Titanium-catalyzed cyclocodimerization of cyclohepta-1,3,5-triene with spiro[cyclopropane-1,7´-norborna-2,5-diene]

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Titanium complexes-catalyzed codimerization of cyclohepta-1,3,5-triene with spiro[cyclopropane-1,7´-norborna-2,5-diene] affords 14-spirocyclopropylhexacyclo[6.5.1.$0^{2,7}$.$0^{3,12}$.$0^{6,10}$.$0^{9,13}$]-tetradec-4-ene and 6-spirocyclopropylpentacyclo[7.5.0.$0^{2,7}$.$0^{3,5}$.$0^{4,8}$]tetradeca-10,12-diene in total yields higher than 80%.

Key words: cyclohepta-1,3,5-triene, metal complex catalysis, norborna-2,5-diene, polycyclic compounds, spiro compounds.

An increased interest in strained polycyclic hydrocarbons is due to their structural features and also wide use as efficient medical and agricultural remedies and in the synthesis of unique polymer materials and products of special design with enormous characteristics.[1—3]

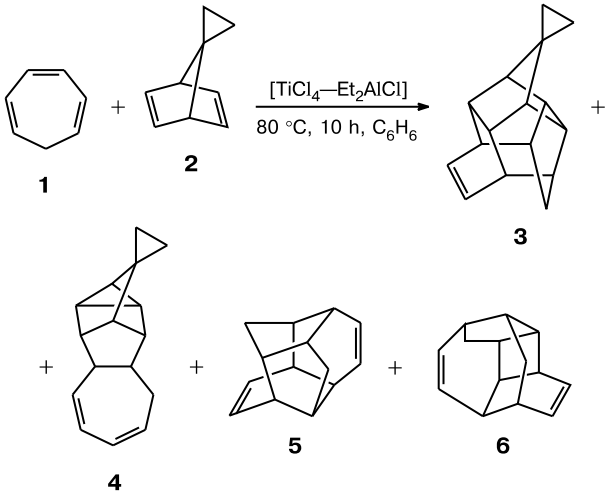
In our opinion, one of the promising monomers for synthesis of strained cage hydrocarbons is cyclohepta-1,3,5-triene (**1**). Thermal and catalytic dimerization of cycloheptatriene **1** with acetylenes, norbornadiene, nitriles, and 1,3-dienes affording rare strained polycycles are rather well studied.[4—7] At the same time, there are no literature data on the influence of the structure of the starting monomers on the direction and structural selectivity of these reactions, as well as the possibility to synthesize codimers of cycloheptatriene **1** with the norbornadiene derivative containing the spirocyclopropane fragment.

In the present work, we aimed at revealing the possibility to synthesize strained polycyclic hydrocarbons of new types and studied the reaction of cycloheptatriene **1** with spiro[cyclopropane-1,7´-norborna-2,5-diene] (**2**).

Interaction of equimolar amounts of compounds **1** and **2** in the presence of $TiCl_4$—Et_2AlCl as the catalyst in benzene at 80 °C for 10 h affords 14-spirocyclopropylhexacyclo[6.5.1.$0^{2,7}$.$0^{3,12}$.$0^{6,10}$.$0^{9,13}$]tetradec-4-ene (**3**) and 6-spirocyclopropylpentacyclo[7.5.0.$0^{2,7}$.$0^{3,5}$.$0^{4,8}$]-tetradeca-10,12-diene (**4**) in equal amounts in a total yield of 82% (Scheme 1). Products **3** and **4** were isolated in the individual state by column chromatography (SiO_2, hexane—benzene (3 : 1) as eluent). Compounds **5** and **6** (homodimers of cycloheptatriene **1**)[4] are also formed in minor amounts (at most 5%).

For compounds **3** and **4**, 1D (^{1}H, ^{13}C, Dept 135°) and 2D (HH COSY, HSQC, HMBC) NMR experiments were carried out. Their structures were additionally confirmed

Scheme 1



by the comparison of their spectral characteristics of the known[7] prototypes: hexacyclo[6.5.1.$0^{2,7}$.$0^{3,12}$.$0^{6,10}$.$0^{9,13}$]-tetradec-4-ene and pentacyclo[7.5.0.$0^{2,7}$.$0^{3,5}$.$0^{4,8}$]tetradeca-10,12-diene synthesized from cycloheptatriene **1** and norborna-2,5-diene.

The presence of spirocyclopropane fragments in the structure of polycycles **3** and **4** is unambiguously confirmed by the characteristic upfield proton AA´BB´ systems (δH = 0.32—0.53 and 0.27—0.56) in the ^{1}H NMR spectra and by the upfield signals in the ^{13}C NMR spectra (δC = 4.97 (CH_2), 5.01 (CH_2), 19.3 (C) and δC = 4.96 (CH_2), 5.66 (CH_2), 23.8 (C)) for compounds **3** and **4**, respectively.

In order to reveal the main regularities of cyclocodimerization of compounds **1** and **2**, we studied the

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Table 1. Influence of the temperature (*T*), reaction duration (*t*), and nature of the solvent and reducing agent on the yield and ratio of codimers **3** and **4**

Reducing agent	Solvent	*t* /h	*T* /°C	Ratio **3** : **4**	Total yield of **3** and **4** (%)
Et_2AlCl	Benzene	10	80	1 : 1	82
	Toluene	10	80	1 : 1	75
	1,2-Dichloro-benzene	10	80	1 : 1	70
	Hexane	10	80	1 : 1	66
	Cyclo-hexane	10	80	1 : 1	50
	THF	10	80	—	—
	Benzene	6	80	1 : 1	71
	Benzene	14	80	1 : 1	82
	Benzene	10	40	1 : 1	19
	Benzene	10	60	1 : 1	33
Bu^i_2AlCl	Benzene	10	80	1 : 2	82
Bu^i_2AlH	Benzene	10	80	1 : 2	50
Bu^i_3Al	Benzene	10	80	1 : 4	85
Et_3Al	Benzene	10	80	1 : 4	80

Note. **1** : **2** : $TiCl_4$: reducing agent = 10 : 10 : 0.1 : 2, solvent (1 mL $mmol^{-1}$).

influence of the nature of the central atom of the catalyst, ligand environment, and the main parameters of the reaction (temperature and duration of experiment) on the yield and ratio of dimers **3** and **4** (Table 1).

It was found that $TiCl_4$ can successfully be replaced by $(Pr^iO)_2TiCl_2$ without considerable change in the composition or yield of the codimers. At the same time, the reaction does not occur when other titanium-based catalysts (Cp_2TiCl_2, $(Pr^iO)_4Ti$) or catalysts based on other transition metals ($ZrCl_4$, Cp_2ZrCl_2, $ZrOCl_2$, $NiCl_2$, $Ni(acac)_2$, $CoCl_2$, $Co(acac)_2$, $Co(acac)_3$, $Fe(acac)_3$) are applied, or in the absence of a catalyst.

The solvent exerts a substantial effect on the ratio of codimers (see Table 1). The nature of a reductant is also essential. For example, the best results were achieved when using Bu^i_2AlCl, Bu^i_2AlH, Bu^i_3Al, and Et_3Al. In the case of $EtAlCl_2$, $AlCl_3$, BuLi, BuMgBr, and $BF_3 \cdot Et_2O$, the yields of polycycles **3** and **4** did not exceed 10—15%. The temperature, duration of experiment, and solvent affect the total yield of the codimers but do not affect their ratio.

The results obtained are planned to use in future for the development of preparative methods of synthesis of polycyclic hydrocarbons by cycloaddition reactions involving cyclohepta-1,3,5-triene.

Experimental

Gas chromatography was carried out on a Chrom-5 instrument (column 1200×3 mm, stationary phase Silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm), helium as carrier gas (47 mL min^{-1})) with temperature programming from 50 to 250 °C with a rate of 8 °C min^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (100 (^{13}C) and 400 MHz (^1H)) in $CDCl_3$ relative to Me_4Si. GC-MS analysis of the compounds was performed on a Finnigan instrument (model 4021, glass capillary column 50 000×0.25 mm, stationary phase HP-5, helium as carrier gas, temperature programming from 50 to 300 °C with a rate of 5 °C min^{-1}, injector temperature 280 °C, ion source temperature 250 °C, 70 eV). Elemental analysis was carried out on a Karlo Erba instrument, model 1106. The yields of products were determined by GLC analysis. The reactions with organometallic compounds were carried out in a flow of dry argon. Prior to use ethereal solvents were distilled over $LiAlH_4$. Aromatic and aliphatic solvents were dried over sodium metal. Commercially available Et_3Al (98%), $EtAlCl_2$ (95%), Et_2AlCl (90%), Bu^iAlCl_2 (96%), Bu^i_2AlH (83%), Bu^i_3Al (92%) (joint-stock company "Redkinskii opytnyi zavod" (Redkino Experimental Plant), $AlCl_3$, Cp_2TiCl_2, $TiCl_4$, $(Pr^iO)_4Ti$, Cp_2ZrCl_2, and cyclohepta-1,3,5-triene (**1**) (Aldrich) were used. 7-Spirocyclopropylnorborna-2,5-diene (**2**) and $(Pr^iO)_2TiCl_2$ were synthesized by the procedures described earlier.[8,9]

Cyclocodimerization of cyclohepta-1,3,5-triene (1) and spiro[cyclopropane-1,7′-norborna-2,5-diene] (2) (general procedure). Cyclohepta-1,3,5-triene (**1**) (10 mmol), spiro[cyclopropane-1,7′-norborna-2,5-diene] (**2**) (10 mmol), a reducing agent (2 mmol) (*e.g.* Et_2AlCl) in benzene (1 mL) (see Table 1), and anhydrous benzene (3 mL) were loaded in a glass ampule, whose temperature was maintained at ~0 °C in an atmosphere of dry argon. The ampule was cooled at the temperature of liquid nitrogen, $TiCl_4$ (0.1 mmole in 1 mL of benzene) was loaded, and the ampule was sealed. After heating for 10 h at 80 °C, the ampule was opened and the contents was diluted with CH_2Cl_2 and poured in water. The organic layer was washed with $NaHCO_3$ and dried with $MgSO_4$. Light solvents were removed *in vacuo*, and the residue was chromatographed on a column with SiO_2 (hexane—benzene (3 : 1) mixture as eluent).

14-Spirocyclopropylhexacyclo[6.5.1.0^{2,7}.0^{3,12}.0^{6,10}.0^{9,13}]-tetradec-4-ene (3). M.p. 121—123 °C. IR, ν/cm^{-1}: 3050, 3015, 3000, 2930, 2850, 1760, 1745, 1600, 1450, 1430, 1340, 1310, 1200, 960, 850, 820, 790, 710, 680, 600, 510. ^1H NMR, δ: 0.27—0.56 (m, 4 H, AA′BB′ system, 2 CH_2); 1.16—1.34 (m, 2 H(11)); 1.50 (m, 2 H, H(2), H(7)); 2.15 (m, 2 H, H(9), H(13)); 2.20 (m, 2 H, H(10), H(12)); 2.65 (m, 2 H, H(3), H(6)); 2.72 (m, 2 H, H(1), H(8)); 6.01 (dd, 2 H, H(4), H(5), ^4J = 3 Hz, ^3J = 5 Hz). ^{13}C NMR, δ: 4.9 (C(2′)); 5.7 (C(3′)); 23.8 (C(14)); 34.9 (C(11)); 41.7 (C(10), C(12)); 42.7 (C(3), C(6)); 47.5 (C(9), C(13)); 49.4 (C(2), C(7)); 53.9 (C(1), C(8)); 130.6 (C(4), C(5)). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 210 $[M]^+$ (3), 195 (9), 181 (11), 167 (17), 155 (13), 143 (31), 129 (48), 117 (100), 105 (17), 91 (82), 77 (18). Found (%): C, 91.19; H, 8.59. $C_{16}H_{18}$. Calculated (%): C, 91.37; H, 8.63.

6-Spirocyclopropylpentacyclo[7.5.0.0^{2,7}.0^{3,5}.0^{4,8}]tetradeca-10,12-diene (4). n_D^{20} 1.5263. IR, ν/cm^{-1}: 3075, 3065, 3030, 2930, 1660, 1545, 1480, 1450, 1370, 1310, 1100, 1010, 960, 850, 840, 760, 710, 690, 650, 590, 530, 505. ^1H NMR, δ: 0.32—0.53 (m, 4 H, AA′BB′ system, 2 CH_2); 0.77 (t, 1 H, H(5), ^3J = 5 Hz); 1.10 (m, 2 H, H(2), H(8)); 1.22 (m, 1 H, H(4)); 1.29 (m, 1 H, H(3)); 2.17 (m, 1 H, H(9)); 2.18 (m, 1 H, H(14)); 2.30 (m, 1 H, H(14)); 2.69 (m, 1 H, H(1), H(7)); 5.87 (m, 1 H, H(13)); 5.93 (m, 1 H, H(11)); 6.10 (d, 1 H, H(10), J = 11.6 Hz); 6.14 (m, 1 H, H(12)). ^{13}C NMR, δ: 4.9 (C(2′)); 5.0 (C(3′)); 12.6 (C(4)); 13.4

(C(3)); 15.4 (C(5)); 19.3 (C(6)); 31.1 (C(14)); 42.6 (C(1)); 47.6 (C(2)); 49.5 (C(8)); 50.1 (C(9)); 55.9 (C(7)); 125.7 (C(12)); 128.1 (C(11)); 133.7 (C(13)); 136.8 (C(10)). MS (EI, 70 eV), m/z (I_{rel} (%)): 210 $[M]^+$ (91), 195 (15), 181 (29), 167 (23), 143 (72), 129 (100), 117 (96), 91 (92), 77 (24). Found (%): C, 91.21; H, 8.69. $C_{16}H_{18}$. Calculated (%): C, 91.37; H, 8.63.

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