, the reaction between TaCl₅ and Et₃Al affords unstable dialkyl tantalum complex **34**, which eliminates an ethane molecule to produce the ethylene complex **35** as a result of β -hydride transfer. The latter transforms into bis-alkene complex **36** containing the ethylene and initial norbornene molecules in the coordination sphere. Intramolecular oxidative cyclization in complex **36** affords labile tantalacyclopentane **37**. Transmetallation reaction of the latter with an additional Et₃Al molecule results in Al,Ta-bimetallic complex **38**, which undergoes transformation into the carboaluminate product **18** after β -hydride transfer.

Scheme 7. Catalytic cycle for the reaction of norbornene with Et_3Al in the presence of $TaCl_5$.

To estimate the thermodynamic probability of the elementary steps of the proposed mechanism for the TaCl₅-mediated norbornene reaction with organoaluminate compounds, we carried out density functional theory (DFT) calculations using the PBE functional¹² and Stevens–Basch–Krauss pseudopotential¹³ implemented in the Priroda 6 program.¹⁴ Density functional methods are efficient tools for the understanding of chemical transformations of palladium,¹⁵ organomagnesium, organoaluminium and zirconium coordination compounds.¹⁶ The calculated harmonic vibrational frequencies characterize the optimized structures as minima of potential energy surfaces. The Gibbs energies of the reactions were calculated as differences between the total energies of products and reactants taking into account thermal corrections (T = 293, all Gibbs energies ΔG are in kJ/mol).

Scheme 8 shows a sequence of elementary steps of the catalytic cycle. Accordingly, the reaction of Et_3Al with $TaCl_5$ results in the formation of organotantalum compound Cl_3TaEt_2 34, which then converts into a π -complex of ethylene and tantalum chloride 35 (reaction 2). Complex formation is endothermic and can occur due to the very high exothermicity of the previous step. Formation of key intermediate 37 (reaction 3) is also an exothermic process.

As we have shown earlier, the reaction between norbornene and Et_3Al in the presence of TaCl₅ leads to the only product **18**, which is characterized by the *exo*-location of the ethylaluminum moiety. To understand the reasons for such chemical behavior of norbornene, we investigated two paths for the reaction between **37** and Et_3Al : a) without breaking the chemical bond between Ta and the norbornyl moiety resulting in **38** (reaction 4), and b) with breaking leading to **39** (reaction 5). DFT calculations showed that both pathways were exothermic and characterized with approximately equal Gibbs energies. The calculated lengths of the non-equivalent Ta–C bonds, being 2.152 and 2.122 Å (Figure 1), confirmed the equal probability of the two possible routes for the reaction between tantalacyclopentane **37** and Et_3Al .

Scheme 8. Elementary steps of the catalytic cycle for the norbornene carboalumination and their calculated Gibbs energies (PBE/SBK, in kJ/mol).

Figure 1. Calculated bond lengths of the tantalacyclopentane moiety in the intermediate 22 (Å). Hydrogen atoms are omitted for clarity.

The greatest differences in the thermodynamic parameters were observed during further transformations of **38** and **39**. According to the proposed Scheme, regeneration of active π -complex **35** occurs in the final steps of the catalytic cycle resulting in **18** and **40**. According to PBE/SBK calculations, these compounds differ in thermodynamic stability, so the Gibbs energies of their formations differ by sign. The formation of **40** (reaction 7) is endothermic in contrast to the exothermic formation of **18** (reaction 6). Therefore, the identification of the only product **18** from the reaction between norbornene and Et₃Al in the chemical experiment is the result of its higher thermodynamic stability.

In conclusion, we have demonstrated a new route to organoaluminate compounds through the carbalumination reaction between 1-alkenes and Et_3Al in the presence of $TaCl_5$ as the catalyst. In contrast to the known zirconium- and titanium-catalyzed procedures, the elaborated method allows synthesis of unusual 3-(R-substituted)-*n*-butylaluminates, thus opening up new possibilities for applications in organic and organometallic chemistry. The stereoselective $TaCl_5$ -catalyzed reaction of bicyclo[2.2.1]hept-2-ene, *endo*-tricyclo[5.2.1.0^{2,6}]dec-3,8-diene, and *exo-endo*-5-

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methylbicyclo[2.1.1]hept-2-ene with Et₃Al affords diethyl[2-exo-(2'-norbornylethyl)]aluminates in high yields. The quantitative evaluation of the Gibbs energy ΔG (293K) for elementary reactions of the proposed catalytic cycle through intermediate tantalacyclopentanes has been carried out by using DFT calculations, which confirmed the thermodynamic preference of the unusual pathway of the carboalumination reaction and the final exo product linking it with steric hindrance in the bulky norbornane moiety. The elaborated method represents a convenient opportunity for functionalization of norbornene-type cyclic olefins.

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Figure(s) (use if uploading high quality figure files)













Figure(s) (use if uploading high quality figure files)





| Entry | Et ₃ Al : 1-octene molar ratio | 1-Octene: TaCl ₅ molar ratio | Solvent | Ligand | Total yield 1b+2b (%) | 1b:2 b molar ratio |
|-------|--|---|----------------|------------------------------------|---------------------------------------|---------------------------------|
| 1 | 1:1 | 100 : 5 | hexane | | 75 | 1:1 |
| 2 | 1:1 | 100 : 3 | hexane | _ | 53 | 1:1 |
| 3 | 2:1 | 100 : 5 | hexane | | 85 | 1:1 |
| 4 | 1:1 | 100 : 10 | hexane | | 81 | 1:1 |
| 5 | 1:1 | 100 : 5 | dichloroethane | | 74 | 2:1 |
| 6 | 1:1 | 100 : 5 | benzene | | 70 | 1:1 |
| 7 | 1:1 | 100 : 5 | toluene | - | 71 | 1:1 |
| 8 | 1:1 | 100 : 5 | hexane | Ph ₃ P | 70 | 5 :4 |
| 9 | 1:1 | 100 : 5 | hexane | $(Pr^iO)_3P$ | 72 | 1:6 |
| 10 | 1:1 | 100 : 5 | hexane | Ph ₂ P PPh ₂ | _ | _ |
| 11 | 1:1 | 100 : 5 | hexane | $P(NMe_2)_3$ | 59 | 1:1 |
| 12 | 1:1 | 100 : 5 | hexane | Et ₃ N | 66 | 3 :2 |
| 13 | 1:1 | 100 : 5 | hexane | N | 65 | 5:1 |
| Tak | ole 1. | | | | | |

Supporting Information

Unusual pathway of the tantalum-catalyzed carboalumination reaction of alkenes with triethylaluminum

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Experimental section

All manipulations of oxygen- and moisture-sensitive materials were conducted with using a standard Schlenk technique or in a dry glove box under an argon atmosphere. Alkenes having a purity of no less than 99,8% were distilled over Bu_3^iAl in under a stream of argon prior to use. Commercially available norbornene and dicyclopentadiene (purity 99,5 %) were purchased from Aldrich. Unavailable commercially *exo-end*o-5-methylnorbornene (*exo/endo* = 2:1) used in experiments was prepared in the laboratory of Prof. R.I. Khusnutdinov. Commercially available TaCl₅ (purity 99,8 %) was purchased from Aldrich. Dry solvents (toluene, benzene, dichloroethane, and hexane) were prepared according to procedures as described in the following: Gordon, A.; Ford, R. Sputnik khimika, Mir, Moscow, 1976. (Russian translation from A. Gordon, R. Ford, The chemist's companion. A handbook of practical data, techniques and references, John Wiley & Sons, 1972). Chromatographic analysis of the hydrolysis and deuterolysis products was performed on SHIMADZU GC-2014 instrument (column 2 m x 3 mm, 5% SE-30 on Chromaton N-AW-HMDS (0.125-0.160 mm) as the stationary phase, helium as a carrier gas (30 mL min⁻¹), temperature programming from 50 to 300 °C at a rate of 8 °C min⁻¹. The one-dimensional (¹H, ¹³C) and two dimensional homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were recorded in CDCl₃ on a spectrometer Bruker Avance 400 [400.13 MHz (¹H) and 100.62 MHz (¹³C)] at 298 K in accordance with standard Bruker pulse sequences. Chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded using FT-IR spectrometer Bruker Vertex 70 v (liquid film). Chromato-mass spectrometric analysis of compounds was performed on SHIMADZU GCMS-QP 2010 instrument (SUPELCO SLBTM-5 ms, 60000 mm x 0.25 mm x 0.25 µm, helium as the carrier gas, temperature programming 260 °C at a rate of 5 °C min⁻¹, the temperature of the ion source 260 ° C [EI, 70 eV]). Elemental analysis of the samples was carried out using Carlo Erba Elemental Analyzer model 1106.

The carboalumination reaction of 1-alkenes with Et_3Al catalyzed by $TaCl_5$ catalyst (general procedure). A glass reactor, under a dry argon atmosphere at 0 °C, was charged under stirring with TaCl₅ (2.5 mmol, ~ 0,9 g), 1-alkene (50 mmol) and Et₃Al (50 mmol, 2 M solution in hexane). Temperature was raised to 20 °C, and the mixture of reactants was stirred for additional 7 h. Then, the reaction mixture was quenched by a 8% DCl in D₂O to identify OACs obtained. The organic layer was separated, washed with NaHCO₃ (until neutral) and dried over MgSO₄. The mixture of products was separated by fractional distillation. Additional separation of compounds from the mixtures was performed by preparative GC.

1-Deutero-3-ethyloctane (**6b**): B.p. 75 °C (30 mm Hg). IR: 2175 (C–D) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 1.12–1.45 (m, 13H, CH₂, CH), 0.86–0.97 (m, 8H, CH₃, CH₂D). ¹³C NMR (100.62 MHz, CDCl₃): δ 36.8 (C⁴), 34.5 (C³), 32.1 (C⁷), 29.8 (C⁶), 29.6 (C²), 27.2 (C⁵), 22.8 (C⁸), 18.9 (C¹⁰,

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t, ${}^{1}J_{C-D} = 19$ Hz), 14.1 (C⁹), 11.3 (C¹). MS, m/z 143 [M]⁺. Elemental Anal. Calc. for: C, 83.92; H, 19.68; D, 1.40. Found: C, 84.20; H+D, 15.49%.

1-Deutero-3-methylnonane (**7b**): B.p. 75 °C (30 mm Hg). IR: 2175 (C–D) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 1.12–1.45 (m, 13H, CH₂, CH), 0.86–0.97 (m, 8H, CH₃, CH₂D). ¹³C NMR (100.62 MHz, CDCl₃): δ 36.8 (C⁴), 34.5 (C³), 32.1 (C⁷), 29.8 (C⁶), 29.5 (C²), 27.2 (C⁵), 22.8 (C⁸), 19.2 (C¹⁰), 14.1 (C⁹), 11.0 (C¹, t, ¹J_{C-D} = 19.0 Hz). MS, *m*/*z* 143 [M]⁺. Elemental Anal. Calc. for: C, 83.92; H, 14.68; D, 1.40. Found: C, 83.79; H+D, 15.97%.

The ¹³C NMR spectrum of regioisomer **6b** exhibits a signal at $\delta(C10)$ 18.9 with a characteristic coupling constant (${}^{1}J_{C-D} = 19.0 \text{ Hz}$) and a diagnostic signal at $\delta(C1)$ 11.3 ppm. The deuterium isotope effect on the ¹H chemical shift of the C10-methyl group caused its shielding compared to that of compound **7b**. This shielding effect results in the chemical shift of δ 0.31 ppm. The ¹³C NMR spectrum of regioisomer **7b** also contained the characteristic triplet signal at $\delta(C1)$ 11.0 ppm (${}^{1}J_{C-D} = 19.0 \text{ Hz}$).

In an analogous fashion, the deuterium isotope effect in compound **7b** caused shielding of the C1-methyl group, which resulted in a chemical shift of δ 0.30 ppm. We also noted the presence of β -isotope effects in both compounds **6b** ($\Delta \delta_{\beta\text{-isotope}} \text{ C3} = 0.06$ ppm) and **7b** ($\Delta \delta_{\beta\text{-isotope}} \text{ C2} = 0.07$ ppm).

Oxidation of OACs from the reaction of 1-alkenes with Et_3Al catalyzed by $TaCl_5$ (general procedure). Oxidation of the OMCs **1b** and **2b**, obtained by the reaction of 1-alkenes with Et_3Al in hexane or benzene in the presence $TaCl_5$, was carried out in a thermostated glass reactor (100 mL) by passing bubbles of pure dry oxygen through the solution. The temperature of solution was maintained at 5–8 °C. After 120 minutes, a 5% HCl solution was added dropwise (0 °C) to the reaction mixture. The resultant mixture was extracted with diethyl ether (3 x 20 mL), dried over MgSO₄. After removal of ether, the residue was analyzed by GLC and then distilled *in vacuo*. Individual alcohols **9** and **10** were separated by preparative GLC.

2-Ethyloctane-1-ol (**9b**): Bp 76–77 °C (3 mm Hg). IR (thin film): 3420 (O–H), 1045 (C–O), 1465, 1375 cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 3.51 (d, ³*J*_{H–H} = 5 Hz, 2H, CH₂O), 1.12–1.41 (m, 13H, CH₂, CH), 0.87–0.89 (m, 6H, CH₃). ¹³C NMR (100.62 MHz, CDCl₃): δ 65.2 (C¹), 31.9 (C⁶), 30.5 (C²), 29.8 (C³), 29.7 (C⁵), 30.0 (C⁴), 23.4 (C⁹), 22.7 (C⁷), 14.1 (C⁸), 11.1 (C¹⁰). MS, *m/z* 158 [M]⁺. Elemental Anal. Calc. for: C, 75.95; H, 13.92; O, 10.13. Found: C, 75.91; H, 13.69%.

3-Methylnonane-1-ol (**10b**): Bp 76–77 °C (3 mm Hg). IR (thin film): 3420 (O–H), 1045 (C–O), 1465, 1375 cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 3.64 (m, 2H, CH₂O), 1.59 and 1.35 (m, 2H, H₂C²), 1.57 (m, 1H, HC³), 1.18–1.31 (m, 10H, CH₂), 0.87–0.89 (m, 6H, CH₃). ¹³C NMR (100.62 MHz, CDCl₃): δ 61.1 (C¹), 40.0 (C²), 37.2 (C⁴), 31.9 (C⁷), 29.8 (C⁶), 29.6 (C³), 26.9 (C⁵), 22.7 (C⁸), 19.7 (C¹⁰), 14.1 (C⁹). MS, *m/z* 158 [M]⁺. Elemental Anal. Calc. for: C, 75.95; H, 13.92; O, 10.13. Found: C, 75.91; H, 13.69%.

In the ¹³C NMR spectrum of regioisomeric alcohol **10b** the carbinol signal appeared at a higher field (δ C1 61.1) compared to the corresponding signal in the spectrum of regioisomeric alcohol **9b** (δ C10 65.2).

Significant differences between the positions of the low field methyl carbon resonance (δ C10 9.7) and the shielded methyl carbon resonance (δ C1 11.1) were observed in the spectra of compounds **10b** and **9b**, respectively. The 1:1 ratio of **9b** and **10b** was calculated through ¹H NMR experiments from integration of unambiguously different proton signals belonging to the hydroxymethylene groups (δ C1<u>H</u>₂ 3.51 and δ C¹<u>H</u>₂ 3.64 for alcohols **9b** and **10b**, respectively).

1-Deutero-3-methylheptane (**7a**): B.p. 56 °C (80 mm Hg). IR: 2180 (C–D) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 1.45 (m, 1H, CH), 1.29 (m, 2H, CH₂), 1.20 (m, 2H, CH₂), 1.16 (m, 2H, CH₂), 1.12 (m, 2H, CH₂), 0.87 (t, 3H, CH₃, ³J = 7.2 Hz), 0.86 (m, 2H, CH₂D), 0.83 (q, 3H, CH₃, ³J = 6.4 Hz). ¹³C NMR (100.62 MHz, CDCl₃): δ 36.6 (C⁴), 34.7 (C³), 29.4 (C²), 28.6 (C⁵), 22.8 (C⁶), 18.6 (C⁸),

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14.1 (C⁹), 10.8 (C¹, t, ${}^{1}J_{C-D} = 19.0$ Hz). MS, m/z 115 [M]⁺. Elemental Anal. Calc. for: C, 83.48; H, 14.78; D, 1.74. Found: C, 83.41; H+D, 16.49%.

1-Deutero-3-methylundecane (**7c**): B.p. 110 °C (30 mm Hg). IR: 2175 (C–D) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 1.43 (m, 1H, CH), 1.35 (m, 16H, CH₂), 0.93 (m, 8H, CH₃, CH₂D). ¹³C NMR (100.62 MHz, CDCl₃): δ 34.4 (C²), 34.4 (C⁴), 32.0 (C⁵), 30.2 (C⁶), 29.8 (C⁷), 29.5 (C³), 29.5 (C⁸), 27.2 (C⁹), 22.7 (C¹⁰), 19.1 (C¹²), 18,8 (C¹, t, ¹J_{C-D} = 19.0 Hz), 14.0 (C¹¹). MS, *m/z* 171 [M]⁺. Elemental Anal. Calc. for: C, 84.21; H, 14.62; D, 1.17. Found: C, 84.18; H+D, 15.71%.

2-Ethylhexane-1-ol (**9a**): B.p. 101 °C (30 mm Hg). IR: 1375, 1465, 1045 (C–O), 3430 (O–H) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 3.52 (q, ³*J*_{H-H} = 4.8 Hz, 2H, CH2O), 1.39 (m, 2H, CH₂), 1.37 (m, 1H, CH), 1.32 (m, 2H, CH₂), 1.28 (m, 4H, CH₂), 0.89 (m, 6H, CH₃). ¹³C NMR (100.62 MHz, CDCl₃): δ 65.1 (C¹), 41.9 (C²), 30.1 (C³), 29.2 (C⁴), 23.3 (C⁷), 23.1 (C⁵), 14.1 (C⁶), 11.1 (C⁸). MS, *m*/*z* 130 [M]⁺. Elemental Anal. Calc. for: C, 73.85; H, 13.84; O, 12.31. Found: C, 73.63; H, 13.75%. 2-Ethyldecane-1-ol (**9c**): Bp 151 °C (30 mm Hg). IR (thin film): 3425 (O–H), 1045 (C–O), 1465, 1375 cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 3.35 (m, 2H, CH₂O), 1.76 (m, 3H, CH₃), 1.45 (m, 1H, CH), 1.17 (m, 16H, CH₂), 0.76 (m, 3H, CH₃). ¹³C NMR (100.62 MHz, CDCl₃): δ 64.3 (C¹), 41.8 (C²), 37.2 (C³), 31.9 (C⁴), 30.4 (C⁵), 29.6 (C⁶), 29.3 (C⁷), 26.9 (C⁸), 23.2 (C¹¹), 22.3 (C⁹), 13.8 (C¹⁰), 10.8 (C¹²). MS, *m*/*z* 186 [M]⁺. Elemental Anal. Calc. for: C, 77.42; H, 13.98; O, 8.60. Found: C, 77.39; H, 13.89%.

3-Methylheptane-1-ol (**10a**): B.p. 97 °C (30 mm Hg). IR: 1375, 1465, 1045 (C–O), 3425 (O–H) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 3.65 (m, 2H, CH₂O), 1.59 (m, 2H, CH₂), 1.52 (m, 1H, CH), 1.28 (m, 6H, CH₂), 0.89 (m, 6H, CH₃). ¹³C NMR (100.62 MHz, CDCl₃): δ 61.1 (C¹), 39.9 (C²), 36.8 (C⁴), 29.5 (C³), 29.1 (C⁵), 22.9 (C⁶), 19.6 (C⁸), 14.0 (C⁷). MS, *m/z* 130 [M]⁺. Elemental Anal. Calc. for: C, 73.85; H, 13.84; O, 12.31. Found: C, 73.71; H, 13.80%.

3-Methylundecane-1-ol (**10c**): Bp 156 °C (30 mm Hg). IR (thin film): 3425 (O–H), 1045 (C–O), 1465, 1375 cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 3.47 (m, 2H, CH₂O), 1.45 (m, 1H, CH), 1.17 (m, 16H, CH₂), 0.76 (m, 6H, CH₃). ¹³C NMR (100.62 MHz, CDCl₃): δ 60.2 (C¹), 39.7 (C²), 31.9 (C⁴), 30.1 (C⁵), 30.0 (C⁶), 29.6 (C⁷), 29.4 (C³), 29.3 (C⁸), 26.9 (C⁹), 22.3 (C¹⁰), 19.4 (C¹²), 13.8 (C¹¹). MS, *m*/*z* 186 [M]⁺. Elemental Anal. Calc. for: C, 77.42; H, 13.98; O, 8.60. Found: C, 77.43; H, 13.85%.

The carboalumination reaction of norbornene with Et_3Al catalyzed by $TaCl_5$ catalyst (general procedure). A glass reactor, under a dry argon atmosphere at 0 °C, was sequentially charged under stirring with hexane (20 mL), norbornene (30 mmol, 2.8 g), triethylaluminum (30 mmol, 4.5 mL), and TaCl₅ (1,5 mmol, 0.54 g). The temperature was raised to 20 °C and the mixture was stirred for additional 6 h. Then, the reaction mixture was quenched by a 8% DCl in D₂O to identify the OAC obtained. The organic layer was separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organics were washed with NaHCO₃ (until neutral) and dried over MgSO₄. The target product **20** was separated by fractional distillation.

2-*exo*-(2-deuteroethyl)bicyclo[2.2.1]heptane (**20**): Bp = 64 °C (30 mm Hg.). IR v (cm⁻¹ in thin film): 2180 (C–D). ¹H NMR (CDCl₃, in ppm, 400.13 MHz): δ = 2.19 (m, 1H, CH), 1.98 (m, 1H, CH), 1.48 (m, 1H, CH), 1.43 (m, 1H, CH), 1.41 (m, 1H, CH), 1.33 (m, 2H, CH₂), 1.31–1.33 (m, 1H, CH), 1.28 (m, 1H, CH), 1.24 (m, 1H, CH), 1.16 (m, 1H, CH), 1.10 (m, 1H, CH), 1.04 (m, 1H, CH), 0.83–0.88 (m, 2H, CH₂D). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz): δ = 44.4 (C²), 40.8 (C¹), 38.0 (C³), 36.5 (C⁴), 35.2 (C⁷), 30.2 (C⁶), 29.5 (C⁸), 28.9 (C⁵), 12.1 (C⁹, ¹J_{C-D} = 19 Hz). MS, *m/z*: 125 (M⁺). Elemental Anal. Calc. for: C, 86.4; H, 12.00; D, 1.60. Found: C, 86.35; H+D, 13.61%.

Oxidation of OACs from the reaction of norbornenes with Et_3Al catalyzed by $TaCl_5$ (general procedure). Oxidation of the OAC **18**, obtained by the reaction of bicycle[2.2.1]-hept-2-ene with Et_3Al in hexane in the presence TaCl₅, was carried out in a thermostated glass reactor (100 mL) by passing bubbles of pure dry oxygen through the solution. The temperature of solution was maintained at 5–8 °C. After 120 minutes, the reaction mixture was poured into a 5% aq. HCl

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solution. The resultant alcohol was extracted with diethyl ether (3 x 50 mL), dried over MgSO₄, and, after removal of ether, was analyzed by GLC. The alcohol **21** was separated by vacuum distillation.

2-*exo*-(2-hydroxyethyl)bicyclo[2.2.1]heptane (**21**): Bp = 135 °C (30 mm Hg). IR v (cm⁻¹ in thin film): 3435 (O–H), 1045 (C–O). ¹H NMR (CDCl₃, in ppm, 400.13 MHz): δ = 3.64 (t, ³J = 7.2 Hz, 2H, CH₂O), 2.21 (m, 1H, CH), 1.98 (m, 1H, CH), 1.59 (m, 1H, CH), 1.50 (m, 1H, CH), 1.49 (m, 1H, CH), 1.47 (m, 1H, CH), 1.45 (m, 1H, CH), 1.38 (m, 1H, CH), 1.31 (m, 1H, CH), 1.15 (m, 1H, CH), 1.10 (m, 3H, CH). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz): δ = 61.7 (C⁹), 41.1 (C¹), 40.0 (C⁸), 38.4 (C²), 38.1 (C³), 36.6 (C⁴), 35.3 (C⁷), 30.1 (C⁵), 28.8 (C⁶). MS, *m/z*: 122 (M⁺-H₂O). Elemental Anal. Calc. for: C, 77.14; H, 11.43; O, 11.43. Found: C, 77.21; H, 11.39%.

The 13 C NMR spectra of products **20** and **21** contain seven resonances assigned to magnetically nonequivalent carbon atoms of the norbornane skeleton. This indicates the effect of the methylene hydrogen substitution at the C2 position. The crosspeaks due to long-range couplings between the norbornane C2 and the protons of the substituent is the further convincing evidence of the structures.

The HMBC spectrum of **20** contains crosspeaks between δ_{C2} 44.4 and δ_H 1.35 and 0.80–0.88, whereas, in the spectrum of **21**, δ_{C2} 38.4 provides crosspeaks with δ_H 1.38, 1.59 and 3.64. The resonances δ_C 44.4, 28.9, and 35.2 for **20** and δ_C 38.4, 30.1, and 35.3 for **21** of the characteristic C2, C5, and C7 clearly indicate the formation of both **20** and **21** having *exo*-substituents, that is, these groups are *cis* to the bridge.

The product mixture of **24** and **25** was isolated by distillation. Bp = 118 °C (30 mm Hg). IR v (cm⁻¹ in thin film): 1370, 1480, 1620, 2190 (C-D), 2860, 2960, 3060. MS, *m/z*: 163 (M⁺). Elemental Anal. Calc. for: C, 88.34; H, 10.43; D, 1.23. Found: C, 88.41; H+ D, 11.60%.

The GC retention times for components of a given mixture were determined as 15.89 and 16.05 min. Two sets of the characteristic carbons in the ¹³C NMR spectra (according to reference data from [10]) clearly indicate the presence of two isomers that are hard to chromatographically separate.

8-*exo*-(1-deuteroethyl)-*endo*-tricyclo[5.2.1.0^{2.6}]dec-3-ene (**24**): ¹H NMR (CDCl₃, in ppm, 400.13 MHz): $\delta = 5.66$ (m, 1H, CH), 5.54 (m, 1H, CH), 2.52 (m, 1H, CH), 2.21 (m, 2H, CH₂), 2.11 (m, 1H, CH), 1.88 (m, 1H, CH), 1.54 (m, 1H, CH), 1.49 (m, 1H, CH), 1.48 (m, 1H, CH), 1.29 (m, 2H, 2CH), 1.23 (m, 2H, CH₂), 0.82 (t, 2H, CH₂D), 0.77 (m, 1H, CH). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz): $\delta = 132.6$ (C⁴), 130.8 (C³), 53.7 (C²), 45.7 (C⁶), 42.5 (C⁷), 41.1 (C¹), 38.4 (C¹⁰), 35.6 (C⁸), 33.6 (C⁹), 32.0 (C⁵), 29.6 (C¹¹), 12.3 (C¹², t, ¹J_{C-D} = 19 Hz).

9-*exo*(1-deuteroethyl)-*endo*-tricyclo[5.2.1.0^{2.6}]dec-3-ene (**25**): ¹H NMR (CDCl₃, in ppm, 400.13 MHz): $\delta = 5.66$ (m, 1H, CH), 5.54 (m, 1H, CH), 2.52 (m, 1H, CH), 2.27 (m, 1H, CH), 2.21 (m, 1H, CH), 2.07 (m, 1H, CH), 1.54 (m, 1H, CH), 1.52 (m, 1H, CH), 1.48 (m, 1H, CH), 1.46 (m, 1H, CH), 1.29 (m, 1H, CH), 1.12 (t, 2H, CH₂), 0.83 (m, 1H, CH), 0.82 (t, 2H, CH₂D). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz): $\delta = 132.6$ (C⁴), 130.4 (C³), 52.4 (C²), 44.1 (C⁶), 41.8 (C⁷), 40.0 (C¹), 38.6 (C⁹), 38.4 (C¹⁰), 32.4 (C⁵), 30.3 (C⁸), 29.2 (C¹¹), 11.9 (C¹², t, ¹J_{C-D} = 19 Hz).

The ¹³C NMR spectrum of the mixture of compounds **24** and **25** contains two resonances at δ_C 11.9 and 12.3 (1:1 intensity ratio) assigned to C12 indicating the formation of only **24** and **25** from four possible dicyclopentene isomers. The 2C intensity signal at δ_C 38.4 belonging to both bridging C10 carbons is indicative of the *exo*-orientation of monodeuterated fragments. The crosspeak between the C12 methylene proton resonance at δ_H 0.82 and the resonance at δ_C 38.6 in the HMBC spectrum of **25** clearly indicate the substitution in the carcass at C9 position, whereas **24** is the C8 substituted isomer due to the correlation between δ_H 0.82 and δ_C 35.6.

The product mixture of **30**, **31**, **32**, and **33** was isolated by distillation. Bp = 78 °C (30 mm Hg). IR v (cm⁻¹ in thin film): 2180 (C–D). MS, *m/z*: 139 (M⁺). Elemental Anal. Calc. for: C, 86.33; H, 12.23; D, 1.44. Found: C, 86.21; H+D, 13.61%.

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The GC retention times t_r for components of a given mixture were determined as 11.34 and 11.52 min with the integral intensity ratio of 2:1, respectively, that agrees with the *exo/endo* ratio of 2:1 for initial *exo-endo*-5-methylbicyclo[2.2.1]-hept-2-ene. However, four sets of the characteristic carbons in the ¹³C NMR spectra (according to reference data from [10]) clearly indicate the presence of two *exo* and two *endo* isomers that are hard to chromatographically separate.

2-*exo*-methyl-6-*exo*-(1-deuteroethyl)bicyclo[2.2.1]heptane (**30**): ¹H NMR (CDCl₃, in ppm, 400.13 MHz): $\delta = 2.15$ (m, 1H, CH), 1.90 (m, 1H, CH), 1.64 (m, 1H, CH), 1.46 (m, 1H, CH), 1.41 (m, 1H, CH), 1.25 (m, 1H, CH), 1.22–1.25 (m, 1H, CH), 1.20 (m, 2H, CH₂), 1.15 (m, 1H, CH), 0.97 (d, 3H, CH₃, ³J = 7.2 Hz), 0.95 (m, 1H, CH), 0.93 (m, 1H, CH), 0.86 (d, 2H, CH₂D, ³J = 7.2 Hz). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz): $\delta = 44.8$ (C⁶), 38.9 (C³), 37.0 (C⁷), 36.9 (C¹), 35.3 (C²), 31.7 (C⁵), 22.3 (C⁹), 16.7 (C⁸), 12.3 (C⁴), 12.1 (C¹⁰, t, ¹J_{C-D} = 19 Hz).

2-*exo*-methyl-5-*exo*-(1-deuteroethylbicyclo[2.2.1]heptane (**31**): ¹H NMR (CDCl₃, in ppm, 400.13 MHz): δ = 2.15 (m, 1H, CH), 1.81 (m, 1H, CH), 1.48 (m, 1H, CH), 1.46 (m, 1H, CH), 1.37 (m, 1H, CH), 1.29 (m, 2H, 2CH), 1.27 (m, 1H, CH), 1.20 (m, 1H, CH), 1.13 (m, 1H, CH), 1.11 (m, 1H, CH), 1.02 (m, 1H, CH), 0.95 (m, 1H, CH), 0.93 (d, 3H, CH₃, ³*J* = 6.8 Hz), 0.86 (d, 2H, CH₂D). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz): δ = 44.9 (C⁵), 43.3 (C⁴), 38.7 (C³), 37.0 (C¹), 37.0 (C⁷), 35.7 (C²), 31.7 (C⁶), 29.4 (C⁹), 17.4 (C⁸), 12.1 (C¹⁰).

1-*endo*-methyl-6-*exo*-(1-deuteroethyl)bicyclo[2.2.1]heptane (**32**): ¹H NMR (CDCl₃, in ppm, 400.13 MHz): $\delta = 2.14$ (m, 1H, CH), 1.94 (m, 1H, CH), 1.90 (m, 1H, CH), 1.80 (m, 2H, 2CH), 1.78 (m, 1H, CH), 1.65 (m, 1H, CH), 1.48 (m, 1H, CH), 1.41 (m, 1H, CH), 0.90 (d, 3H, CH₃, ³J = 7.2 Hz), 0.86 (d, 2H, CH₂D), 0.84 (m, 1H, CH), 0.57 (m, 1H, CH), 0.55 (m, 1H, CH). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz)): $\delta = 47.6$ (C⁵), 41.9 (C⁴), 39.1 (C⁷), 37.9 (C¹), 37.6 (C³), 34.1 (C²), 30.7 (C⁶), 29.6 (C⁹), 22.2 (C⁸), 12.1 (C¹⁰).

1-*endo*-methyl-5-*exo*-(1-deuteroethyl)bicyclo[2.2.1]heptane, (**33**): ¹H NMR (CDCl₃, in ppm, 400.13 MHz): $\delta = 1.90$ (m, 1H, CH), 1.80 (m, 1H, CH), 1.46 (m, 1H, CH), 1.41 (m, 1H, CH), 1.40 (m, 1H, CH), 1.25 (m, 1H, CH), 1.15 (m, 1H, CH), 0.97 (m, 3H, CH₂, CH), 0.90 (d, 3H, CH₃, ³*J* = 7.2 Hz), 0.86 (m, 2H, CH₂D), 0.84 (m, 1H, CH). ¹³C NMR (CDCl₃, in ppm, 100.62 MHz): $\delta = 46.4$ (C⁶), 41.8 (C⁴), 40.2 (C⁷), 38.2 (C³), 37.9 (C¹), 33.3 (C²), 30.7 (C⁵), 29.3 (C⁹), 22.0 (C⁸), 12.1 (C¹⁰).

The ¹³C DEPT135 NMR spectrum contains two typical resonances δ_{C6} 44.8 and δ_{C5} 44.9 for *exo* epimers **30** and **31** as well as the other two δ_{C6} 46.4 and δ_{C5} 47.6 for *endo* isomers **32** and **33**.

The bridging C7 carbon atoms in *exo* isomers **30** and **31** are accidentally isochronous and manifest themselves at δ_C 37.0, while the resonances δ_{C7} 39.1 and 40.2 are clearly distinguishable for the *endo* epimers **32** and **33**.