ELSEVIER

Journal of Organometallic Chemistry 636 (2001) 76–81

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

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

Usein M. Dzhemilev*, Askhat G. Ibragimov, Leyla O. Khafizova, Ilfir R. Ramazanov, Dina F. Yalalova, Genrikh A. Tolstikov

Institute of Petrochemistry and Catalysis, Bashkortostan Republic Academy of Sciences, Ufa Scientific Centre of Russian Academy of Sciences, 450075, Ufa, Russia

Received 26 February 2001; accepted 28 July 2001

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

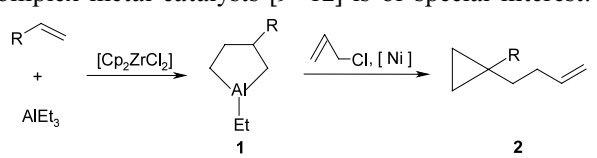
Abstract

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 aluminacyclopentenes, respectively, was developed. Five-membered organoaluminium compounds obtained without preliminary isolation are transformed to cyclopropanes under the effect of $Ni(acac)_2$ in combination with allylhalogenides in the case of aluminacyclopentanes and alkylsulphates in experiments with aluminacyclopentenes. © 2001 Elsevier Science B.V. All rights reserved.

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

1. Introduction

Carbene reactions, such as cyclopropanation according to Simmons–Smith [1] halogencyclopropanation 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 aluminacyclopentenes by cycloalumination of α-olefins and acetylenes effected by complex metal catalysts [9–12] is of special interest.



* Corresponding author. Fax: +7-3472-312750.
E-mail address: ink@anrb.ru (U.M. Dzhemilev).

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 $Ni(acac)_2$ and allylchloride, without preliminary isolation from the reaction mixture.

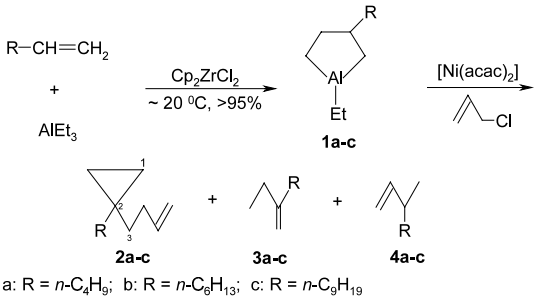
2. Results and discussion

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 aluminacyclopentenes [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-

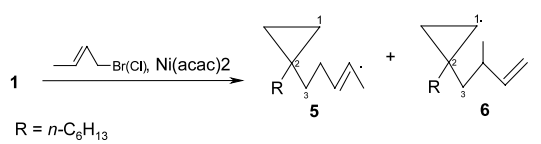
PII: S0022-328X(01)01168-8

clopentanes in the presence of 5 mol% freshly sublimated $Ni(acac)_2$ and three-fold excess of allylchloride as reoxidant (reaction conditions: 20 °C, 8 h, solvent—$(C_2H_5)_2O$).

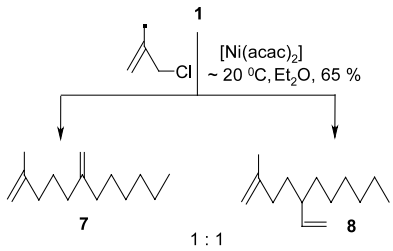


Thus, 1-ethyl-3-(*n*-hexyl)aluminacyclopentane (**1b**) obtained in situ by the reaction of oct-1-ene with $AlEt_3$, under conditions [13] using freshly sublimated $Ni(acac)_2$ and allylchoride, affords 1-(but-3-enyl)-1-(*n*-hexyl)cyclopropane (**2b**), 3-methylenenonane (**3b**) and 3-methylnonene (**4b**)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

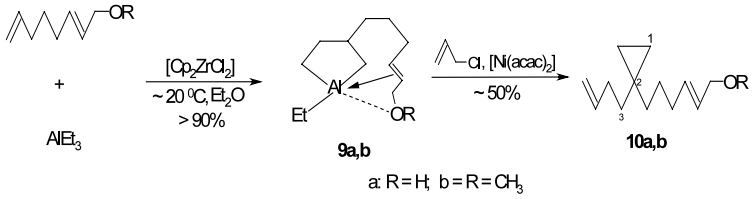


The direction of the aforesaid catalytic reaction completely changes when metallylchloride is used as allylhaloid (reoxidant). For example, under selected optimal conditions ACP (**1**) turns into regioisomeric hydrocarbons—2-methyl-6-methylenedodec-1-ene (**7**) and 2-methyl-5-vinylundec-1-ene (**8**)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



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

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-dienes 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 $Ni(acac)_2$ leading to corresponding 1,1-disubstituted oxygen-containing cyclopropanes **10a**,**b** in ca. 50% yield.

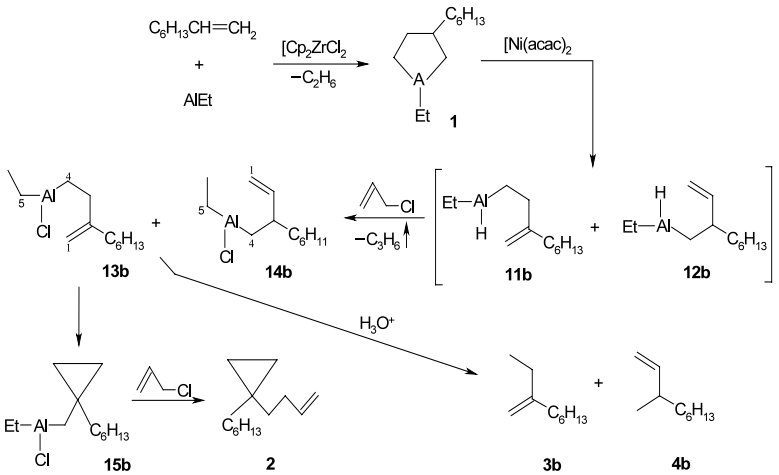


To determine the structure of intermediate compounds obtained during transformation of aluminacyclopentanes to 1,1-disubstituted cyclopropanes we have studied the reaction **1** with allylchloride in the presence of $Ni(acac)_2$ by dynamic NMR-spectroscopy along with identification of compounds formed. Experiments were carried out in an inert gas flow, by mixing of aluminacyclopentane (**1**) with allylchloride and a catalytic amount of $Ni(acac)_2$ 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 ([Al]–CH_2CHCH_2Cl = 1:3) in the presence of 5 mol% $Ni(acac)_2$ 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 Ni(acac)$_2$. Signals disappear completely in 24 h. Probably, under selected conditions intramolecular carboalumination in **13b** takes place leading to cyclopropylhalogenalane (**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 Ni(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].

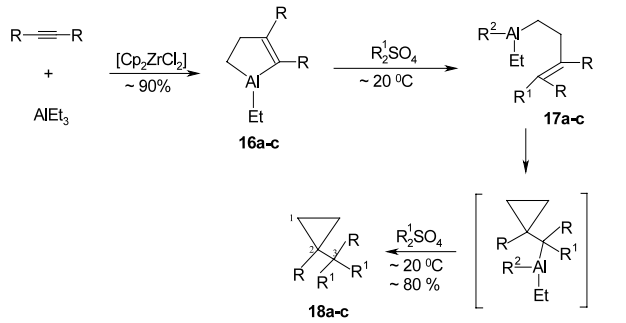
At the same time under above conditions (catalyst Ni(acac)$_2$, ca. 20 °C, 8 h; solvent—Et_2O) aluminacyclopentenes (**16**) were found to react with allylchloride non-selectively leading upon hydrolysis to the mixture of hydrocarbons, the content of substituted cyclopropanes in which does not exceed 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 $(CH_3)_2SO_4$ 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].

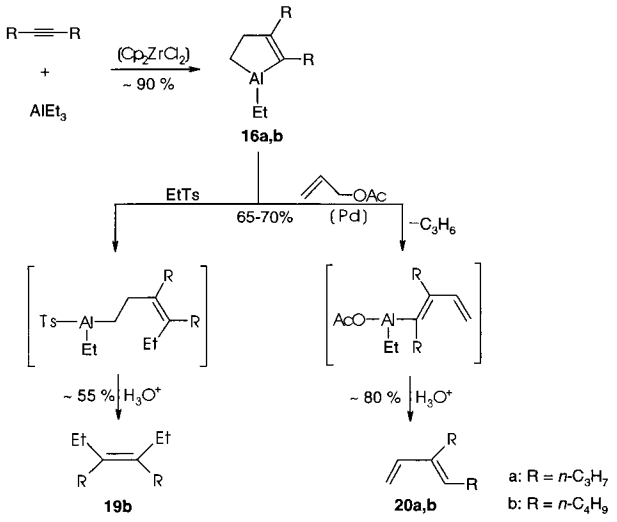
The mechanistic study of transformation **16** into **18** by the model interaction between **16a** and $(CH_3)_2SO_4$ using the dynamic NMR-spectroscopy method revealed that typical for aluminacyclopentene ring resonance peaks have disappeared in 60 min after beginning of the reaction. At the same time ^{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.



a: R = *n*-C_3H_7, R^1 = CH_3; b: R = *n*-C_4H_9, R^1 = CH_3;
c: R = *n*-C_4H_9, R^1= C_2H_5; R^2 = SO_4R^1

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 [Pd(acac)$_2$–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 synthesises 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. ^{1}H- 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 ^{1}H) and 'Bruker AM-300' (75.46 MHz for ^{13}C and 300 MHz for ^{1}H). 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 $Ni(acac)_2$ (0.5 mmol) and allylchloride (metallylchloride, 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. ^{1}H-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, CH=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. ^{1}H-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, CH=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. ^{1}H-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, CH=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. ^{1}H-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, CH=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. ^{1}H-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, CH_2=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. ^{1}H-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, CH_2=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}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, CH_2=C, CH_2=CH). ^{13}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}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}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}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}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 hydrolized 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}H-NMR (δ ppm): 0.14 (m, 2H, BB^1); 0.35 (m, 2H, AA^1); 0.73 (s, 6H, C(7)H_3, C(7′)H_3); 0.83–0.88 (m, 6H, C(6)H_3, C(10)H_3); 1.01–1.52 (m, 8H, C(4)H_2, C(5)H_2, C(8)H_2, C(9)H_2). ^{13}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}H-NMR (300 MHz, δ ppm): 0.12 (BB^1, $^3J_{BB',\ cis} = 9.5$, $^2J_{AB,\ gem} = -5.4$, $^3J_{AB',\ trans} = 5.5$, 2H); 0.33 (AA^1, $^3J_{AA',\ cis} = 9.5$, $^2J_{AB,\ gem} = -5.4$, $^3J_{AB',\ trans} = 5.5$, 2H,); 0.70 (c, 6H, C(8)H_3, C(8′)H_3); 0.83–0.93 (m, 6H, C(7)H_3, C(12)H_3); 1.05–1.57 (m, 12H, C(4)H_2–C(6)H_2, C(9)H_2–C(11)H_2). ^{13}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}H-NMR (δ ppm): 0.10 (m, 2H, BB^1); 0.40 (m, 2H, AA^1); 0.76 (t, 6H, C(9)H_3, C(9′)H_3, $J = 7.81$ Hz); 1.17–1.34 (m, 10H, C(7)H_3, C(8)H_3, C(8′)H_3, C(13)H_3); 1.40–1.62 (m, 12H, C(4)H_2–C(6)H_2, C(10)H_2–C(12)H_2). ^{13}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-5Z-ene ***(19b)***

b.p. 113 °C (14 Torr). ^{1}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}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-1Z,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 $Pd(acac)_2$ (0.3 mmol) were added to the mixture at −5 °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. 63–64 °C (25 Torr). ^{1}H-NMR (δ ppm): 0.92 (t, 6H, CH_3, $^3J_{CH} = 6.8$); 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, $^3J_{CH} = 7.3$); 6.12–6.43 (m, 1H, CH). M^+ 138.

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

b.p. 80–81 °C (10 Torr). ^{1}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, $^3J_{CH} = 7.3$); 6.09–6.40 (m, 1H, CH). M^+ 166.

Acknowledgements

The research work was sponsored by Russian Federation for Basic Research (grant Nos. 00-15-97312, 00-03-32736).

References

[1] H.E. Simmons, R.D. Smith, J. Am. Chem. Soc. 80 (1958) 5323.
[2] O.M. Nefedov, A.I. Jioffe, L.G. Menchikov, The Chemistry of Carbenes, Khimiya, Moscow, 1990.
[3] E.A. Shapiro, A.B. Dyatkin, O.M. Nefedov, Diazoesters, Nauka, Moscow, 1992.
[4] E. Negishi, C. Coperet, S. Ma, S.-Y. Liov, F. Liu, Chem. Rev. 96 (1996) 365.
[5] I. Ojima, M. Tzamarioudaki, Z. Li, R.J. Donovan, Chem. Rev. 96 (1996) 635.
[6] E. Negishi, J.-L. Montchamp, L. Anastasia, A. Elizarov, D. Choveiry, Tetrahedron Lett. 39 (1998) 2503.
[7] J.-L. Montchamp, E. Negishi, J. Am. Chem. Soc. 120 (1998) 5345.
[8] U.M. Dzhemilev, A.G. Ibragimov, A.P. Zolotarev, R.R. Muslukhov, G.A. Tolstikov, Izv. Acad. Nauk SSSR, Ser. Khim. (1990) [Bull. Acad. Sci. USSR, Div. Chem. Sci. 39 (1990) 1071 (Engl. Transl.)].
[9] U.M. Dzhemilev, A.G. Ibragimov, J. Organometal. Chem. 466 (1994) 1.
[10] U.M. Dzhemilev, Tetrahedron 51 (1995) 4333.
[11] U.M. Dzhemilev, A.G. Ibragimov, Russian Chem. Bull. 47 (1998) 786.
[12] U.M. Dzhemilev, A.G. Ibragimov, Russian Chem. Rev. 69 (2000) 121.
[13] U.M. Dzhemilev, A.G. Ibragimov, A.P. Zolotarev, Izv. Acad. Nauk SSSR, Ser. Khim. (1989) 207 [Bull. Acad. Sci. USSR, Div. Chem. Sci. 38 (1989) 194 (Engl. Transl.)].
[14] U.M. Dzhemilev, A.G. Ibragimov, A.P. Zolotarev, Mendeleev Commun. 4 (1992) 135.
[15] U.M. Dzhemilev, A.G. Ibragimov, A.P. Zolotarev, G.A. Tolstikov, Izv. Acad. Nauk SSSR, Ser. Khim. (1990) 2831 [Bull. Acad. Sci. USSR, Div. Chem. Sci. 39 (1990) 2570 (Engl. Transl.)].