

Tantalum-catalyzed reaction of disubstituted acetylenes with EtAlCl_2

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Tetraalkyl-substituted (*E,E*)-buta-1,3-dienes were synthesized regio- and stereoselectively by the tantalum(v) chloride-catalyzed reaction of dialkyl-substituted acetylenes with EtAlCl_2 and sodium metal in toluene followed by hydrolysis or deuterolysis. A mechanism of these transformations was suggested. The *in situ* generated organoaluminum intermediates reacted with methylsulfonyl chloride and iodine to give tetraalkyl-substituted (*Z,Z*)-1,4-dichlorobuta-1,3-dienes and 1,4-diiodobuta-1,3-dienes, respectively.

Key words: acetylenes, sodium metal, (*E,E*)-buta-1,3-dienes, tantalum(v) chloride, diethylaluminum chloride.

Transition metal-catalyzed carboalumination of acetylenic compounds with organoaluminum compounds is the efficient tool for the C—C bond formation.^{1,2} On the whole, a combination of carbometallation and cross-coupling of the *in situ* generated organometallic intermediates is one of the general approaches to different classes of organic compounds.³ Currently, carboalumination of acetylenes includes two main strategies. The first strategy is the Cp_2ZrCl_2 -catalyzed methylalumination using Me_3Al under the Negishi conditions⁴ and the second strategy is the Cp_2ZrCl_2 -catalyzed cycloalumination using Et_3Al under the Dzhemilev conditions.^{5,6} The analysis of the literature on carboalumination of the functionally substituted acetylenes indicated that the methylalumination reaction is limited to terminal acetylenes,⁷ hetero-substituted arylacetylenes bearing the O, S, Cl, and Si⁸ atoms, and homopropargylic alcohols.⁹ We have shown earlier that cycloalumination of such functionally-substituted acetylenic compounds as 2-alkynylamines, 3-alkynols,¹⁰ (1-alkynyl)phosphines,¹¹ (1-alkynyl)phosphine sulfides¹², 1-alkynyl selenides,¹³ and 1-alkynyl sulfides¹⁴ as well as methylalumination of 1-alkynyl sulfones¹⁵ and ethylalumination of (1-alkenyl)phosphine oxides¹² is a very effective approach to regio- and stereoselective synthesis of *N*-, *O*-, *P*-, *Se*-, and *S*-containing trisubstituted olefins. The obtained experimental data show that the use of Cp_2ZrCl_2 allows carboalumination of both non-functionalized and functionally substituted triple bond. The zirconium-catalyzed cycloalumination of acetylenes is of special

interest due to its effectiveness in the construction of the (2-aluminioethyl)aluminum structural unit bearing two active Al—C bonds. Subsequent reaction of the *in situ* generated organoaluminum intermediates with electrophilic reagents can serve as simple and convenient one-step synthetic approach to different polyfunctionalized olefins. Another advantage of the Cp_2ZrCl_2 — Et_3Al system is the possibility to synthesize the buta-1,3-diene derivatives. We also have demonstrated¹⁶ that the reaction of Cp_2ZrCl_2 with 2 equiv. of Et_3Al in toluene enables regio- and stereoselective intramolecular coupling of (1-alkynyl)trimethylsilanes to give high yields of 1,4-bis(trimethylsilyl)-substituted buta-1,3-dienes. We believe that the formation of the diene systems is based on the homocoupling of two acetylene molecules that occur on Cp_2Zr generated by the reaction of Cp_2ZrCl_2 with 2 equiv. of Et_3Al . However, this method is limited only to (1-alkynyl)-methylsilanes. For instance, the reaction of dec-5-yne with 0.5 equiv. of Cp_2ZrCl_2 and 2 equiv. of Et_3Al carried out in toluene for 18 h quantitatively gave ethylalumination product, (*Z*)-5-ethyldec-5-ene.¹⁶ Despite the thorough studies of the reaction of acetylenes with the Et_3Al — Cp_2ZrCl_2 system, no efficient methods for the zirconium-catalyzed intramolecular coupling of the acetylene derivatives are known. Thus, Negishi *et al.*⁴ described the reaction of diphenylacetylene with Et_3Al in the presence of 10 mol.% of Cp_2ZrCl_2 in benzene at 55 °C that resulted in a 1 : 1 mixture of ethyl-substituted olefin and diene in 90% total yield. However, the Cp_2ZrCl_2 -catalyzed carboalumination of dec-5-yne

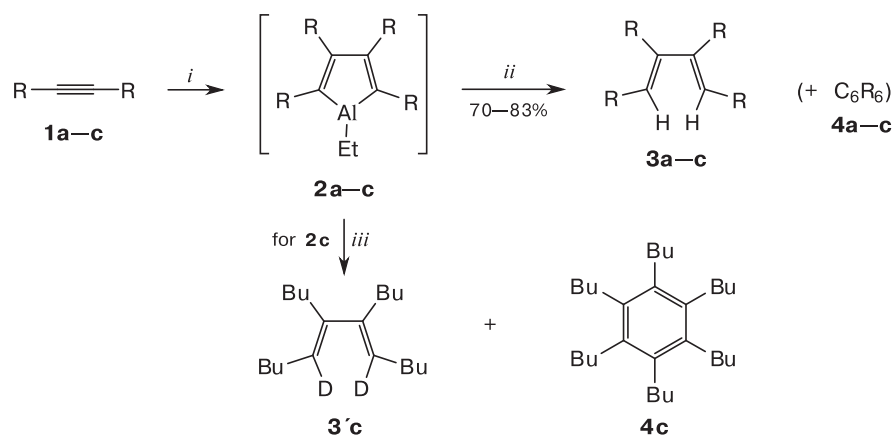
described by Negishi *et al.*⁴ and the reaction of dec-5-yne with Et₃Al in the presence of 0.5 equiv. of Cp₂ZrCl₂ described by us¹⁶ produced only ethyl-substituted olefin, (*Z*)-5-ethyldec-5-ene. To develop new catalytic systems for homocoupling of acetylenic compounds, we studied herein the TaCl₅-catalyzed reaction of acetylenes with EtAlCl₂ and described the first results of the tantalum-catalyzed homocoupling of symmetrical dialkyl-substituted acetylenes under the organoaluminum synthesis conditions.

We found that the reaction of dialkyl-substituted acetylenes **1a–c** with 3 equiv. of EtAlCl₂ and 2 equiv. of magnesium metal in the presence of 5 mol.% of TaCl₅ in toluene at room temperature followed by hydrolysis (or deuterohydrolysis) gave regio- and stereoselectively tetraalkyl-substituted (*E,E*)-buta-1,3-dienes **3a–c** with the *E* configuration of the double bond (Scheme 1). The structures of the products of hydrolysis **3a–c** and deuterohydrolysis **3'c** were established by 1D and 2D NMR spectroscopy. The discovered reaction is accompanied by trimerization of alkynes to give 5–9% of cyclic trimers, namely, hexaalkylbenzenes **4a–c**. Increasing the loading of TaCl₅ to 10 mol.% increased the fraction of cyclic trimer **4c** to 20% (see Scheme 1). When the reaction was carried out in the absence of Mg, the fraction of trimer **4c** dramatically increased to 77%.

The closest electronic analog of tantalum is niobium. Narula and coworkers have described¹⁷ the reduction of niobium(v) chloride with magnesium activated by HgCl₂ to niobium(III) chloride. Siemeling and Gibson¹⁸ have synthesized the niobium(III) complex by the reac-

tion of Nb(η⁵-C₅Me₅)Cl₄ with Mg. It was assumed^{19–21} that the TaCl₅-catalyzed carbomagnesiation of the olefins proceeded *via* the generation of alkene–TaCl₃ complexes. The described by us earlier selective synthesis of (*Z*)-2-alkenylamines by the NbCl₅–EtMgBr-catalyzed reduction of propargylamines with Et₂Zn²² is apparently initiated by NbCl₃ stabilized by the ethylene ligand.²³ The literature on the reduction of alkynes with the TaCl₅–Mg²⁴ and TaCl₅–Zn²⁵ systems indicated that the reduction of TaCl₅ with Mg and Zn gave tantalum(III) chloride. The closest analogs of the considered herein TaCl₅-catalyzed reaction of homocoupling of dialkyl-substituted acetylenes are the TaCl₅-catalyzed carbocationic of terminal olefins with diethylzinc²⁶ and TaCl₅-catalyzed carbomagnesiation of olefins with alkylmagnesium.²⁰ According to these publications, the exchange reaction between TaCl₅ and Et₂Zn (or EtMgBr) gave unstable complex Et₂TaCl₃, which disproportionated to generate low-valence complex of TaCl₃ with the ethylene ligand. The suggested by us approach to buta-1,3-dienes based on the TaCl₅-catalyzed intramolecular coupling of disubstituted acetylenes in the presence of EtAlCl₂ and Mg closely resembles the earlier described synthesis of alumina-cyclopenta-2,4-dienes by the Cp₂ZrCl₂-catalyzed homocoupling of disubstituted acetylenes in the presence of EtAlCl₂ and Mg (Scheme 2).²⁷ According to a suggested mechanism,²⁷ the acetylene homocoupling is initiated by the Cp₂Zr complex generated by the reduction of Cp₂ZrCl₂ with Mg. Subsequent coupling of two acetylene molecules on low-valence Cp₂Zr gave zircona-

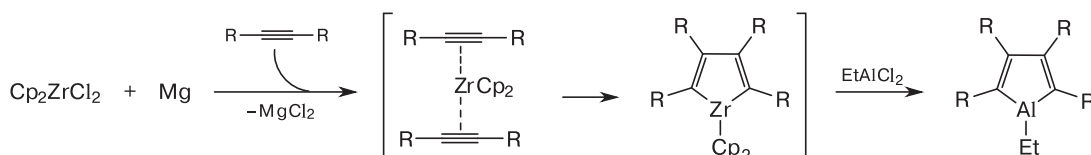
Scheme 1



R = Et (**a**), Pr (**b**), Bu (**c**)

Reagents, conditions, and yields: *i.* TaCl₅ (5 mol.%), Mg (2 equiv.), EtAlCl₂ (3 equiv.), toluene, ~20 °C, 0.5 h; *ii.* KOH, H₂O; *iii.* KOH, D₂O; yields: **3'c** 77%, **4c** 9% (25 mol.% TaCl₅, 2 equiv. Mg); **3'c** 59%, **4c** 20% (10 mol.% TaCl₅, 2 equiv. Mg); **3'c** 7%, **4c** 77% (5 equiv.% TaCl₅).

Scheme 2



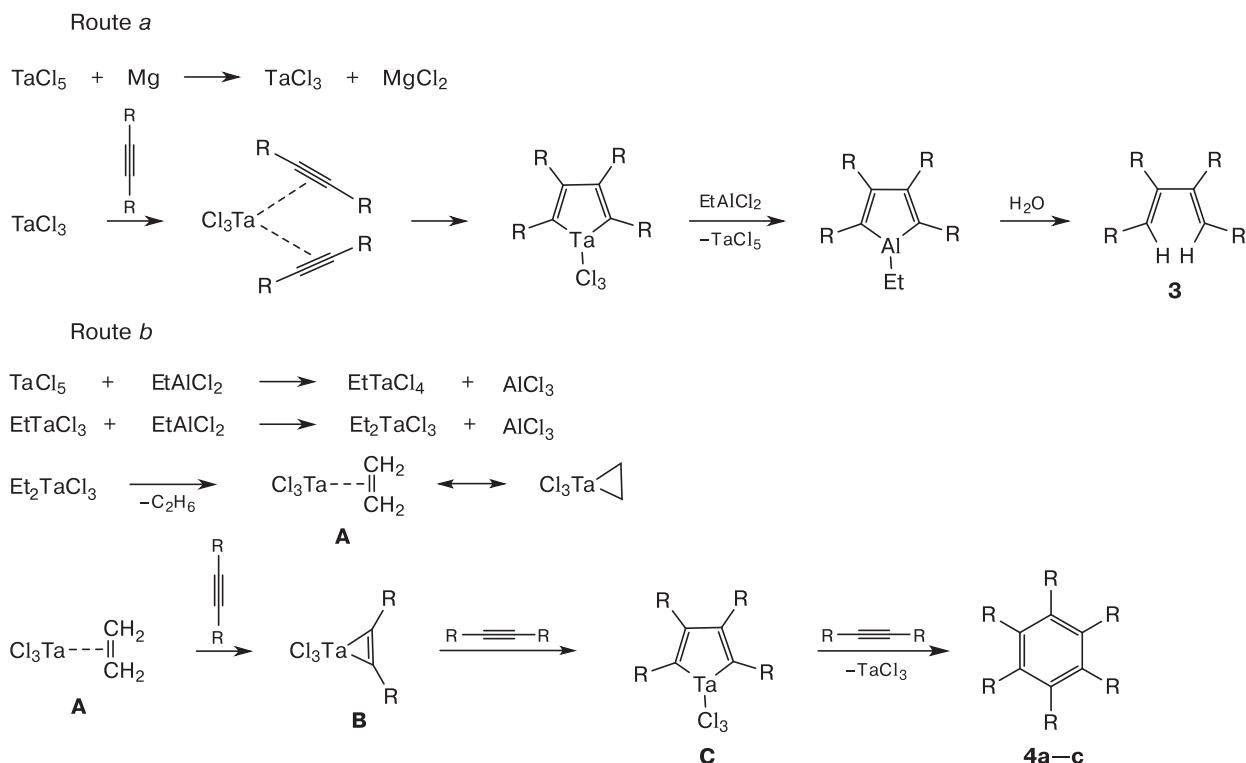
cyclopentadiene, which underwent transmetalation with EtAlCl_2 to give aluminacyclopentadiene.

Thus, we suggested that the discovered by us Ta-catalyzed intramolecular coupling of alkynes proceeded *via* the following mechanism. Homocoupling of alkynes is initiated by low-valence TaCl_3 generated upon reduction of TaCl_5 with Mg (Scheme 3, route *a*). Next, similarly to the Zr-catalyzed homocoupling of alkynes in the presence of EtAlCl_2 and Mg, the coupling of two alkyne molecules coordinated to TaCl_3 took place to give tantalacyclopentadiene.²⁷ Transmetalation of tantalacyclopentadiene with EtAlCl_2 resulted in the replacement of tantalum by aluminum to give aluminacyclopentadiene, which further hydrolyzed to the target tetraalkyl-substituted butadiene derivatives of the type **3**. Formation of aluminacyclopentadiene is supported by such experimental facts as low conversion of dec-5-yne (**1c**) ($\leq 5\%$) in its reaction

with Mg catalyzed by 10 mol.% of TaCl_5 in the absence of EtAlCl_2 and described below functionalization of the intermediate aluminacyclopentadienes with methylsulfonyl chloride (Scheme 4).

In the absence of Mg, the reaction path is altered to give rise to 1,2,3,4,5,6-hexabutylbenzene **4c** in 77% yield (see Scheme 1). The observed transformation of dec-5-yne (**1c**) can reflect the generation of the tantalum–ethylene complex **A** that resulted from the alkylation of TaCl_5 with EtAlCl_2 and subsequent disproportionation (see Scheme 3, route *b*). The similar reaction of TaCl_5 with Et_2Zn that generated the tantalum–ethylene complex **A** has been described earlier.²⁶ Displacement of ethylene from the coordination sphere of tantalum in the tantalum–ethylene complex **A** by the stronger nucleophile can result in tantalacyclopentadiene complex **B**. Cotton and Hall²⁸ have described the synthesis and X-ray diffraction analysis of tantalacyclo-

Scheme 3



propene complex ($[\text{pyH}][\text{TaCl}_4(\text{py})(\text{PhC}\equiv\text{CPh})]$) bearing the similar tricyclic moiety. According to the suggested by us Scheme 3, the generated tantalacyclopentadiene complex **B** reacted with the second molecule of acetylene to give tantalacyclopentadiene **C**. The first cyclopentadiene derivative obtained by the reduction of $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$ (DIPP is 2,6-diisopropylphenoxy) with sodium amalgam in the presence of hex-3-yne has been characterized by NMR spectroscopy by Wigley and coworkers.²⁹ Subsequent coordination of the tantalum atom in tantalacyclopentadiene complex **C** with dec-5-yne (**1c**) can result in cyclotrimerization product, hexabutylbenzene **4c**. The similar mechanism of trimerization of dialkyl-substituted acetylenes upon the reaction of $\text{Ta}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ with acetylenes has been described by Cotton and coworkers.³⁰

Our experience showed that the reaction of (1-alkenyl)alanes with hetero derivatives of sulfonic acids (trialkylsilyl sulfonates, *S*-methyl thiosulfonate, and sulfonyl halides) is a versatile one-pot method to convert acetylenes to halo- and sulfur-containing olefins of various structure.^{15,31,32} In the present work, we involved the generated *in situ* organoaluminum intermediates in the reaction with methylsulfonyl chloride (see Scheme 4). The reaction of dialkyl-substituted acetylenes **1b,c** with Mg (2 equiv.) and EtAlCl_2 (3 equiv.) catalyzed by TaCl_5 (5 mol.%) in toluene at room temperature followed by addition of methylsulfonyl chloride

(4 equiv.) within 8 h gave high yields of tetraalkyl-substituted (*Z,Z*)-1,4-dichlorobuta-1,3-dienes **5b,c** (see Scheme 4). It is of note that the cross-coupling of organomagnesium compounds with alkyl- and arylsulfonyl chlorides catalyzed by the iron and palladium catalysts proceeded with the formation of the carbon—carbon but not the carbon—heteroatom bond.^{32–35}

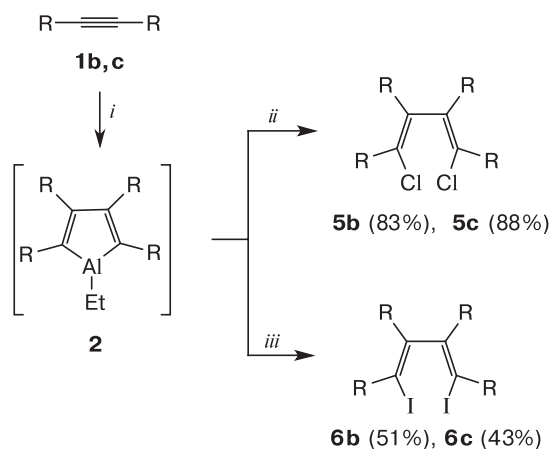
To additionally confirm the structures of the synthesized substituted buta-1,3-dienes **3**, we performed iodinolysis of organoaluminum intermediates **2b,c**, generated *in situ* by TaCl_5 -catalyzed reaction of acetylenes **1b,c** with 3 equiv. of EtAlCl_2 , using 13 equiv. of I_2 to give (4*Z*,6*Z*)-4,7-diiodo-5,6-dipropyldeca-4,6-diene (**6b**) and (5*Z*,7*Z*)-6,7-dibutyl-5,8-diiodododeca-5,7-diene (**6c**), respectively (see Scheme 4).

In summary, we first showed that the reaction of dialkyl-substituted acetylenes with EtAlCl_2 and Mg catalyzed by tantalum(v) chloride in toluene regio- and stereoselectively gave the tetraalkyl-substituted (*E,E*)-buta-1,3-dienes. The selective synthesis of tetraalkyl-substituted (*Z,Z*)-1,4-dichlorobuta-1,3-dienes by the reaction of methylsulfonyl chloride with organoaluminum intermediates generated *in situ* by the TaCl_5 -catalyzed reaction of dialkyl-substituted acetylenes with EtAlCl_2 and Mg was developed.

Experimental

Gas chromatography was carried out on a Shimadzu GC-9A instrument equipped with a 2000×2 -mm column, stationary phase was silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125–0.160 mm), carrier gas was helium (30 mL min^{-1}), temperature programming: heating from 50 to 300 °C at a heating rate of 8 deg min^{-1} . ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker Avance-400 (working frequencies of 100 (^{13}C) and 400 MHz (^1H)) and Bruker Avance-500 (working frequencies of 125 (^{13}C) and 500 MHz (^1H)) spectrometers. The chemical shifts are given in the δ scale relative to Me_4Si . Numbering of the carbon atoms in compounds **3b,c** and **5b,c** is given in Fig. 1. Gas chromatography-mass spectrometry was performed on a Shimadzu GCMS-QP2010 Plus instrument (glass capillary column SLB-5ms $60000 \times 0.25 \text{ mm} \times 0.25 \text{ m}$ (Supelco, USA), ion source temperature was 200 °C, 70 eV). Elemental analysis was carried out on a Karlo Erba model 1106 elemental analyzer. IR spectra were recorded on a Bruker VERTEX 70V FTIR spectrometer for the liquid samples. Yields of the products were determined by gas chromatography. Monomers with purity no less than 90% were used. Toluene was refluxed and distilled over sodium metal under argon. Argon (pure grade; State Standard GOST 10157-73) was used to provide the inert atmosphere. The following commercially available reagents were used: tantalum(v) chloride, sodium metal, mag-

Scheme 4



1, 2, 5, 6: R = Pr (**b**), Bu (**c**)

Reagents and conditions: *i.* TaCl_5 (5 mol.%), Mg (2 equiv.), EtAlCl_2 (3 equiv.), toluene, 30 min, ~ 20 °C; *ii.* 0 \rightarrow 20 °C, MeSO_2Cl (4 equiv.), ~ 20 °C; *iii.* 1) I_2 (13 equiv.), -78 °C \rightarrow 20 °C, 18 h; 2) KOH (25%), $\text{Na}_2\text{S}_2\text{O}_3$ (saturated aqueous solution).

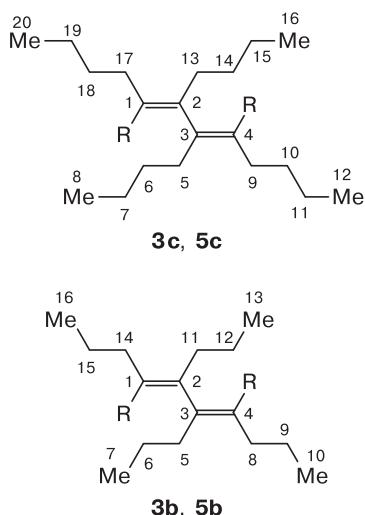


Fig. 1. Numbering of the carbon atoms in compounds **3b,c** and **5b,c** used for the NMR spectra interpretation.

nesium, EtAlCl_2 (OJSC Redkinskii Opytnyi Zavod), hex-3-yne, oct-4-yne, and dec-5-yne (Sigma—Aldrich). The ^1H and ^{13}C spectral data of compounds **3a**, **4c**, and **6b,c** are in good agreement with those published previously.³⁶ Tantalum(v) chloride was purified and dried as earlier described.³⁷

(5E,7E)-6,7-Dibutyldeca-5,7-diene (3c), Ta-Mg-catalyzed reaction of acetylenes with EtAlCl_2 . A glass reactor filled with dry argon was successively charged with dec-5-yne (**1c**) (276 mg, 2 mmol), TaCl_5 (35.8 mg, 0.1 mmol), magnesium metal (96 mg, 4 mmol), and a 0.5 M solution of EtAlCl_2 in hexane (0.82 mL, 6 mmol of EtAlCl_2). The obtained mixture was stirred at 23 °C for 30 min, diluted with diethyl ether (5 mL), treated dropwise with 25% aqueous KOH (3 mL), and stirred at room temperature for 1 h. The aqueous layer was extracted with diethyl ether (3×5 mL), the combined organic layers were washed with brine (10 mL), and dried with anhydrous CaCl_2 . The drying agent was filtered off, the solvent was removed *in vacuo*. Vacuum distillation of the residue afforded 63 mg (83%) of product **3c**. B.p. 138–140 °C (1.5 Torr), colorless liquid. ^1H NMR (CDCl_3), δ : 0.91–0.96 (m, 12 H, C(8)H₃, C(12)H₃, C(16)H₃, C(20)H₃); 1.29–1.38 (m, 16 H, C(6)H₂, C(7)H₂, C(10)H₂, C(11)H₂, C(14)H₂, C(15)H₂, C(18)H₂, C(19)H₂); 2.07–2.11 (m, 4 H, C(5)H₂, C(9)H₂); 2.16–2.19 (t, 4 H, C(13)H₂, C(17)H₂, $J = 7.2$ Hz), 5.35–5.37 (t, 2 H, C(1)H, C(4)H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3), δ : 14.06 (C(8), C(12), C(16), C(20)); 22.47 (C(7), C(11)); 22.79 (C(13), C(17)); 27.72 (C(6), C(10)); 27.91 (C(5), C(9)); 31.17 (C(14), C(18)); 32.31 (C(13), C(17)); 125.91 (C(1), C(4)); 141.21 (C(2), C(3)). MS (EI), m/z : 204 (15) $[\text{M}]^+$, 161 (11), 147 (13), 117 (18), 105 (100). Found (%): C, 86.45; H, 13.60. $\text{C}_{20}\text{H}_{38}$. Calculated (%): C, 86.25;

H, 13.75. IR, ν/cm^{-1} : 2958, 2930, 2872, 1753, 1688, 1607, 1564, 1465, 1378, 731.

(4E,6E)-5,6-Dipropyldeca-4,6-diene (3b) was synthesized similarly from oct-4-yne (**1b**) (220 mg, 2 mmol). Yield 311 mg (70%). B.p. 98–100 °C (1.6 Torr), colorless liquid. ^1H NMR (CDCl_3), δ : 0.88–0.95 (m, 12 H, C(7)H₃, C(10)H₃, C(13)H₃, C(16)H₃); 1.31–1.37 (m, 4 H, C(6)H₂, C(9)H₂); 1.39–1.45 (m, 4 H, C(12)H₂, C(15)H₂); 2.05–2.09 (q, 4 H, C(5)H₂, C(8)H₂, $J = 14.1$ Hz, $J = 7.2$ Hz); 2.14–2.17 (t, 4 H, C(13)H₂, C(17)H₂, $J = 7.3$ Hz); 5.36–5.38 (t, 2 H, C(1)H, C(4)H, $J = 7.0$ Hz). ^{13}C NMR (CDCl_3), δ : 13.93 (C(7), C(10)), 14.11 (C(13), C(16)), 22.05 (C(12), C(15)), 23.21 (C(6), C(9)), 30.06 (C(5), C(8)), 30.31 (C(11), C(14)), 126.00 (C(1), C(4)), 141.27 (C(2), C(3)). Calculated (%): C, 86.40; H, 13.60. $\text{C}_{16}\text{H}_{30}$. Found (%): C, 86.20; H, 13.8. IR, ν/cm^{-1} : 2960, 2933, 2873, 1709, 1464, 1379, 1362, 1100, 1020, 613.

(5Z,7Z)-6,7-Dibutyl-5,8-dichlorodeca-5,7-diene (5c).

A glass reactor filled with dry argon was successively charged with dec-5-yne (**1c**) (276 mg, 2 mmol), TaCl_5 (35.8 mg, 0.1 mmol), magnesium metal (96 mg, 4 mmol), and a 0.5 M solution of EtAlCl_2 in hexane (0.82 mL, 6 mmol of EtAlCl_2). The obtained mixture was stirred at 23 °C for 30 min, cooled to 0 °C, treated with methylsulfonyl chloride (916 mg, 8 mmol), and stirred at room temperature for 6 h. The mixture was diluted with diethyl ether (5 mL), cooled to 0 °C, and treated dropwise with 5% HCl (3 ml). The mixture was stirred at room temperature for 1 h, the aqueous layer was extracted with diethyl ether (3×5 mL), the combined organic layers were washed with brine (10 mL), dried with anhydrous CaCl_2 . The drying agent was filtered off, and the solvent was removed *in vacuo*. Vacuum distillation of the residue afforded 299 mg (88%) of product **5c**. B.p. 201–203 °C (2 Torr), colorless liquid. ^1H NMR (CDCl_3), δ : 0.91–0.97 (m, 12 H, C(8)H₃, C(12)H₃, C(13)H₃, C(17)H₃); 1.28–1.41 (m, 12 H, C(6)H₂, C(7)H₂, C(10)H₂, C(11)H₂, C(15)H₂, C(19)H₂); 1.58–1.63 (m, 4 H, C(14)H₂, C(18)H₂); 2.03–2.09 (m, 2 H, C(5)H_A, C(9)H_A); 2.27–2.33 (m, 2 H, C(5)H_B, C(9)H_B); 2.39–2.47 (m, 4 H, C(13)H₂, C(17)H₂). ^{13}C NMR (CDCl_3), δ : 13.91 (C(16), C(20)), 14.00 (C(8), C(12)), 22.03 (C(15), C(19)), 23.04 (C(7), C(11)), 29.92 (C(6), C(10)), 30.22 (C(14), C(18)), 31.90 (C(13), C(17)), 34.76 (C(5), C(9)), 131.41 (C(1), C(4)), 135.43 (C(2), C(3)). Found (%): C, 69.36; H, 10.31. $\text{C}_{20}\text{H}_{36}\text{Cl}_2$. Calculated (%): C, 69.15; H, 10.45. IR, ν/cm^{-1} : 2958, 2930, 2872, 2861, 1426, 1379, 1216, 1100, 761, 670, 613.

(4Z,6Z)-4,7-Dichloro-5,6-dipropyldeca-4,6-diene (5b) was synthesized similarly from oct-4-yne (**1b**) (220 mg, 2 mmol). Yield 483 mg (83%). B.p. 98–100 °C (1.6 Torr), colorless liquid. ^{13}C NMR (CDCl_3), δ : 0.92–0.98 (m, 12 H, C(7)H₃, C(10)H₃, C(13)H₃, C(16)H₃); 1.47–1.52 (m, 4 H, C(12)H₂, C(15)H₂); 1.62–1.68 (m, 4 H, C(6)H₂, C(9)H₂); 2.02–2.08 (m, 4 H, C(5)H₂, C(8)H₂); 2.25–2.31 (m, 4 H, C(11)H₂, C(14)H₂). ^{13}C NMR (CDCl_3), δ : 13.33 (7, 10), 14.45 (C(13), C(16)), 20.95 (C(12), C(15)), 21.44 (C(6), C(9)), 34.42 (C(11), C(14)), 36.79 (C(5), C(9)), 131.32 (C(1),

C(4)), 135.72 (C(2), C(3)). Found (%): C, 65.76; H, 9.56. C₁₆H₂₈Cl₂. Calculated (%): C, 65.97; H, 9.69. IR, ν/cm^{-1} : 2962, 2933, 2873, 1649, 1463, 1379, 1216, 1150, 1115, 760, 613.

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No human or animal subjects were used in this research.

The authors declare no competing interests.

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