Codimerization of quadricyclane with *endo,exo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradec-12-ene catalyzed by the $Pd(PPh_3)_4$ complex

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endo,exo-Hexacyclo[9.2.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradec-12-ene (**1**) undergoes cyclocodimerization with quadricyclane (Q) in the presence of the $Pd(PPh_3)_4$ complex to give *exo,exo,endo,exo*-decacyclo[9.9.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,20}$.$0^{13,18}$.$0^{14,16}$.$0^{15,19}$]heneicosane (**2**) and *endo,exo,endo,exo*-decacyclo[9.9.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,20}$.$0^{13,18}$.$0^{14,16}$.$0^{15,19}$]heneicosane (**3**) in a ratio of 10 : 7 (yield up to 26 %). Simultaneously, homocyclotrimerization of Q occurs to give three known C_{21} hydrocarbons (**4—6**). The yields of compounds **2** and **3** and the selectivity of the process depend considerably on the reaction conditions and the molar ratio of **1** and Q. Compounds **2** and **3** that were obtained were characterized by ^{13}C NMR spectra.

Key words: synthesis, metallocomplex catalysis, palladium, polycyclic strained hydrocarbons.

Polycyclic strained C_{21} hydrocarbons of the norbornane series, trimers of norbornadiene (NBD), are usually synthesized either by homocyclotrimerization of NBD or its valence isomer quadricyclane (Q) or by codimerization of NBD and Q with stereoisomeric [2π+2π]- and [2π+2π+2π]-dimers of NBD in the presence of homogeneous metallocomplex catalysts.[1—7] By the start of the present study, we were aware that codimerization of NBD and Q with four of the seven unsaturated NBD dimers had been performed,[2—7] whereas the other three NBD dimers, whose common feature is the presence of a bulky *endo*-substituent, including *endo,exo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradec-12-ene (**1**), could not be involved in codimerization with NBD or Q.

To obtain new types of polycyclic strained hydrocarbons and to develop highly active metallocomplex catalysts that would be able to provide selective codimerization of Q with [2π+2π+2π]-dimers of NBD, we studied codimerization of dimer **1** with Q in the presence of the zero-valence palladium complex $Pd(PPh_3)_4$. This complex, after being exposed to air for 1—2 h, displays high activity toward codimerization of compound **1** with Q.

Due to the occurrence of the competing reaction of homocyclotrimerization of Q, the composition of the reaction mixture is rather complex. It contains two new

Scheme 1

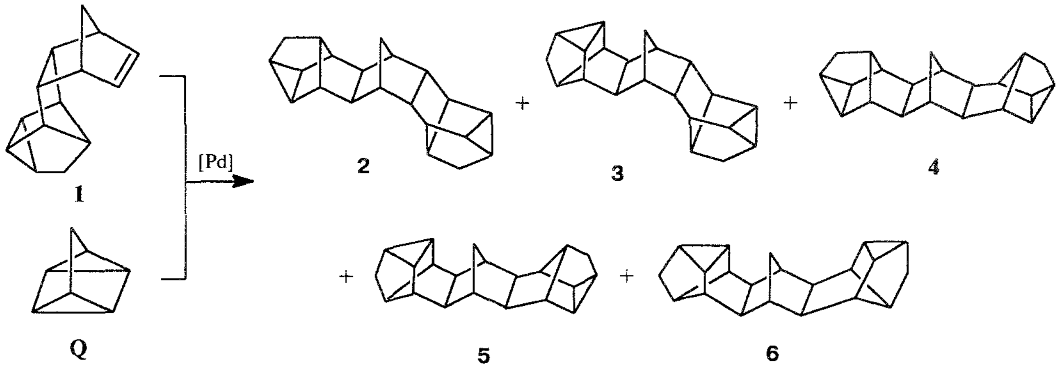

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Table 1. Dependence of the yield and isomeric composition of norbornadiene trimers on the reaction conditions ([Pd] : [Q] = 1 : 100, in toluene, $Pd(PPh_3)_4$ as catalyst)

T/°C	τ/h	Q : (1)	Yield (%)	
		mol : mol	**2—6**	**2, 3**
70	6	1 : 1	10	3
70	6	1 : 2	29	11
70	6	1 : 3	51	20
100	6	1 : 1	17	7
100	10	1 : 1	19	8
100	6	1 : 2	46	18
100	6	1 : 3	67	26
120	6	1 : 3	64	19

Note. T, reaction temperature; τ, reaction time.

trimers (**2**, **3**) formed by codimerization of **1** with Q, along with three C_{21} hydrocarbons (**4**—**6**) known to be products of the homocyclotrimerization of Q.[7]

The selectivity of the process and the yields of trimers **2** and **3** are primarily determined by the molar ratio of Q and **1** and by the reaction conditions (see Table 1).

According to data of capillary gas chromatography and ^{13}C NMR spectroscopy, the codimers of Q with **1** are represented by two isomers (**2** and **3**), whose ratio does not change from one experiment to another and equals 10 : 7. The structures of trimers **2** and **3** were determined by analyzing the ^{13}C NMR spectra and by comparing the latter with those available in the literature for dimers and trimers of NBD incorporating similar structural moieties.[6,7] In particular, a set of signals in the spectrum of compound **2**, namely, δ 16.96 (C(14), C(15)), 11.68 (C(16)), 29.81 (C(17)), 38.88 (C(18)), indicates that a molecule of this trimer incorporates an *exo*-disubstituted tetracyclo[4.3.$0^{2,4}$.$0^{3,7}$]nonane moiety,[6,7] which allows us to assign an *exo,exo,endo,exo*-configuration to this compound. The ^{13}C NMR spectrum of trimer **3** displays a group of signals (13.48 (C(14), C(15)), 17.16 (C(16)), 28.22 (C(17)), 44.20 C(18)) typical of an *endo*-disubstituted tetracyclo[4.3.$0^{2,4}$.$0^{3,7}$]nonane fragment, which provides reasons to attribute it to the *endo,exo,endo,exo*-series.

Trimers **2** and **3** were characterized as a mixture, since our attempts to isolate them in the pure state by GLC and HPLC were unsuccessful.

Experimental

Quadricyclane and dimer 1 were obtained by well-known procedures.[10,11] The $Pd(PPh_3)_4$ complex was synthesized according to a procedure described previously.[12] The ^{13}C NMR spectrum was recorded on a Jeol FX-90Q spectrometer (22.5 MHz) in $CDCl_3$ with Me_4Si as the standard. Chromatographic analyses were carried out on a Chrom 5 chromatograph equipped with a 50 m × 0.2 mm capillary column with an SE-30 phase in a stream of helium (40 mL min^{-1}) and an evaporator temperature of 300 °C. The temperature was varied from 100 to 300 °C, and the heating rate was 6 deg min^{-1}. The retention times were: **2**, 23.02 min; **3**, 23.5 min; **4**—**6**, 24.12—24.20 min.

Codimerization of quadricyclane with *endo,exo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradec-12-ene (1). Compound Q (0.16 g, 1.72 mmol) was added at ~20 °C to dimer **1** (0.32 g, 1.73 mmol) and $Pd(PPh_3)_4$ (0.02 g, 0.017 mmol) in toluene (1 mL), and the mixture was heated at 70—120 °C for 6—10 h. The reaction mixture was cooled and passed through Al_2O_3, the solvent was evaporated, and the residue was distilled *in vacuo*.

***exo,exo,endo,exo*-Decacyclo[9.9.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,20}$.$0^{13,18}$.$0^{14,16}$.$0^{15,19}$]heneicosane (2).** ^{13}C NMR, δ: 41.88 (d, C(1), C(11)); 49.98 (d, C(2), C(10)); 42,86 (d, C(3), C(9)); 18.58 (d, C(4), C(5)); 13.64 (d, C(6)); 33.84 (t, C(7)); 38.77 (d, C(8)); 47.84 (d, C(12), C(20)); 46.53 (d, C(13), C(19)); 16.96 (d, C(14), C(15)); 11.68 (d, C(16)); 29.81 (t, C(17)); 38.88 (d, C(18)); 38.88 (t, C(21)).

***endo,exo,endo,exo*-Decacyclo[9.9.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,20}$.$0^{13,18}$.$0^{14,16}$.$0^{15,19}$]heneicosane (3).** ^{13}C NMR, δ: 40.55 (d, C(1), C(11)); 50.96 (d, C(2), C(10)); 42.81 (d, C(3), C(9)); 18.64 (d, C(4), C(5)); 13.64 (d, C(6)); 33.84 (t, C(7)); 38.42 (d, C(8)); 42.81 (d, C(12), C(20)); 47.49 (d, C(13), C(19)); 13.48 (d, C(14), C(15)); 17.16 (d, C(16)); 28.22 (t, C(17)); 44.03 (d, C(18)); 43.28 (t, C(21)).

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