$TiCl_4$—Et_2AlCl-Catalyzed cycloaddition of 1,2-dienes to 1,3,5-cycloheptatriene

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A reaction of 1,3,5-cycloheptatriene with 1,2-dienes in the presence of the two-component catalytic system $TiCl_4$—Et_2AlCl leads to regio- (~99%) and stereoselective (>85%) formation of substituted *endo*-bicyclo[4.2.1]nona-2,4-dienes in up to 80% yields.

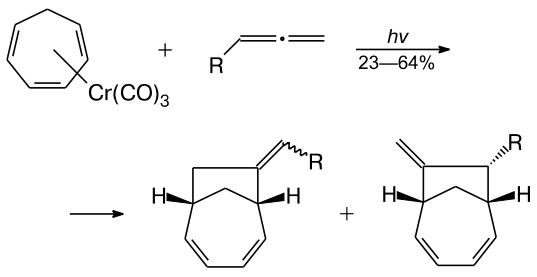
Key words: cycloheptatriene, metal complex catalysis, 1,2-dienes, bicyclo[4.2.1]nonanes, allenes, cycloaddition.

Transition metal complex-catalyzed cycloaddition attract attention due to a possibility to accomplish efficient and stereoselective synthesis of polycyclic hydrocarbons of desired structure.[1—3]

Reactions of catalytic [6π+2π] or [6π+4π] cycloaddition of 1,3-dienes, norborna-2,5-dienes, and acetylenes to 1,3,5-cycloheptatriene (CHT) are well studied. These processes are successfully used in the construction of various cyclic systems,[4—7] as well as in stereoselective synthesis of diverse practically useful natural compounds.[8—10]

However, analysis of literature data showed that [6π+2π] cycloaddition of 1,2-dienes (allenes) to CHT is represented by the only example of photochemical reaction of (η^6-cycloheptatriene)chromium(0) tricarbonyl with allenes leading to bicyclo[4.2.1]nonanes in 23—64% yields (Scheme 1).[11] In addition, in the most cases the reaction proceeds with low regio- and stereoselectivity, which in turn considerably depends on the steric and electronic effects of substituents on the allene group.

Scheme 1



Z + *E* (~50 : 50%)

R = Ar, Het, *cyclo*-Alk

In continuation of our works on the synthesis of polycyclic compounds on the basis of homo- and codimers of 1,3,5-cycloheptatriene,[5—7,12] in the present work we accomplished cycloaddition of a number of substituted 1,2-dienes to CHT in the presence of the two-component catalytic system $TiCl_4$—Et_2AlCl, possessing high activity and selectivity in the [6π+2π] and [6π+4π] cycloaddition reactions of 1,3-dienes, norborna-2,5-dienes, and acetylenes to 1,3,5-cycloheptatriene.[7] Allenes of acyclic (Table 1) and cyclic series have been chosen as objects for the study.

At the beginning, it was found that the reaction of 1,3,5-cycloheptatriene with terminal 1,2-dienes taken in the molar ratio 1 : 1.1 upon the action of a $TiCl_4$—Et_2AlCl catalyst (1 mol.%) in benzene for 8 h at 80 °C results in the formation of *endo*-bicyclo[4.2.1]nona-2,4-dienes **1**—**4** in 60—81% yields, which were isolated by column chromatography as a mixture of *E*/*Z*-isomers (Scheme 2, see Table 1). In the case of cycloaddition of allenes to CHT taken in equimolar amounts and under conditions described above, formation of homodimers of CHT (*cf.* Ref. 7) in amounts below 3—5% is observed together with the target bicycles **1**—**4**.

Table 1. Cycloaddition of terminal 1,2-dienes to CHT

Entry	1,2-Diene	R	*E* : *Z**	Yield (%)
1	Hepta-1,2-diene	Bu	3 : 1	60
2	Nona-1,2-diene	C_6H_{13}	3 : 1	65
3	Phenylpropa-1,2-diene	Ph	10 : 1	81
4	Phenylbuta-1,2-diene	Bn	12 : 1	77

* Ratios of *E*- and *Z*-isomers (**1a**—**4a** and **1b**—**4b**) obtained were determined by chromatography (GLC) and ^{1}H NMR spectroscopy.

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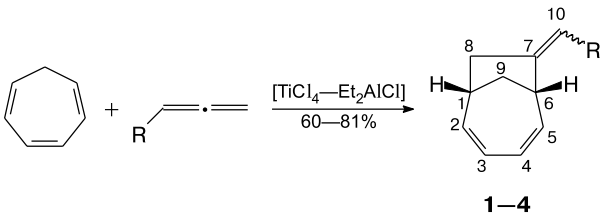
Scheme 2



R = Bu (**1**), C_6H_{13} (**2**), Ph (**3**), Bn (**4**)

The structures of compounds **1—4** were confirmed by single-dimensional (^{1}H, ^{13}C) and two-dimensional (COSY, NOESY, HSQC, HMBC) NMR spectroscopy. Thus, the ^{13}C NMR spectrum of compound **3** exhibits two sets of signals with relative intensities 10 : 1, which are related to the two isomers at the alkylidene C(7)=C(10) double bond with the *E*- and *Z*-orientation of the phenyl group in the side chain of molecules **3a** and **3b**. Signals for the main and minor isomers coincide with accuracy to 0.1—0.2 ppm with the known[11] resonances of *E*- and *Z*-isomers of 7-benzylidenebicyclo[4.2.1]nona-2,4-diene obtained earlier in the ratio 55 : 45.

Positions of the resonance lines for the allyl carbon atoms C(6) and C(8) are the indicative signals for determination of configuration of the C(7)=C(10) double bond, since in the case of steric shielding they are shifted to the high fields in the ^{13}C NMR spectrum: δ 43.92 (C(8), **3a**) contrary to δ 48.99 (C(8), **3b**) and δ 47.80 (C(6), **3a**) contrary to δ 42.03 (C(6), **3b**).

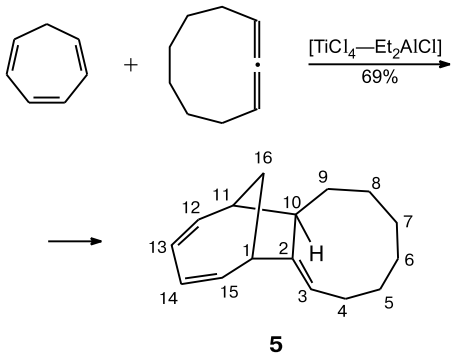
A high-field shielding of the methylene proton HC(6) (δ 3.50) for the main component of the mixture *E*-**3a** should be also noted, whereas in the spectrum of the minor product *Z*-**3b**, the signal for δHC(6) is found at δ 3.77; integral intensities of the signals observed confirm the ratio of isomers **3a** : **3b** = 10 : 1.

Benzylidene derivatives **4a** and **4b** show a decrease in the content of the minor component to the ratio **4a** : **4b** = 12 : 1, whereas in the case of cycloaddition of alkylallenes to CHT for bicycles **1a,b** and **2a,b**, a considerable change in the ratio in favor of *Z*-isomer was found (see Table 1).

When the methodology under study was extended to alicyclic allene, it was found that 1,3,5-cycloheptatriene can be involved into the reaction with 1,2-cyclononadiene under conditions given above with the formation of tricyclo[9.4.1.0^{2,10}]hexadeca-2(3),12,14-triene (**5**) in 69% yield (Scheme 3). The ^{1}H and ^{13}C NMR spectra of compound **5** exhibit a single set of signals each, whose proton spin system is related to the corresponding carbon atoms in the COSY, HSQC, and HMBC experiments.

Configuration of the annulated cyclononene fragment was established based on the spin-spin constant value $^3J_{H(9),H(10)}$ = 11 Hz, which corresponds to the *trans*-arrangement of the interacting protons.[13]

Scheme 3



The high-field shielding of the bridged carbon atom C(16) (δ 30.0) as compared to the chemical shifts for the corresponding bridged carbon atoms in compounds **1—4** indicates the *exo*-position of the C(9)—C(10) bond, whereas in the case of *endo*-addition, the signal for C(16) would have had the low-field value more than 32 ppm.[14,15]

The study of the main parameters of catalytic codimerization of CHT and 1,2-dienes showed that replacement of benzene with other aromatic or aliphatic solvents (for example, toluene, 1,2-dichlorobenzene, heptane, cyclohexane) has no considerable effect on the yields of codimers.

The temperature elevation and longer experiment time do not affect the ratio of *E*- and *Z*-isomers, but lead to a significant decrease in the yield of codimers, apparently, due to the side decomposition and polymerization processes.

In conclusion, catalytic codimerization of 1,3,5-cycloheptatriene with 1,2-dienes in the presence of the two-component catalytic system $TiCl_4$—Et_2AlCl proved an efficient method for the synthesis of substituted *endo*-bicyclo[4.2.1]nona-2,4-dienes.

Experimental

IR spectra were recorded on a Vertex 70V FTIR spectrometer (Bruker). Chromatographic analysis was performed on a Shimadzu GC-9A instrument using a 2000×2 mm column with the silicon SE-30 (5%) on Chromaton P-AW-HMDS (0.125—0.160 mm) as a stationary phase and helium as a carrier gas (30 mL min^{-1}), the temperature was programmed from 50 to 300 °C at the rate 8 °C min^{-1}. ^{1}H and ^{13}C spectra were recorded on a Bruker Avance-400 spectrometer (^{13}C, 100 MHz; ^{1}H, 400 MHz) in $CDCl_3$, chemical shifts are given with respect to the Me_4Si. MS-GLC analysis was performed on a Finnigan instrument (model 4021, a 50000×0.25 mm glass capillary column, the HP-5 as a stationary phase, helium as a carrier gas, the temperature was programmed from 50 to 300 °C at the rate 5 °C min^{-1}, the injector temperature was 280 °C, the temperature of the source of ions was 250 °C, EI, 70 eV). Elemental composition of the samples was determined on a Karlo Erba

analyzer (model 1106). The yields of the products were determined by GLC-analysis. Reactions of catalytic cycloaddition were carried out in the flow of dry argon. Ether solvents were distilled over $LiAlH_4$ just before use. Aromatic and aliphatic solvents were dried with Na. Commercially available Et_2AlCl (90%) (OAO Redkinskii Experimental Factory), $TiCl_4$, 1,3,5-cycloheptatriene (Aldrich) were used in the work. 1,2-Dienes were obtained according to the procedures described earlier.[16,17]

Cycloaddition 1,2-dienes to 1,3,5-cycloheptatriene (general procedure). 1,3,5-Cycloheptatriene (10 mmol), 1,2-diene (11 mmol), Et_2AlCl, (2 mmol), benzene (1 mL), and anhydrous benzene (3 mL) were placed into a thermostated (~0 °C) glass tube under dry argon. The tube was cooled to the temperature of liquid nitrogen, followed by addition of $TiCl_4$ (0.1 mmol) in benzene (1 mL)) and sealing. After heating at 80 °C for 8 h, the tube was unsealed, the content was diluted with CH_2Cl_2 and poured into water. The organic layer was washed with $NaHCO_3$ and dried with $MgSO_4$. The light solvents were evaporated *in vacuo*, the residue was subjected to column chromatography on SiO_2 (eluent: cyclohexane, 100%) to separate the mixture of *E*- and *Z*-isomers from the minor by-products of the reaction.

7-Pentylidenebicyclo[4.2.1]nona-2,4-diene (1a,b) (*E* : *Z* = = 3 : 1), R_f = 0.64. IR, ν/cm^{-1}: 3010, 2925, 2858, 1732, 1675, 1598, 1458, 1379, 987, 890, 750, 720. ^{1}H NMR, δ: 0.91 (t, 3 H, Me, *J* = 7 Hz); 1.16—1.25 (m, 4 H, CH_2); 1.31—1.33 (m, 1 H, C(11)H$_2$); 1.92—1.94 (m, 1 H, C(11)H$_2$); 1.93 (d, 1 H, C(9)H$_2$, *J* = 12 Hz); 2.21 (dt, 1 H, C(9)H$_2$, J_d = 12 Hz, J_t = 7 Hz); 2.46 (dd, 1 H, C(8)H$_2$, *J* = 7 Hz); 2.54 (d, 1 H, C(8)H$_2$, *J* = 16 Hz); 2.77 (q, C(1)H, *J* = 8 Hz); (*E*) 3.29—3.31 (m, 1 H, C(6)H); (*Z*) 3.42—3.44 (m, 1 H, C(6)H); 5.15 (t, 1 H, C(10)H, *J* = 7 Hz); 5.60—5.62 (m, 2 H, C(3)H, C(4)H); 6.04—6.07 (m, 2 H, C(2), C(5)H). ^{13}C NMR, δ: (*E*): 14.08 (C(14)), 22.63 (C(13)), 31.73 (C(12)), 32.19 (C(9)), 32.14 (C(11)), 38.56 (C(1)), 42.24 (C(8)), 45.46 (C(6)), 120.92 (C(10)), 123.09 (C(4)), 123.47 (C(3)), 138.2 (C(5)), 138.80 (C(2)), 151.31 (C(7)); (*Z*): 14.08 (C(14)), 22.63 (C(13)), 31.53 (C(11)), 31.73 (C(12)), 32.91 (C(9)), 39.16 (C(1)), 47.31 (C(8)), 43.13 (C(6)), 118.98 (C(10)), 123.64 (C(4)), 124.30 (C(3)), 136.67 (C(5)), 137.93 (C(2)), 149.52 (C(7)). MS, *m*/*z* (I_{rel} (%)): 188 [M]$^+$ (31), 145 (37), 131 (48), 117 (62), 105 (19), 91 (100), 77 (21), 67 (23). Found (%): C, 89.15; H, 10.69. $C_{14}H_{20}$. Calculated (%): C, 89.29; H, 10.71.

7-Heptylidenebicyclo[4.2.1]nona-2,4-diene (2a,b) (*E* : *Z* = = 3 : 1), R_f = 0.62. IR, ν/cm^{-1}: 3015, 2925, 2855, 1732, 1671, 1599, 1458, 1377, 987, 890, 752, 720. ^{1}H NMR, δ: 0.9 (t, 3 H, Me, *J* = 7 Hz); 1.18—1.29 (m, 8 H, CH_2); 1.30—1.32 (m, 1 H, C(11)H$_2$); 1.91—1.92 (m, 1 H, C(11)H$_2$); 1.94 (d, 1 H, C(9)H$_2$, *J* = 12 Hz); 2.22 (dt, 1 H, C(9)H$_2$, J_d = 12 Hz, J_t = 7 Hz); 2.46 (dd, 1 H, C(8)H$_2$, *J* = 7 Hz); 2.56 (d, 1 H, C(8)H$_2$, *J* = 16 Hz); 2.75 (q, C(1)H, *J* = 8 Hz); (*E*) 3.27—3.29 (m, 1 H, C(6)H); (*Z*) 3.41—3.42 (m, 1 H, C(6)H); 5.14 (t, 1 H, C(10)H, *J* = 7 Hz); 5.60—5.63 (m, 2 H, C(3)H, C(4)H); 6.01—6.02 (m, 2 H, C(2)H, C(5)H). ^{13}C NMR, δ: (*E*): 14.09 (C(16)), 22.66 (C(15)), 29.40 (C(13)), 29.46 (C(12)), 31.78 (C(14)), 32.18 (C(9), C(11)), 38.59 (C(1)), 42.24 (C(8)), 45.47 (C(6)), 120.93 (C(10)), 123.09 (C(4)), 123.47 (C(3)), 138.2 (C(5)), 138.80 (C(2)), 151.3 (C(7)); (*Z*): 14.09 (C(16)), 22.66 (C(15)), 29.40 (C(13)), 29.46 (C(12)), 31.51 (C(11)), 31.78 (C(14)), 32.93 (C(9)), 39.18 (C(1)), 47.30 (C(8)), 43.11 (C(6)), 118.95 (C(10)), 123.64 (C(4)), 124.30 (C(3)), 136.67 (C(5)), 137.93 (C(2)), 149.50 (C(7)). MS, *m*/*z* (I_{rel} (%)): 216 [M]$^+$ (23), 175 (22), 145 (41), 131 (42), 117 (68), 105 (23), 91 (100), 79 (23), 67 (23). Found (%): C, 88.76; H, 11.16. $C_{16}H_{24}$. Calculated (%): C, 88.82; H, 11.18.

7-Benzylidenebicyclo[4.2.1]nona-2,4-diene (3a,b) (*E* : *Z* = = 10 : 1), R_f = 0.53. IR, ν/cm^{-1}: 3022, 2928, 2248, 1946, 1722, 1681, 1598, 1493, 1448, 1317, 910, 733, 698, 649, 599, 515. ^{1}H NMR, δ: 2.03 (d, 1 H, C(9)H$_2$, *J* = 12 Hz); 2.31 (dt, 1 H, C(9)H$_2$, J_d = 12 Hz, J_t = 7 Hz); 2.81—2.83 (m, 1 H, C(8)H$_2$); 2.85—2.88 (m, C(1)H); 3.00 (d, 1 H, C(8)H$_2$, *J* = 16 Hz); (*E*) 3.49—3.51 (m, 1 H, C(6)H); (*Z*) 3.69—3.72 (m, 1 H, C(6)H); 5.66—5.69 (m, 2 H, C(3)H, C(4)H); 6.05—6.06 (m, 2 H, C(2)H, C(5)H); 6.25 (s, 1 H, C(10)H), 7.18—7.37 (m, 5 H, Ph). ^{13}C NMR, δ: (*E*): 31.25 (C(9)), 39.22 (C(1)), 43.92 (C(8)), 47.80 (C(6)), 120.81 (C(10)), 123.69 (C(4)), 123.87 (C(3)), 125.84 (C(14)), 128.14 (C(12), C(16)), 128.16 (C(13), C(15)), 137.09 (C(5)), 138.45 (C(11)), 138.80 (C(2)), 154.31 (C(7)); (*Z*): 33.47 (C(9)), 37.43 (C(1)), 42.03 (C(6)), 48.99 (C(8)), 120.73 (C(10)), 124.40 (C(4)), 123.87 (C(3)), 125.84 (C(14)), 127.59 (C(12)), 128.14 (C(16)), 128.16 (C(13), C(15)), 134.86 (C(5)), 138.35 (C(11)), 138.42 (C(2)), 152.16 (C(7)). MS, *m*/*z* (I_{rel} (%)): 208 [M]$^+$ (89), 193 (30), 179 (29), 167 (44), 154 (25), 129 (45), 117 (99), 115 (96), 91 (100), 89 (26), 77 (21), 65 (18). Found (%): C, 92.09; H, 7.75. $C_{16}H_{16}$. Calculated (%): C, 92.26; H, 7.74.

7-(2-Phenylethylidene)bicyclo[4.2.1]nona-2,4-diene (4a,b) (*E* : *Z* = 12 : 1), R_f = 0.49. IR, ν/cm^{-1}: 3025, 2931, 2248, 1949, 1723, 1681, 1596, 1493, 1448, 1319, 910, 735, 698, 652, 599, 518. ^{1}H NMR, δ: 2.03 (d, 1 H, C(9)H$_2$, *J* = 12 Hz); 2.32 (dt, 1 H, C(9)H$_2$, J_d = 12 Hz, J_t = 7 Hz); 2.61 (dd, 1 H, C(8)H$_2$, *J* = 17 Hz, *J* = 7 Hz); 2.78 (d, 1 H, C(8)H$_2$, *J* = 17 Hz); 2.87 (t, C(1)H, *J* = 8 Hz); 3.34 (d, 1 H, C(11)H$_2$, *J* = 7 Hz); (*E*) 3.39—3.41 (m, 1 H, C(6)H); (*Z*) 3.60—3.62 (m, 1 H, C(6)H); 5.40 (t, 1 H, C(10)H, *J* = 7 Hz); 5.68—5.74 (m, 2 H, C(3), C(4)H); 6.04—6.09 (m, 2 H, C(2)H, C(5)H); 7.21—7.34 (m, 5 H, Ph). ^{13}C NMR, δ: (*E*): 32.24 (C(9)), 35.69 (C(11)), 38.64 (C(1)), 42.45 (C(8)), 45.44 (C(6)), 119.31 (C(10)), 123.41 (C(4)), 123.66 (C(3)), 125.80 (C(15)), 128.32 (C(13), C(17)), 128.37 (C(14), C(16)), 137.90 (C(5)), 138.71 (C(2)), 141.36 (C(12)), 152.48 (C(7)); (*Z*): 33.00 (C(9)), 35.05 (C(11)), 37.69 (C(1)), 41.37 (C(6)), 47.40 (C(8)), 119.45 (C(10)), 123.55 (C(4)), 123.75 (C(3)), 125.86 (C(15)), 127.20 (C(13), C(17)), 128.37 (C(14), C(16)), 136.20 (C(5)), 138.02 (C(2)), 140.39 (C(12)), 150.74 (C(7)). MS, *m*/*z* (I_{rel} (%)): 222 [M]$^+$ (39), 193 (6), 181 (100), 179 (12), 167 (16), 153 (8), 131 (53), 129 (40), 115 (22), 91 (87), 77 (13), 65 (13). Found (%): C, 91.73; H, 8.13. $C_{17}H_{18}$. Calculated (%): C, 91.84; H, 8.16.

Tricyclo[9.4.1.0^{2,10}]hexadeca-2,12,14-triene (5), n_D^{20} 1.5479, R_f = 0.59. IR, ν/cm^{-1}: 3014, 2922, 2863, 1727, 1682, 1449, 1293, 1018, 982, 718, 699. ^{1}H NMR, δ: 1.28—1.59 (m, 8 H, CH_2); 1.37—1.38 (m, 1 H, C(9)H$_2$); 1.61—1.63 (m, 1 H, C(9)H$_2$); 1.86 (d, 1 H, C(16)H$_2$, *J* = 12 Hz); 2.11—2.13 (m, 1 H, C(4)H$_2$); 2.24—2.26 (m, 1 H, C(4)H$_2$); 2.33—2.35 (m, 1 H, C(1)H); 2.43 (dt, 1 H, C(16)H$_2$, J_d = 12 Hz, J_t = 7 Hz); 2.87 (d, 1 H, C(10)H, *J* = 11 Hz); 3.50 (t, 1 H, C(11)H); 5.22 (q, 1 H, C(3)H, *J* = 6 Hz); 5.60—5.62 (m, 1 H, C(13)H); 5.64—5.66 (m, 1 H, C(14)H); 5.97—5.99 (m, 1 H, C(15)H); 6.16—6.18 (m, 1 H, C(12)H). ^{13}C NMR, δ: 21.5 (C(8)), 27.6 (C(6)), 27.7 (C(7)), 29.2 (C(4)), 30.0 (C(16)), 30.5 (C(5)), 33.84 (C(9)), 43.57 (C(11)), 50.26 (C(1)), 58.76 (C(10)), 123.01 (C(3)), 123.25 (C(13), C(14)), 137.62 (C(15)), 139.82 (C(12)), 155.94 (C(2)). MS, *m*/*z* (I_{rel} (%)): 214 [M]$^+$ (39), 157 (11), 143 (24), 129 (53), 117 (80), 104 (19), 91 (100), 79 (28), 67 (18). Found (%): C, 89.59; H, 10.36. $C_{16}H_{22}$. Calculated (%): C, 89.65; H, 10.35.

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