

‘One-pot’ synthesis of 1,1-disubstituted cyclopropanes in the presence of metal complex catalysts

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Dedicated to Academician Oleg M. Nefedov on his 70th birthday

Abstract

A ‘one-pot’ catalytic method for the synthesis of 1,1-disubstituted cyclopropanes starting from olefins, acetylenes and AlEt_3 in the presence of Cp_2ZrCl_2 , via a step involving in situ formation of aluminacyclopentanes and aluminacyclopentenenes, respectively, was developed. Five-membered organoaluminium compounds obtained without preliminary isolation are transformed to cyclopropanes under the effect of $\text{Ni}(\text{acac})_2$ in combination with allylhalogenides in the case of aluminacyclopentanes and alkylsulphates in experiments with aluminacyclopentenenes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Substituted cyclopropanes; Olefins; Acetylenes; Aluminacyclopentanes; Aluminacyclopentenenes; Catalysis

1. Introduction

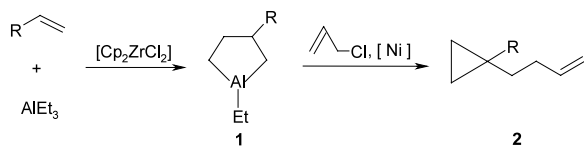
Carbene reactions, such as cyclopropanation according to Simmons–Smith [1] halogenycyclopropanation using halogensubstituted carbenes [2] and synthesis of cyclopropanecarbenic acid derivatives by thermocatalytic reactions of diazo esters [3] are reported to be well-known methods for a synthesis of cyclopropanes and their derivatives. The recent papers on cyclic carboalumination of unsaturated compounds using organopalladium, -zinc and -aluminium reagents have determined the new technique for a synthesis of substituted cyclopropanes [4–8]. The synthesis of cyclopropanes [6,8] based on skeleton transformations of forming in situ aluminacyclopentanes and aluminacyclopentenenes by cycloalumination of α -olefins and acetylenes effected by complex metal catalysts [9–12] is of special interest.

According to [8] a limited number of the simplest aluminacyclopentanes generated in situ from α -olefins and AlEt_3 in the presence of catalyst Cp_2ZrCl_2 was involved in this reaction. Five-membered organoaluminium compounds OAC **1**, synthesized by the present method, could be transformed into the corresponding 1,1-disubstituted cyclopropanes **2** using catalytic amounts of $\text{Ni}(\text{acac})_2$ and allylchloride, without preliminary isolation from the reaction mixture.

2. Results and discussion

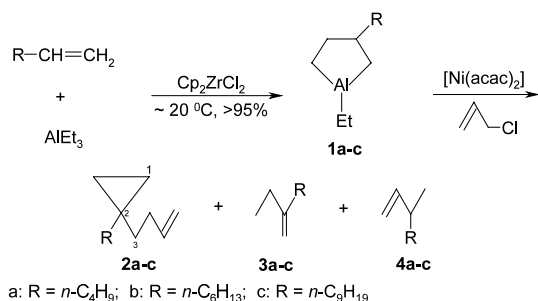
To extend the area of reaction developed [8] as well as to investigate the structural effect of initial five-membered OAC, the nature of the central atom of a catalyst and the effect of reaction conditions on yield and selectivity of cyclopropanes, we studied skeleton transformations of aluminacyclopentanes [13] and aluminacyclopentenenes [14], using Ni- and Ti-containing complex catalysts.

In the course of preliminary experiments it was established that the highest yields of 1,1-disubstituted cyclopropanes were allowed from the reaction of aluminacy-

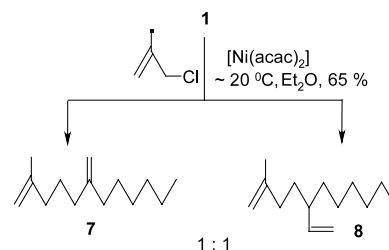


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clopentanes in the presence of 5 mol% freshly sublimated $\text{Ni}(\text{acac})_2$ and three-fold excess of allylchloride as reoxidant (reaction conditions: 20 °C, 8 h, solvent— $(\text{C}_2\text{H}_5)_2\text{O}$).

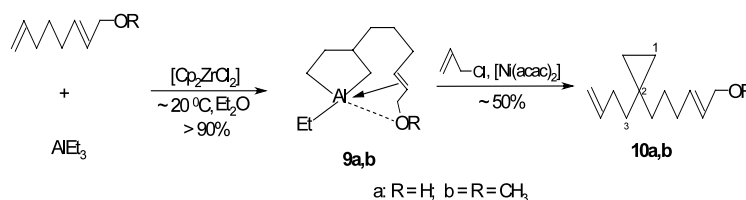


Thus, 1-ethyl-3-(*n*-hexyl)aluminacyclopentane (**1b**) obtained in situ by the reaction of oct-1-ene with AlEt_3 , under conditions [13] using freshly sublimated $\text{Ni}(\text{acac})_2$ and allylchloride, affords 1-(but-3-enyl)-1-(*n*-hexyl)cyclopropane (**2b**), 3-methylenenonane (**3b**) and 3-methylnonene (**4b**) in total yield ca. 80% (quoted



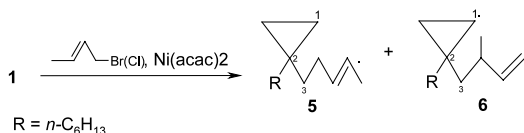
Apparently, the formation of substituted cyclopropanes has not ever been observed with the use of metallychloride.

Under selected conditions functionally substituted five-membered OAC react with allylhalides to afford 1,1-disubstituted cyclopropanes. For example, during the interaction of 1-hydroxy- or 1-methoxyocta-2*E*,7-di- enes with AlEt_3 over the catalyst Cp_2ZrCl_2 aluminacyclopentanes (**9a,b**) [15] are formed, which further react in situ with allylchloride in the presence of $\text{Ni}(\text{acac})_2$ leading to corresponding 1,1-disubstituted oxygen-containing cyclopropanes **10a,b** in ca. 50% yield.



yields were obtained after distillation) and in a ratio of ca. 12:1:3, respectively. The analogous results were obtained during the study of the reaction of 1-ethyl-3-(*n*-butyl)- and 1-ethyl-3-(*n*-nonyl)aluminacyclopentanes (**1a,c**) with allylchloride over the catalyst $\text{Ni}(\text{acac})_2$ leading to cyclopropanes **2a,c** and olefins **3a,c** and **4a,c**, respectively in 75–85% yields.

The replacement of allylchloride by crotylbromide leads to the formation of regioisomeric by alkenyl substituent 1,1-disubstituted cyclopropanes **5**, **6** in ratio ca. 1:1 and in total yield of ca. 60%.



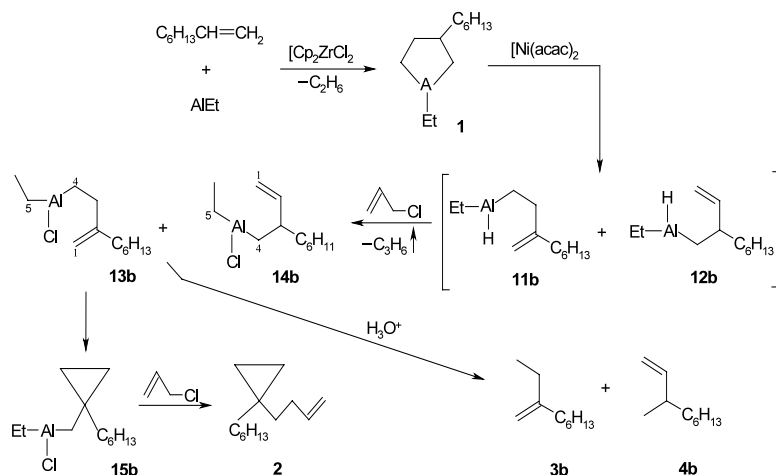
The direction of the aforesaid catalytic reaction completely changes when metallychloride is used as allylhaloid (reoxidant). For example, under selected optimal conditions ACP (**1**) turns into regioisomeric hydrocarbons—2-methyl-6-methylenedodec-1-ene (**7**) and 2-methyl-5-vinylundec-1-ene (**8**) over the catalyst $\text{Ni}(\text{acac})_2$ in the presence of metallychloride.

To determine the structure of intermediate compounds obtained during transformation of aluminacyclopentanes to 1,1-disubstituted cyclopropanes we have studied the reaction **1** with allylchloride in the presence of $\text{Ni}(\text{acac})_2$ by dynamic NMR-spectroscopy along with identification of compounds formed. Experiments were carried out in an inert gas flow, by mixing of aluminacyclopentane (**1**) with allylchloride and a catalytic amount of $\text{Ni}(\text{acac})_2$ in Et_2O solution at -5°C in the glass reactor, with subsequent injection of the reaction mixture into the NMR spectrometer cell. Spectra were recorded at ca. 20 °C.

The model interaction reaction of 1-ethyl-3-(*n*-hexyl)aluminacyclopentane (**1**) with an excess of allylchloride ($[\text{Al}]-\text{CH}_2\text{CHCH}_2\text{Cl} = 1:3$) in the presence of 5 mol% $\text{Ni}(\text{acac})_2$ reveals that initially Al–C bond in ACP (**1**) is opened as a result of β -hydrogen abstraction effected by low-valence Ni complexes to afford hydride complexes **11**, **12**. At the same time stoichiometric amount of propylene is isolated, thus indicating the evidence of alkenylhalogenalanes **13**, **14** formation.

Above-mentioned is confirmed by following results. NMR-spectrum of reaction mixture shows a significant decrease in signal intensity at 155.1 and 107.1 ppm assigned to carbon atoms of methylene double bond in

OAC **13b** in 60 min after the beginning of reaction between **1b** and allylchloride over the catalyst $\text{Ni}(\text{acac})_2$. Signals disappear completely in 24 h. Probably, under selected conditions intramolecular carboalumination in **13b** takes place leading to cyclopropylhalogenane (**15b**) with subsequent cross-coupling with allylchloride to afford 1,1-disubstituted cyclopropane **2b**. In contrast to OAC **13b** compound **14b** seems not to undergo aforesaid transformations and retains its structure.



Apparently homoallylic OAC **13b** is the key intermediate in the above reaction; subsequent transformations of this compound over $\text{Ni}(\text{acac})_2$ afford 1,1-disubstituted cyclopropane.

Developed by us the catalytic method of skeleton transformations of aluminacyclopentanes to disubstituted cyclopropanes was applied to 2,3-disubstituted aluminacyclopentenes (**16**) synthesized by cycloalumination of 1,2-disubstituted acetylenes using AlEt_3 over the catalyst Cp_2ZrCl_2 [14].

At the same time under above conditions (catalyst $\text{Ni}(\text{acac})_2$, ca. 20 °C, 8 h; solvent— Et_2O) aluminacyclopentenes (**16**) were found to react with allylchloride non-selectively leading upon hydrolysis to the mixture of hydrocarbons, the content of substituted cyclopropanes in which does not exceed ca. 30%.

Dialkylsulphates (MeSO_4 , Et_2SO_4) were used as alkylating agents.

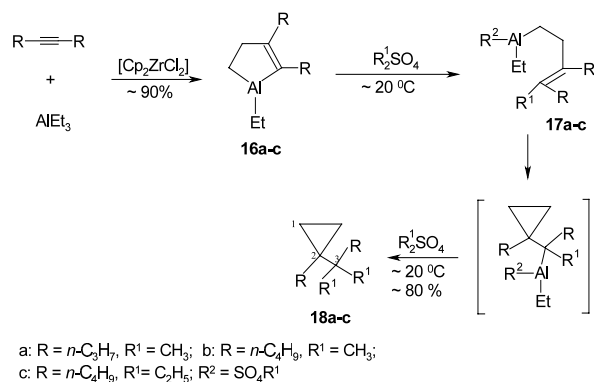
The interaction of 1-ethyl-2,3-di(*n*-propyl)- or 1-ethyl-2,3-di(*n*-butyl)-aluminacyclopent-2-enes (**16a,b**) with four-fold excess of $(\text{CH}_3)_2\text{SO}_4$ under optimal conditions (ca. 20 °C, 12 h, hexane) was established to afford 1-propyl-1-(2-methylpentane-2-yl)cyclopropanes (**18a,b**) in > 80% yields.

The nature of solvents used (hexane, cyclohexane, benzene, toluene, diethyl ester, tetrahydrofuran) almost have no influence on the yield of **16a,b**, however at first

reaction step the use of aliphatic or aromatic solvents (hexane, cyclohexane, toluene) is required [14].

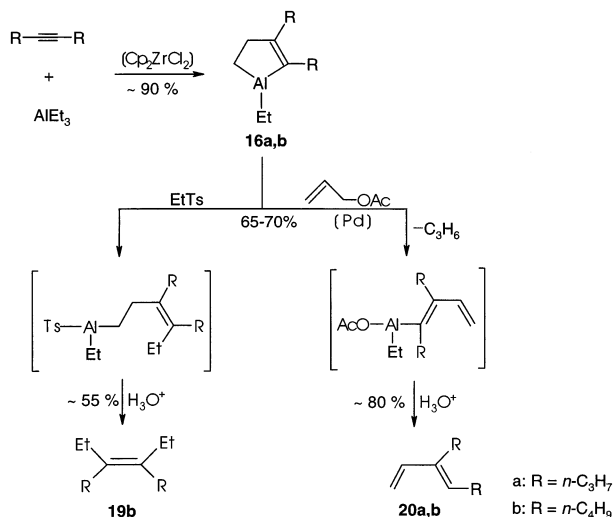
The mechanistic study of transformation **16** into **18** by the model interaction between **16a** and $(\text{CH}_3)_2\text{SO}_4$ using the dynamic NMR-spectroscopy method revealed that typical for aluminacyclopentene ring resonance peaks have disappeared in 60 min after beginning of the reaction. At the same time ^{13}C -NMR-spectrum of reaction mixture shows the peaks assigned to homoallylic OAC **17a** and cyclopropane **18a**. Reaction is completed

in ca. 5 h. Thus, on basis of experimental data the formation of **18** from **16** could be represented by the following Scheme.



We have shown the possibility of aluminacyclopentenes (**16**) transformation into corresponding tetrasubstituted olefins **19** and conjugated dienes **20** with high yields under the influence of alkyltosilates or alkylacetates effected by complex palladium catalyst $[\text{Pd}(\text{acac})_2\text{-PPh}_3]$.

The examples of 'one-pot' synthesis of 1,1-disubstituted cyclopropanes from α -olefines and acetylene via formation in situ five-membered OAC are a great evidence of synthetic capability of this method.



3. Experimental

All reactions were carried out under argon. For all syntheses dry solvents were used. The compounds obtained were analyzed by a Chrom-5 chromatograph (1200 × 3 mm column packed with 5% of SE-30 and 15% of PEG-6000 on Chromosorb N-AW, flame-ionization detector, carrier-gas—helium, working temperature 50–170 °C). Mass spectral measurements were performed on Finnigan 4021 gas chromatograph–mass spectrometer at 70 eV. ^1H - and ^{13}C -NMR spectra were recorded as CDCl_3 solutions on spectrometers ‘Jeol FX-90Q’ (22.5 MHz for ^{13}C and 90 MHz for ^1H) and ‘Bruker AM-300’ (75.46 MHz for ^{13}C and 300 MHz for ^1H). Internal standard: Me_4Si ; for cyclopropane derivatives— C_6D_6 . ^{13}C -NMR spectra were recorded using complete and partially proton-decoupled mode, and with the use of INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) technique.

3.1. Synthesis of 1-alkyl-1-(but-3-enyl)cyclopropanes from α -olefines

A glass reactor was charged with Cp_2ZrCl_2 (0.5 mmol), α -olefin (10 mmol) and AlEt_3 (12 mmol) under dried nitrogen at 0 °C; the reaction mixture was stirred for 8 h at 21–23 °C. To resulted 1-ethyl-3-(alkyl)aluminacyclopentane Et_2O (8 ml), freshly sublimated $\text{Ni}(\text{acac})_2$ (0.5 mmol) and allylchloride (metallychloride, crotylbromide) (36 mmol) were added at –5 °C; the reaction mixture was stirred for 8–10 h at room temperature (r.t.). The mixture was treated then by 10% HCl , washed by water to neutral reaction. An organic layer was separated from aqueous. Resulted solution was dried over calcined Na_2SO_4 . After evaporation of solvents the crude product was purified by vacuum distillation.

3.1.1. 1-(*n*-Butyl)-1-(but-3-enyl)cyclopropane (2a)

b.p. 63–64 °C (10 Torr), n_{D}^{22} 1.4390. IR $\tilde{\nu}$ (cm^{-1}): 3085, 2970, 2940, 2870, 1650, 1470, 1385, 1025, 1015, 925. ^1H -NMR (δ ppm): 0.22 (s, 4H, CH_2 cycl); 0.89 (m, 3H, CH_3); 1.20–1.39 (m, 4H, CH_2CH_2); 1.39–1.68 (m, 4H, CH_2CCH_2); 1.81–2.11 (m, 2H, CH_2CH); 4.68–5.70 (m, 3H, $\text{CH}=\text{CH}_2$). ^{13}C -NMR (δ ppm): 12.1 (C_1), 19.2 (C_2), 35.6 (C_3), 31.1 (C_4), 139.3 (C_5), 113.8 (C_6), 35.7 (C_7), 28.9 (C_8), 23.1 (C_9), 14.2 (C_{10}). M^+ 152.

3.1.2. 1-(*n*-Hexyl)-1-(but-3-enyl)cyclopropane (2b)

b.p. 73–74 °C (5 Torr), n_{D}^{22} 1.4445. ^1H -NMR (δ ppm): 0.18 (s, 4H, CH_2 cycl); 0.88 (m, 3H, CH_3); 1.18–1.29 (m, 8H, CH_2); 1.40–1.65 (m, 4H, CH_2CCH_2); 1.70–2.03 (m, 2H, CH_2); 4.52–5.55 (m, 3H, $\text{CH}=\text{CH}_2$). ^{13}C -NMR (δ ppm): 12.1 (C_1), 19.2 (C_2), 35.6 (C_3), 31.1 (C_4), 139.4 (C_5), 113.8 (C_6), 36.0 (C_7), 26.6 (C_8), 29.7 (C_9), 32.0 (C_{10}), 22.5 (C_{11}), 14.1 (C_{12}). M^+ 180.

3.1.3. 1-(*n*-Nonyl)-1-(but-3-enyl)cyclopropane (2c)

b.p. 89–90 °C (2 Torr), n_{D}^{22} 1.4499. ^1H -NMR (δ ppm): 0.21 (s, 4H, CH_2 cycl); 0.88 (m, 3H, CH_3); 1.15–1.30 (m, 14H, CH_2); 1.38–1.66 (m, 4H, CH_2CCH_2); 2.08–2.20 (m, 2H, CH_2); 4.70–5.80 (m, 3H, $\text{CH}=\text{CH}_2$). ^{13}C -NMR (δ ppm): 12.1 (C_1), 19.2 (C_2), 35.5 (C_3), 31.1 (C_4), 139.4 (C_5), 113.9 (C_6), 36.1 (C_7), 26.6 (C_8), 29.6 (C_9), 29.7 (C_{10} , C_{11}), 29.4 (C_{12}), 32.0 (C_{13}), 22.8 (C_{14}), 14.1 (C_{15}). M^+ 222.

3.1.4. 1-(*n*-Hexyl)-1-(trans-pent-3-enyl)cyclopropane (5)

b.p. 79–80 °C (2 Torr), n_{D}^{22} 1.4621. ^1H -NMR (δ ppm): 0.84 (t, 3H, CH_3 , $J = 6.4$ Hz); 1.11–1.35 (m, 12H, CH_2); 0.04 (s, 4H, CH_2 cycl); 1.74–2.02 (m, 2H, CH_2); 1.45–1.69 (m, 3H, CH_3); 4.66–5.59 (m, 2H, $\text{CH}=\text{CH}$). ^{13}C -NMR (δ ppm): 10.3 (C_1), 18.6 (C_2), 38.2 (C_3), 25.8 (C_4), 131.5 (C_5), 124.6 (C_6), 17.9 (C_7), 37.24 (C_8), 28.1 (C_9), 29.6 (C_{10}), 32.1 (C_{11}), 22.8 (C_{12}), 14.1 (C_{13}). M^+ 194.

3.1.5. 1-(*n*-Hexyl)-1-(2-methyl-trans-but-3-enyl)-cyclopropane (6)

b.p. 74–75 °C (2 Torr), n_{D}^{22} 1.4541. ^1H -NMR (δ ppm): 0.83 (t, $J = 6.4$ Hz, 3H, CH_3); 1.04–1.30 (m, 12H, CH_2); 0.15 (s, 4H, CH_2 cycl); 0.88–1.04 (m, 3H, CH_3); 1.80–2.10 (m, 1H, CH); 4.66–5.59 (m, 3H, $\text{CH}_2=\text{CH}$). ^{13}C -NMR (δ ppm): 11.4 (C_1), 19.7 (C_2), 45.2 (C_3), 35.0 (C_4), 143.3 (C_5), 114.2 (C_6), 19.3 (C_7), 43.7 (C_8), 28.5 (C_9), 29.2 (C_{10}), 32.1 (C_{11}), 22.8 (C_{12}), 14.2 (C_{13}). M^+ 194.

3.1.6. 2-Methyl-6-methylenedodec-1-ene (7)

b.p. 99–100 °C (5 Torr), n_{D}^{22} 1.4421. ^1H -NMR (δ ppm): 0.81 (t, $J = 6.1$ Hz, 3H, CH_3); 1.04–1.34 (m, 10H, CH_2); 1.01 (s, 3H, CH_3); 1.86–2.01 (m, 6H, CH_2); 4.40–5.67 (m, 4H, $\text{CH}_2=\text{C}$). ^{13}C -NMR (δ ppm):

14.2, 21.1, 25.9, 27.2, 29.2, 29.5, 32.0, 35.7, 36.2, 37.6, 108.7, 109.9, 146.0, 150.1. M^+ 194.

3.1.7. 2-Methyl-5-vinylundec-1-ene (**8**)

b.p. 80–81 °C (2 Torr), n_D^{22} 1.4422. $^1\text{H-NMR}$ (δ ppm): 0.81 (t, $J = 6.1$ Hz, 3H, CH_3); 1.02–1.42 (m, 12H, CH_2); 1.82–1.93 (m, 2H, CH_2C); 1.93–2.10 (m, 1H, CH); 4.40–5.67 (m, 5H, $\text{CH}_2=\text{C}$, $\text{CH}_2=\text{CH}$). $^{13}\text{C-NMR}$ (δ ppm): 14.2, 22.5, 25.4, 29.6, 29.8, 32.0, 33.0, 35.2, 35.5, 43.9, 109.6, 114.4, 143.4, 146.4. M^+ 194.

3.1.8. 1-(But-3-enyl)-1-(6-hydroxyhex-4-enyl)cyclopropane (**10a**)

b.p. 120–121 °C (1 Torr), n_D^{22} 1.4902. IR $\tilde{\nu}$ (cm^{-1}): 3360, 3080, 3010, 2935, 2865, 1645, 1470, 1105, 1030, 985, 925. $^1\text{H-NMR}$ (δ ppm): 0.24 (s, 4H, CH_2 cycl); 1.10–1.62 (m, 8H, CH_2); 1.84–2.20 (m, 4H, CH_2CH); 4.06 (d, $J = 4.0$ Hz, 2H, CH_2OH); 4.82–5.90 (m, 5H, olefinic). $^{13}\text{C-NMR}$ (δ ppm): 12.0 (C_1), 19.0 (C_2), 35.4 (C_3), 31.0 (C_4), 139.3 (C_5), 113.9 (C_6), 35.5 (C_7), 26.1 (C_8), 32.4 (C_9), 129.0 (C_{10}), 133.6 (C_{11}), 63.8 (C_{12}). M^+ 194.

3.1.9. 2-(*n*-Hexyl)-4-(ethylchloroaluminia)-but-1-ene (**13b**)

$^{13}\text{C-NMR}$ (δ ppm): 107.1 (C_1), 155.1 (C_2), 40.5 (C_3), 16.2 (C_4), 1.2 (C_5), 9.0 (C_6), 36.5 (C_7), 28.7 (C_8), 30.0 (C_9), 32.6 (C_{10}), 23.4 (C_{11}), 14.5 (C_{12}).

3.1.10. 3-(*n*-Hexyl)-4-(ethylchloroaluminia)-but-1-ene (**14b**)

$^{13}\text{C-NMR}$ (δ ppm): 111.5 (C_1), 148.2 (C_2), 41.8 (C_3), 16.2 (C_4), 1.2 (C_5), 9.0 (C_6), 32.7 (C_7), 28.4 (C_8), 30.3 (C_9), 32.1 (C_{10}), 23.4 (C_{11}), 14.5 (C_{12}).

3.2. Synthesis of 1,1-dialkylcyclopropanes from acetylenes

To the mixture of disubstituted acetylene (2 mmol) and Cp_2ZrCl_2 (0.01 mmol) in dried hexane (5 ml), Et_3Al (5 mmol) was added under argon at 0 °C; the solution was stirred for 10 h at ca. 20 °C. To the resulting mixture, dialkylsulphate (8 mmol) was added dropwise at 0 °C, and the reaction solution was stirred for 12 h at 20 °C. Hexane (5 ml) was then added, and the reaction mixture was hydrolyzed by 5% HCl. The organic layer was extracted with diethyl ether, washed with Na_2CO_3 to neutral reaction and dried over CaCl_2 . After removing the solvent the residue was distilled.

3.2.1. 1-(2-Methylpentane-2-yl)-1-propylcyclopropane (**18a**)

b.p. 86–87 °C (15 Torr). $^1\text{H-NMR}$ (δ ppm): 0.14 (m, 2H, BB^1); 0.35 (m, 2H, AA^1); 0.73 (s, 6H, $\text{C}(7)\text{H}_3$, $\text{C}(7')\text{H}_3$); 0.83–0.88 (m, 6H, $\text{C}(6)\text{H}_3$, $\text{C}(10)\text{H}_3$); 1.01–1.52 (m, 8H, $\text{C}(4)\text{H}_2$, $\text{C}(5)\text{H}_2$, $\text{C}(8)\text{H}_2$, $\text{C}(9)\text{H}_2$). $^{13}\text{C-NMR}$ (δ ppm): 7.1 (C_1 , C_1'), 24.9 (C_2), 35.2 (C_3), 35.4

(C_4), 20.1 (C_5), 15.3 (C_6), 25.2 (C_7 , C_7'), 43.5 (C_8), 17.8 (C_9), 15.1 (C_{10}). M^+ 168.

3.2.2. 1-(*n*-Butyl)-1-(2-methylhexane-2-yl)cyclopropane (**18b**)

b.p. 102–103 °C (9 Torr). $^1\text{H-NMR}$ (300 MHz, δ ppm): 0.12 (BB^1 , $^3J_{\text{BB}^1, \text{cis}} = 9.5$, $^2J_{\text{AB}, \text{gem}} = -5.4$, $^3J_{\text{AB}', \text{trans}} = 5.5$, 2H); 0.33 (AA^1 , $^3J_{\text{AA}', \text{cis}} = 9.5$, $^2J_{\text{AB}, \text{gem}} = -5.4$, $^3J_{\text{AB}', \text{trans}} = 5.5$, 2H); 0.70 (c, 6H, $\text{C}(8)\text{H}_3$, $\text{C}(8')\text{H}_3$); 0.83–0.93 (m, 6H, $\text{C}(7)\text{H}_3$, $\text{C}(12)\text{H}_3$); 1.05–1.57 (m, 12H, $\text{C}(4)\text{H}_2$ – $\text{C}(6)\text{H}_2$, $\text{C}(9)\text{H}_2$ – $\text{C}(11)\text{H}_2$). $^{13}\text{C-NMR}$ (δ ppm): 6.97 (C_1 , C_1'), 25.0 (C_2), 35.0 (C_3), 32.0 (C_4), 29.2 (C_5), 23.9 (C_6), 14.3 (C_7), 25.2 (C_8 , C_8'), 40.7 (C_9), 26.7 (C_{10}), 23.7 (C_{11}), 14.3 (C_{12}). M^+ 196.

3.2.3. 1-(*n*-Butyl)-1-(3-ethylheptane-3-yl)cyclopropane (**18c**)

$^1\text{H-NMR}$ (δ ppm): 0.10 (m, 2H, BB^1); 0.40 (m, 2H, AA^1); 0.76 (t, 6H, $\text{C}(9)\text{H}_3$, $\text{C}(9')\text{H}_3$, $J = 7.81$ Hz); 1.17–1.34 (m, 10H, $\text{C}(7)\text{H}_3$, $\text{C}(8)\text{H}_3$, $\text{C}(8')\text{H}_3$, $\text{C}(13)\text{H}_3$); 1.40–1.62 (m, 12H, $\text{C}(4)\text{H}_2$ – $\text{C}(6)\text{H}_2$, $\text{C}(10)\text{H}_2$ – $\text{C}(12)\text{H}_2$). $^{13}\text{C-NMR}$ (δ ppm): 5.3 (C_1 , C_1'), 20.7 (C_2), 39.0 (C_3), 32.4 (C_4), 26.1 (C_5), 24.0 (C_6), 14.3 (C_7), 26.0 (C_8 , C_8'), 8.50 (C_9 , C_9'), 33.3 (C_{10}), 28.8 (C_{11}), 23.8 (C_{12}), 14.3 (C_{13}). M^+ 224.

3.3. Synthesis of (*Z*)-1,2-dialkyl-1,2-diethylethylenes from acetylenes

To the mixture of disubstituted acetylene (10 mmol) and Cp_2ZrCl_2 (0.3 mmol) in dried hexane (8 ml), Et_3Al (15 mmol) was added under dried argon at 0 °C; the solution was stirred for 8 h at r.t. Ethyltosylate (50 mmol) was then added to the mixture of forming *in situ* cyclic OAC at 0 °C; the reaction solution was stirred for 18 h at r.t. The reaction mixture was hydrolyzed with 5% HCl, the organic layer was extracted with diethyl ether, washed with Na_2CO_3 to neutral reaction and dried over CaCl_2 . After removing the solvent the residue was distilled in vacuo.

3.3.1. 5,6-Diethyldec-5*Z*-ene (**19b**)

b.p. 113 °C (14 Torr). $^1\text{H-NMR}$ (δ ppm): 0.66–0.96 (m, 12H, CH_3); 1.00–1.23 (m, 8H, CH_2); 1.30 (q, 4H, CH_2 , $J = 7.1$ Hz); 1.90 (t, 4H, CH_2 , $J = 7.3$ Hz). $^{13}\text{C-NMR}$ (δ ppm): 14.1 (C_1), 24.4 (C_2), 31.1 (C_3), 31.6 (C_4), 134.5 (C_5), 23.2 (C_6), 13.9 (C_7). M^+ 196.

3.4. Synthesis of 1,2-dialkyl-1*Z*,3-butadienes from acetylenes

To the mixture of disubstituted acetylene (10 mmol) and Cp_2ZrCl_2 (0.3 mmol) in dried hexane (8 ml), Et_3Al (15 mmol) was added under dried argon at 0 °C; the solution was stirred for 8 h at r.t. THF (20 mmol),

allylacetate (40 mmol) and $\text{Pd}(\text{acac})_2$ (0.3 mmol) were added to the mixture at $-5\text{ }^\circ\text{C}$; the reaction solution was stirred for 10 h at r.t. The reaction mixture was hydrolyzed with 5% HCl, the organic layer was separated from the aqueous layer, washed with Na_2CO_3 to neutral reaction and dried over CaCl_2 . After removing the solvent the residue was distilled in vacuo.

3.4.1. (3E)-3-propylhepta-1,3-diene (20a)

b.p. $63\text{--}64\text{ }^\circ\text{C}$ (25 Torr). $^1\text{H-NMR}$ (δ ppm): 0.92 (t, 6H, CH_3 , $^3J_{\text{CH}} = 6.8$); 1.22–1.63 (m, 4H, CH_2); 1.98–2.29 (m, 4H, CH_2); 4.84–5.19 (m, 2H, CH_2); 5.47 (t, 1H, CH, $^3J_{\text{CH}} = 7.3$); 6.12–6.43 (m, 1H, CH). M^+ 138.

3.4.2. (3E)-3-butylocta-1,3-diene (20b)

b.p. $80\text{--}81\text{ }^\circ\text{C}$ (10 Torr). $^1\text{H-NMR}$ (δ ppm): 0.71–1.10 (m, 6H, CH_3); 1.14–1.60 (m, 8H, CH_2); 1.99–2.29 (m, 4H, CH_2); 4.82–5.16 (m, 2H, CH_2); 5.42 (t, 1H, CH, $^3J_{\text{CH}} = 7.3$); 6.09–6.40 (m, 1H, CH). M^+ 166.

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