1016 Russian Chemical Bulletin, International Edition, Vol. 62, No. 4, pp. 1016—1019, April, 2013

Synthesis of Si- and N-containing bicyclo[4.2.1]nona-2,4-dienes and bicyclo[4.2.1]nona-2,4,7-trienes*

V. A. D´yakonov,⋆ D. I. Kolokol´tsev, G. N. Kadikova, and U. M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347) 284 2750. E-mail: DyakonovVA@rambler.ru

A [6π+2π] cycloaddition of Si- and N-containing alkynes and 1,2-dienes to cyclohepta-1,3,5-trienes in the presence of the two-component catalytic system $(acac)_2TiCl_2$—Et_2AlCl gives rise to the corresponding bicyclo[4.2.1]nona-2,4-diene and bicyclo[4.2.1]nona-2,4,7-triene derivatives.

Key words: cyclohepta-1,3,5-trienes, propargylamines, 1,2-dienes, metal complex catalysis, medium size cycles, cycloaddition, organoaluminum compounds, organosilicon compounds.

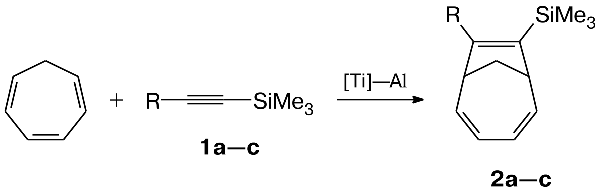
Development of efficient methods for the construction of medium size cycles is among the most important problems of organic chemistry because of their wide application in the composition of medicines exhibiting antitumor, antiviral, and other activities.[1]

Recently, we pioneered to show that 1,2-dienes selectively underwent the [6π+2π] cycloaddition to cyclohepta-1,3,5-trienes (CHT) in the presence of the catalytic system $TiCl_4$—Et_nAlCl_{3-n} (n = 1—3) with the formation of practically important bicyclo[4.2.1]nonadienes in high yields.[2,3]

To continue this research and examine a possibility of the [6π+2π] cycloaddition between functionally substituted 1,2-dienes and acetylenes to cyclohepta-1,3,5-trienes, we studied reactions of CHT and 7-alkyl(phenyl)cyclohepta-1,3,5-trienes with Si-containing allenes and disubstituted acetylenes, as well as with propargylamines, catalyzed by Ti complexes in combination with trialkyl- and alkylhaloalanes.

To search for the optimal catalyst for this reactions, we studied a number of titanium complexes: (Cp_2TiCl_2, $(Pr^iO)_2TiCl_2$, $(Bu^tO)_2TiCl_2$, $Ti(acac)_2Cl_2$, $(Pr^iO)_4Ti$) in combination with such cocatalysts as Et_3Al, $Bu^i{}_3Al$, Et_2AlCl, $Bu^i{}_2AlCl$, and $Bu^i{}_2AlH$ used previously for the transformation of unsaturated compounds. The selection was carried out for the model reaction of 1-phenyl-2-trimethylsilylacetylene (**1a**) with CHT (Scheme 1). The highest yields (>70%) of the [6π+2π]-adducts **2a** were observed in the case of $(RO)_2TiCl_2$ and $Ti(acac)_2Cl_2$ reduced with Et_2AlCl or $Bu^i{}_2AlCl$ at 80 °C, in the benzene solution and at the concentration of the catalyst of 6 mol.%. The best yields of adducts **2** under the conditions of choice (CHT : Si—alkyne : $Ti(acac)_2Cl_2$: Et_2AlCl = = 1 : 2 : 0.06 : 0.4, benzene, 80 °C, 8 h) were 84 (**2a**), 71 (**2b**), and 78% (**2c**) (see Scheme 1).

Scheme 1



R = Ph (**a**), Hex (**b**), Oct (**c**)

The high efficiency of the $Ti(acac)_2Cl_2$—Et_2AlCl catalytic system, in contrast to the catalyst $TiCl_4$—Et_2AlCl reported in the literature[4] for the use in the homodimerization of cyclohepta-1,3,5-triene, was demonstrated for the [6π+2π] cycloaddition of propargylamine **3a—c** to cyclohepta-1,3,5-triene. Using of this catalytic system, nitrogen-containing bicyclo[4.2.1]nona-2,4,7-trienes **4a—c** were obtained in high yields 61—78% (Scheme 2). It should be noted that in the case of $TiCl_4$ and $(RO)_2TiCl_2$ in combination with organoaluminum reducing agents mentioned above did not lead to the target cycloadducts were not formed.

Note that no cycloaddition of propargylamine to CHT was previously reported.

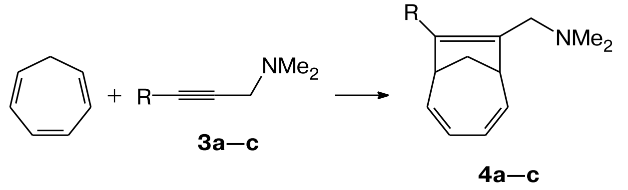
We also showed that Si- and N-containing acetylenes similarly add to 7-substituted CHT (CHT : Si—alkyne : : $Ti(acac)_2Cl_2$: Et_2AlCl = 1 : 2 : 0.06 : 0.4, benzene, 80 °C, 8 h; CHT : N—alkyne : $Ti(acac)_2Cl_2$: Et_2AlCl =

---

* Dedicated to Academician of the Russian Academy of Sciences I. P. Beletskaya on the occasion of her anniversary.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 1015—1018, April, 2013.

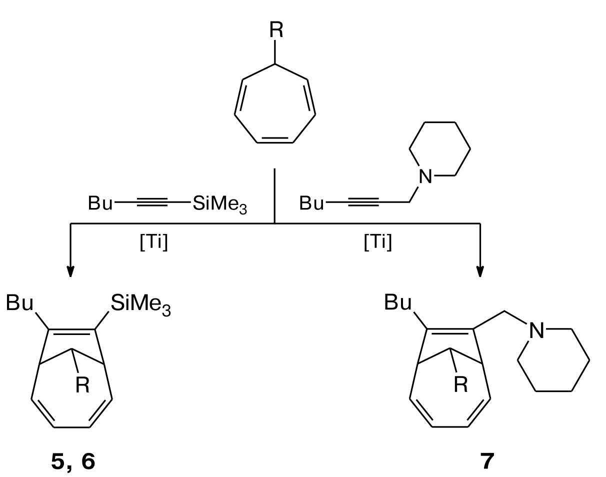
Scheme 2



R = Bu (**a**), Oct (**b**), Ph (**c**)

= 1 : 1 : 0.07 : 0.5, benzene, 80 °C, 8 h) in the presence of $Ti(acac)_2Cl_2—Et_2AlCl$ to give products **5—7** in 74, 52, and 81% yields, respectively (Scheme 3).

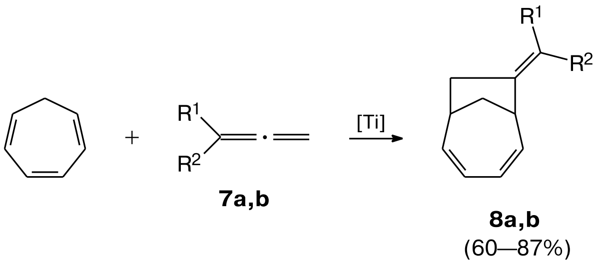
Scheme 3



R = Et (**5**, **7**), Ph (**6**)

The systems selected also catalyzed [6π+2π] cycloaddition of CHT to allenes (Scheme 4). Thus, the Si-containing 1,2-dienes **7a**,**b** added to CHT in the presence of the catalyst $Ti(acac)_2Cl_2—R_nAlCl_{3-n}$ (R = Et, Bu^i; n = 2, 3) affording alkylidene-substituted bicyclo[4.2.1]nona-2,4-dienes **8a**,**b** in 60—87% yields.

Scheme 4



7a, 8a: $R^1 = CH_2TMS$, R^2 = H
7b, 8b: R^1 = Bu, $R^2 = CH_2TMS$

The structure of compounds obtained was confirmed by ^1D (^1H, ^{13}C) and 2D (COSY, NOESY) NMR spectroscopy and mass spectrometry.

In conclusion, we developed an efficient synthesis of Si- and N-containing bicyclo[4.2.1]nona-2,4-dienes and bicyclo[4.2.1]nona-2,4,7-trienes based on the [6π+2π] cycloaddition of functionally substituted alkynes and allenes to cyclohepta-1,3,5-trienes in the presence of the new two-component catalytic system $(acac)_2TiCl_2—Et_2AlCl$. The results obtained show that such catalytic systems seem promising for cycloaddition between heterocyclic analogs of CHT and for the preparation of practically important natural compounds.

Experimental

Chromatographic analysis was carried out on a Shimadzu GC-9A instrument, using a 2000×2-mm column, silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm) as the stationary phase, carrier gas helium (30 mL min^{-1}), the temperature regime from 50 to 300 °C at the rate of 8 deg min^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (100 MHz for ^{13}C and 400 MHz for ^1H) in $CDCl_3$ relative to Me_4Si. Mass spectrometric analysis was carried out on a Shimadzu GCMS-QP2010 Plus spectrometer (glass capillary column SLB-5ms 60000×0.25mm×0.25 μm (Supelco, USA), carrier gas helium, the temperature regime from 40 to 280 °C at the rate of 5 deg min^{-1}, the injector temperature 280 °C, the source of ions temperature 200 °C, 70 eV). Elemental analysis was performed on a Carlo Erba model 1108 analyzer. The yields of the products were determined by GLC. The catalytic cycloaddition was carried out under dry argon. Aromatic solvents were dried with Na. Commercial Et_2AlCl (90%) and $Bu^i{}_3Al$ (92%) were available from Redkino Experimental Factory Inc., cyclohepta-1,3,5-triene was purchased from Aldrich. Titanium chlorobis(acetylacetonate), trimethylsilylacetylenes, propargylamines, and 1,2-dienes were synthesized as described.[5,6] 7-Ethylcyclohepta-1,3,5-triene and 7-phenylcyclohepta-1,3,5-triene were obtained according to the literature.[7]

Cycloaddition of Si-containing acetylenes to cyclohepta-1,3,5-trienes (general procedure). Cycloheptatriene (1 mmol), acetylene compound **1** (2 mmol), $Ti(acac)_2Cl_2$ (0.06 mmol), and dry benzene (3 mL) were placed into a temperature controlled (~0 °C) glass tube under dry argon. The tube was cooled to temperature of liquid nitrogen, Et_2AlCl (0.4 mmol) was added, and the tube was sealed. After heating at 80 °C for 8 h, the tube was unsealed, the content was treated with EtOH. The light solvents were evaporated *in vacuo*, the residue was subjected to chromatography on a column with silica gel (eluent light petroleum, 100%).

Trimethyl(8-phenylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)silane (2a). R_f 0.52 (SiO_2, light petroleum, 100%). ^1H NMR, δ: –0.73 (s, 9 H, $SiMe_3$); 1.69 (d, 1 H, $C(9)H_2$, J = 12 Hz); 2.33 (dt, 1 H, $C(9)H_2$, J_d = 12 Hz, J_t = 7 Hz); 3.31 (t, 1 H, C(1)H, J = 7 Hz); 3.54 (t, 1 H, C(6)H, J = 7 Hz); 5.84—5.91 (m, 2 H, C(3,4)H); 5.99—6.04 (m, 1 H, C(5)H); 6.20—6.24 (m, 1 H, C(2)H); 7.17—7.30 (m, 5 H, Ph). ^{13}C NMR, δ: 0.60 ($SiMe_3$), 31.64 (C(9)), 49.22 (C(1)), 51.62 (C(6)), 123.63 (C(3)), 124.70 (C(4)), 126.89 (C(13)), 127.49 (C(12), C(14)), 129.10 (C(11), C(15)), 135.20 (C(10)), 138.01 (C(5)), 139.00 (C(2)), 147.24 (C(7), C(8)). MS, *m/z*: 266 [M]$^+$. Found (%): C, 80.91; H, 8.33. $C_{18}H_{22}Si$. Calculated (%): C, 81.14; H, 8.32.

(8-Hexylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)trimethylsilane (2b). R_f 0.59 (SiO_2, light petroleum, 100%). ^{1}H NMR, δ: 0.17 (s, 9 H, $SiMe_3$); 0.91 (t, 3 H, CH_3, $J = 6$ Hz); 1.20—1.46 (m, 8 H, C(11—14)H_2); 1.56 (d, 1 H, C(9)H_2, $J = 12$ Hz); 2.08—2.14 (m, 2 H, C(10)H_2); 2.23—2.32 (m, 1 H, C(9)H_2); 3.08 (t, 1 H, C(1)H, $J = 7$ Hz); 3.26 (t, 1 H, C(6)H, $J = 7$ Hz); 5.70—5.83 (m, 2 H, C(3,4)H); 6.05—6.17 (m, 2 H, C(2,5)H). ^{13}C NMR, δ: 0.63 (3 C, $SiMe_3$), 14.07 (C(15)), 22.64 (C(14)), 29.49 (C(11)), 29.57 (C(12)), 30.30 (C(13)), 31.44 (C(9)), 31.83 (C(10)), 48.31 (C(1)), 48.36 (C(6)), 123.05 (C(3)), 124.32 (C(4)), 132.61 (C(7)), 138.62 (C(5)), 139.91 (C(2)), 149.87 (C(8)). MS, *m/z*: 274 [M]$^+$. Found (%): C, 78.49; H, 10.99. $C_{18}H_{30}Si$. Calculated (%): C, 78.75; H, 11.02.

Trimethyl(8-octylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)silane (2c). R_f 0.63 (SiO_2, light petroleum, 100%). ^{1}H NMR, δ: 0.17 (s, 9 H, $SiMe_3$); 0.91 (t, 3 H, CH_3, $J = 6$ Hz); 1.21—1.48 (m, 12 H, C(11—16)H_2); 1.56 (d, 1 H, C(9)H_2, $J = 12$ Hz); 2.05—2.14 (m, 2 H, C(10)H_2); 2.22—2.33 (m, 1 H, C(9)H_2); 3.08 (t, 1 H, C(1)H, $J = 7$ Hz); 3.25 (t, 1 H, C(6)H, $J = 7$ Hz); 5.70—5.83 (m, 2 H, C(3,4)H); 6.05—6.17 (m, 2 H, C(2,5)H). ^{13}C NMR, δ: 0.64 (3 C, $SiMe_3$), 14.10 (C(17)), 22.67 (C(16)), 29.48 (C(11)), 29.91 (C(13)), 29.57 (C(12)), 29.91 (C(13)), 30.33 (C(15)), 31.44 (C(9)), 31.88 (C(10)), 48.30 (C(1)), 48.35 (C(6)), 123.03 (C(3)), 124.31 (C(4)), 132.61 (C(7)), 138.65 (C(5)), 139.94 (C(2)). MS, *m/z*: 302 [M]$^+$. Found (%): C, 79.15; H, 11.30. $C_{20}H_{34}Si$. Calculated (%): C, 79.39; H, 11.33.

(8-Butyl-9-ethylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)trimethylsilane (5). R_f 0.66 (SiO_2, light petroleum, 100%). ^{1}H NMR, δ: 0.13 (s, 9 H, $SiMe_3$); 0.84 (t, 3 H, C(11)H_3, $J = 7$ Hz); 0.93 (t, 3 H, C(15)H_3, $J = 7$ Hz); 1.11—1.33 (m, 2 H, C(10)H_2); 1.34—1.57 (m, 4 H, C(13,14)H_2); 2.05—2.28 (m, 3 H, C(9)H, C(12)H_2); 2.87 (t, 1 H, C(1)H, $J = 7$ Hz); 3.10 (t, 1 H, C(6)H, $J = 7$ Hz); 5.83—5.91 (m, 4 H, C(2—5)H). ^{13}C NMR, δ: 0.71 (3 C, $SiMe_3$), 13.16 (C(11)), 14.09 (C(15)), 20.87(C(10)), 22.98 (C(14)), 29.76 (C(12)), 32.58 (C(13)), 40.68 (C(9)), 50.67 (C(1)), 50.74 (C(6)), 124.96 (C(3)), 126.26 (C(4)), 134.76 (C(7)), 136.09 (C(2)), 137.33 (C(5)), 151.82(C(8)). MS, *m/z*: 274 [M]$^+$. Found (%): C, 78.69; H, 11.00. $C_{18}H_{30}Si$. Calculated (%): C, 78.75; H, 11.02.

(8-Butyl-9-phenylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)trimethylsilane (6). R_f 0.59 (SiO_2, light petroleum, 100%). ^{1}H NMR, δ: 0.26 (s, 9 H, $SiMe_3$); 1.02 (t, 3 H, CH_3, $J = 6$ Hz); 1.39—1.51 (m, 2 H, C(12)H_2); 1.59—1.70 (m, 2 H, C(10)H_2); 2.23—2.44 (m, 2 H, C(11)H_2); 3.51—3.60 (m, 2 H, C(1,6)H); 3.72—3.81 (m, 1 H, C(9)H); 5.67—5.76 (m, 2 H, C(3,4)H); 6.14—6.23 (m, 2 H, C(2,5)H); 7.43—7.44 (m, 5 H, Ph). ^{13}C NMR, δ: 0.80 (3 C, $SiMe_3$), 14.21 (C(13)), 23.09 (C(12)), 29.80 (C(11)), 32.67 (C(10)), 44.18 (C(6)), 49.98 (C(9)), 50.01 (C(1)), 125.14 (C(3)), 125.22 (C(17)), 126.35 (C(4)), 127.19 (C(15), C(19)), 128.40 (C(16), C(18)), 133.66 (C(14)), 136.57 (C(2)), 137.69 (C(5)), 141.64 (C(7)), 150.57 (C(8)). MS, *m/z*: 322 [M]$^+$. Found (%): C, 81.74; H, 9.34. $C_{22}H_{30}Si$. Calculated (%): C, 81.92; H, 9.37.

Cycloaddition of N-containing acetylenes to cyclohepta-1,3,5-trienes (general procedure). Cyclohepta-1,3,5-triene (1 mmol), propargylamine **3** (1 mmol), $Ti(acac)_2Cl_2$ (0.07 mmol), and dry benzene (3 mL) were placed into a temperature controlled (~0 °C) glass tube under dry argon. The tube was cooled to temperature of liquid nitrogen, Et_2AlCl (0.5 mmol) was added, and the tube was sealed. After heating at 80 °C for 8 h, the tube was unsealed, the content was treated with aqueous KOH (25%). The reaction products were extracted with benzene, dried with KOH, the target compounds were isolated by fractional distillation.

***N*-[(8-Butylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)methyl]-*N*,*N*-dimethylamine (4a).** ^{1}H NMR, δ: 0.91 (t, 3 H, CH_3, $J = 7$ Hz); 1.28—1.46 (m, 6 H, C(10,11,12)H_2); 1.62 (d, 1 H, C(9)H_2, $J = 11$ Hz); 2.19 (s, 6 H, $(CH_3)_2N$); 2.23—2.30 (m, 1 H, C(9)H_2); 2.69 (d, 1 H, C(14)H_2, $J = 13$ Hz); 3.13 (t, 1 H, C(6)H, $J = 7$ Hz); 3.19 (d, 1 H, C(14)H_2, $J = 13$ Hz); 3.29 (t, 1 H, C(1)H, $J = 7$ Hz); 5.73—5.78 (m, 2 H, C(3,4)H); 6.14—6.18 (m, 1 H, C(5)H); 6.24—6.27 (m, 1 H, C(2)H). ^{13}C NMR, δ: 14.03 (C(13)), 22.71 (C(12)), 25.87 (C(11)), 30.61 (C(9)), 31.84 (C(10)), 45.43 ($(CH_3)_2N$)), 45.47 (C(6)), 46.75 (C(1)), 54.59 (C(14)), 123.76 (C(4)), 124.06 (C(3)), 132.86 (C(7)), 139.02 (C(8)), 139.81 (C(5)), 140.80 (C(2)). MS, *m/z*: 231 [M]$^+$. Found (%): C, 82.92; H, 10.87; N, 6.01. $C_{16}H_{25}N$. Calculated (%): C, 83.06; H, 10.89; N, 6.05.

***N*,*N*-Dimethyl-*N*-[(8-octylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)methyl]amine (4b).** ^{1}H NMR, δ: 0.90 (t, 3 H, CH_3, $J = 7$ Hz); 1.28—1.46 (m, 14 H, C(10—16)H_2); 1.61 (d, 1 H, C(9)H_2, $J = 12$ Hz); 2.20 (s, 6 H, $(CH_3)_2N$); 2.22—2.29 (m, 1 H, C(9)H_2); 2.66 (d, 1 H, C(18)H_2, $J = 13$ Hz); 3.12 (t, 1 H, C(6)H, $J = 7$ Hz); 3.19 (d, 1 H, C(18)H_2, $J = 13$ Hz); 3.28 (t, 1 H, C(1)H, $J = 7$ Hz); 5.72—5.75 (m, 2 H, C(3,4)H); 6.13—6.17 (m, 1 H, C(5)H); 6.22—6.26 (m, 1 H, C(2)H). ^{13}C NMR, δ: 14.09 (C(17)), 22.66 (C(16)), 26.11 (C(11)), 29.28 (C(14)), 29.50 (C(13)), 29.62 (C(12)), 30.61 (C(9)), 31.83 (C(10)), 31.88 (C(15)), 45.52 ($(CH_3)_2N$), 44.11 (C(6)), 46.77 (C(1)), 54.69 (C(18)), 123.71 (C(4)), 124.06 (C(3)), 132.85 (C(7)), 139.00 (C(8)), 139.78 (C(5)), 140.79 (C(2)). MS, *m/z*: 287 [M]$^+$. Found (%): C, 83.29; H, 11.53; N, 4.84. $C_{20}H_{33}N$. Calculated (%): C, 83.56; H, 11.57; N, 4.87.

***N*,*N*-Dimethyl-*N*-[(8-phenylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)methyl]amine (4c).** ^{1}H NMR, δ: 1.75 (d, 1 H, C(9)H_2, $J = 12$ Hz); 2.18 (s, 6 H, $(CH_3)_2N$); 2.40—2.43 (m, 1 H, C(9)H_2); 2.75 (d, 1 H, C(16)H_2, $J = 12$ Hz); 3.31 (d, 1 H, C(16)H_2, $J = 16$ Hz); 3.50 (t, 1 H, C(6)H, $J = 7$ Hz); 3.55 (t, 1 H, C(1)H, $J = 7$ Hz); 5.81—5.90 (m, 2 H, C(3,4)H); 6.17 (t, 1H, C(5)H, $J = 8$ Hz); 6.31 (t, 1 H, C(2)H, $J = 8$ Hz); 7.24—7.39 (m, 5 H, Ph). ^{13}C NMR, δ: 30.61 (C(9)), 45.55 ($(CH_3)_2N$), 45.93 (C(1)), 48.96 (C(6)), 55.01 (C(16)), 124.40 (C(3), C(4)), 126.69 (C(13)), 127.94 (C(12), C(14)), 129.28 (C(11), C(15)), 135.16 (C(10)), 136.44 (C(8)), 137.60 (C(7)), 139.59 (C(5)), 139.93 (C(2)). MS, *m/z*: 251 [M]$^+$. Found (%): C, 85.81; H, 8.39; N, 5.59. $C_{18}H_{21}N$. Calculated (%): C, 86.01; H, 8.42; N, 5.57.

1-[(8-Butyl-9-ethylbicyclo[4.2.1]nona-2,4,7-trien-7-yl)methyl]piperidine (7). ^{1}H NMR, δ: 0.83 (t, 3 H, C(15)H_3, $J = 7$ Hz); 0.92 (t, 3 H, C(13)H_3, $J = 7$ Hz); 1.26—1.48 (m, 8 H, C(10—12,14)H_2); 1.66—1.70 (m, 1 H, C(9)H); 2.00—2.12 (m, 10 H, C(17—21)H_2); 2.78 (d, 2 H, C(16)H_2, $J = 7$ Hz); 2.85—2.95 (m, 1 H, C(1)H); 3.00—3.12 (m, 1 H, C(6)H); 5.65—5.72 (5.80—5.87) (m, 2 H, C(3,4)H); 5.94—5.99 (6.09—6.12) (m, 1 H, C(5)H); 6.14—6.18 (6.28—6.33) (m, 1 H, C(2)H). ^{13}C NMR, δ: 12.40 (C(15)), 12.91 (C(13)), 20.61 (C(14)), 22.72 (C(12)), 22.77 (C(19)), 25.81 (C(11)), 26.28 (C(18)), 26.67 (C(20)), 31.55 (C(10)), 31.88 (C(9)), 48.22 (49.11) (C(6)), 50.92 (51.86) (C(1)), 53.68 (C(16)), 54.26 (C(17)), 54.62 (C(21)), 123.29 (124.00) (C(4)), 125.61 (126.24) (C(3)), 134.12 (C(7)), 136.62 (138.40) (C(5)), 137.59 (C(8)), 138.82 (140.61) (C(2)).

MS, *m/z*: 299 $[M]^+$. Found (%): C, 84.01; H, 11.07; N, 4.62. $C_{21}H_{33}N$. Calculated (%): C, 84.22; H, 11.11; N, 4.68.

Cycloaddition of Si-containing allenes to cyclohepta-1,3,5-triene (general procedure). Cyclohepta-1,3,5-triene (1 mmol), allene **7** (1.1 mmol), $Ti(acac)_2Cl_2$ (0.06 mmol), and dry benzene (3 mL) were placed into a temperature controlled (~0 °C) glass tube under dry argon. The tube was cooled to temperature of liquid nitrogen, R_nAlCl_{3-n} (R = Et, Bu^i; *n* = 2, 3) (0.2 mmol) was added, and the tube was sealed. After heating at 80 °C for 8 h, the tube was unsealed, the content was treated with EtOH. The light solvents were evaporated *in vacuo*, the residue was subjected to chromatography on a column with silica gel (eluent light petroleum, 100%) to separate a mixture of *E*- and *Z*-isomers from the minor reaction products.

[2-(Bicyclo[4.2.1]nona-2,4-dien-7-ylidene)ethyl]trimethylsilane (*E* : *Z* = 1 : 1) (8a). R_f 0.62 (SiO_2, light petroleum, 100%). ^{1}H NMR, δ: 0.01 (s, 9 H, $SiMe_3$); 1.35 (d, 2 H, $C(11)H_2$, *J* = 8 Hz); 1.54 (d, 1 H, $C(9)H_2$, *J* = 11 Hz); 1.97 (d, 1 H, $C(9)H_2$, *J* = 12 Hz); 2.42—2.53 (m, 2 H, $C(8)H_2$); 2.71—2.75 (m, 1 H, C(1)H); 3.19—3.29 (m, 1 H, C(6)H); 5.18 (t, 1 H, C(10)H, *J* = 8 Hz); 5.56—5.88 (m, 2 H, C(3,4)H); 5.96—6.24 (m, 2 H, C(2,5)H).

***E*-Isomer.** ^{13}C NMR, δ: –1.55 ($SiMe_3$), 22.60 (C(11)), 31.69 (C(9)), 38.85 (C(1)), 42.31 (C(6)), 45.52 (C(8)), 118.16 (C(10)), 122.85 (C(3)), 123.58 (C(4)), 138.74 (C(5)), 139.49 (C(2)), 149.21 (C(7)).

***Z*-Isomer.** ^{13}C NMR, δ: –1.65 ($SiMe_3$), 20.16 (C(11)), 32.41 (C(9)), 39.22 (C(1)), 43.04 (C(6)), 46.06 (C(8)), 116.64 (C(10)), 123.41 (C(3)), 124.35 (C(4)), 134.46 (C(5)), 139.36 (C(2)), 144.15 (C(7)). MS, *m/z*: 218 $[M]^+$. Found (%): C, 76.84; H, 10.12. $C_{14}H_{22}Si$. Calculated (%): C, 76.99; H, 10.15.

[2-(Bicyclo[4.2.1]nona-2,4-dien-7-ylidene)hex-1-yl]trimethylsilane (*E* : *Z* = 1 : 1) (8b). R_f 0.64 (SiO_2, light petroleum, 100%). ^{1}H NMR, δ: 0.05 (s, 9 H, $SiMe_3$); 0.93—0.99 (m, 2 H, $C(14)H_2$); 1.30—1.64 (m, 6 H, $C(12,13,15)H_2$); 1.93—2.13 (m, 1 H, $C(11)H_2$); 2.17—2.27 (m, 2 H, $C(9)H_2$); 2.42—2.63 (m, 1 H, $C(8)H_2$); 2.72—2.74 (m, 1 H, C(1)H); 3.45—3.49 (m, 1 H, C(6)H); 5.57—5.68 (m, 2 H, C(3,4)H); 5.97—6.14 (m, 2 H, C(2,5)H).

***E*-Isomer.** ^{13}C NMR, δ: –0.32 ($SiMe_3$), 14.13 (C(14)), 22.77 (C(13)), 24.59 (C(15)), 30.34 (C(12)), 32.79 (C(9)), 36.29 (C(11)), 39.28 (C(1)), 42.95 (C(6)), 45.13 (C(8)), 122.92 (C(4)), 123.46 (C(3)), 127.65 (C(10)), 138.14 (C(2)), 137.31 (C(5)), 141.56 (C(7)).

***Z*-Isomer.** ^{13}C NMR, δ: –0.26 ($SiMe_3$), 14.07 (C(14)), 22.20 (C(13)), 23.01 (C(15)), 30.04 (C(12)), 33.02 (C(9)), 33.99 (C(11)), 39.35 (C(1)), 42.38 (C(6)), 43.93 (C(8)), 123.35 (C(4)), 123.53 (C(3)), 127.65 (C(10)), 136.63 (C(5)), 138.06 (C(2)), 141.56 (C(7)). MS, *m/z*: 274 $[M]^+$. Found (%): C, 78.60; H, 11.00. $C_{18}H_{30}Si$. Calculated (%): C, 78.75; H, 11.02.

This work was finacially supported by the Russian Foundation for Basic Research (Project No. 13-03-00167).

References

1. N. A. Petasis, M. A. Patane, *Tetrahedron*, 1992, **48**, 5757.
2. V. A. D´yakonov, G. N. Kadikova, U. M. Dzhemilev, *Tetrahedron Lett.*, 2011, **52**, 2780.
3. V. A. D´yakonov, G. N. Kadikova, L. M. Dzhemilev, *Russ. Chem. Bull.* (*Int. Ed.*), 2011, **60**, 499 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2011, 489].
4. K. Mach, H. Antropiusová, F. Tureèek, V. Hanuš, P. Sedmera, *Tetrahedron Lett.*, 1980, **21**, 4879.
5. U. M. Dzhemilev, N. R. Popod´ko, E. V. Kozlova, *Metallokompleksnyi kataliz v organicheskom sinteze* [*Metal Complex Catalysis in Organic Synthesis*], Khimiya, Moscow, 1999, 631 pp. (in Russian).
6. *Best Synthetic Methods: Acetilenes, Allenes and Cumulenes*, Ed. L. Brandsma, Elsevier, Amsterdam, 2003, p. 502.
7. K. Conrow, *J. Am. Chem. Soc.*, 1961, **83**, 2343.

Received January 25, 2013;
in revised form February 22, 2013