# SYNTHESIS OF NEW TYPES OF STRAINED HYDROCARBONS BY CYCLO-CODIMERIZATION OF QUADRICYCLANE WITH NORBORNENES AND THEIR DERIVATIVES, CATALYZED BY PALLADIUM COMPLEXES

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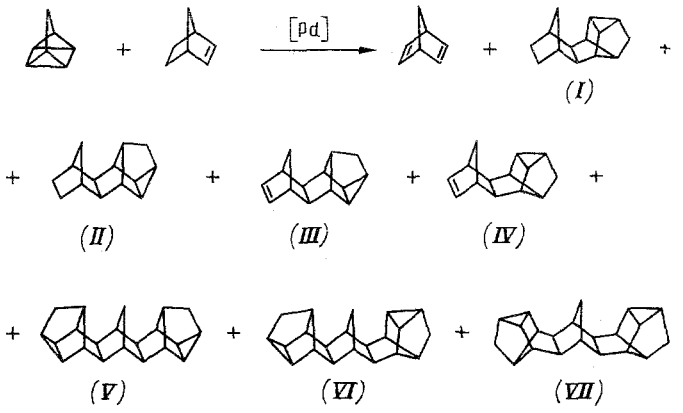
The codimerization of quadricyclane (QC), the valence isomer of norbornadiene (NBD), with norbornene compounds was studied in the presence of Pd(0) complexes. Codimerization of QC with norbornene, 5-methyl- and 5-methylenenorbornene, exo-tricyclo[3.2.1.$0^{2,4}$]octene-6, tetracyclo[4.2.0.$0^{2,4}$.$0^{3,7}$]nonene-8, and penta- and hexacyclic NBD dimers was carried out in the presence of $PPh_3$-activated $Pd_2(DBA)_3 \cdot CHCl_3$ to afford a new class of hexa- to nonacyclic strained hydrocarbons with exo- and endo-tetracyclo[4.2.0.$0^{2,4}$.$0^{3,7}$]nonane fragments.

Recently we carried out homo-, di-, and trimerization of quadricyclane (QC), the valence isomer of norbornadiene (NBD), into polycyclic $C_{14}$-$C_{21}$ hydrocarbons in the presence of Pd complexes [1]. We proposed [1] that these types of compounds are formed as a result of cyclocodimerization of QC with NBD or its dimers, which are formed in the course of the reaction.

In order to confirm this hypothesis, and also to investigate the possibility of cyclocodimerization of QC with norbornenes of various structures and the synthesis of new types of strained polycyclic hydrocarbons, we studied the catalytic reaction of QC with cycloolefins (VIII)-(XVII) in the presence of the complex $Pd_2(DBA)_3 \cdot CHCl_3$–$PPh_3$ (DBA = dibenzylideneacetone), which is widely used in cycloaddition processes.

Thus, norbornene (NB) and QC, in the presence of $Pd_2(DBA)_3 \cdot CHCl_3$–$PPh_3$ ($C_6H_6$, 20°C, 5 h), form two codimers (I) and (II) in a ratio of 56:44 with an overall yield of ~28%, along with the known dimers (III) and (IV) and NBD or QC trimers (V)-(VII) [1]. Under these reaction conditions, a part of the QC (up to 5%) is converted to NBD.




The yield of compounds (I)-(VII) depends on the activator ligand, the reaction conditions, and the molar ratio of NB to QC and Pd(0) to ligand. $PPh_3$ is the most effective activator ligand in this reaction. When the $PPh_3$ concentration of the catalyst is increased ($PPh_3$:Pd(0) ≥ 1-4), the proportion of codimers (I) and (II) increases to ~40%; however, the

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TABLE 1. Effect of the Molar Ratio of Norbornene to Quadricyclane on the Composition of Reaction Products ($Pd_2(DBA)_3 \cdot CHCl_3$–$PPh_3$ = 1:2, 60°C, 2 h, toluene, QC:Pd(0) = 100:1)

| NB:QC | Overall yield* of (I)-(VII), % | Composition, % | | |
|---|---|---|---|---|
| | | ((I)+(II)) | ((III)+(IV)) | ((V)+(VI)+(VII)) |
| † | 96 | 0 | 84 | 16 |
| 1 | 97 | 5 | 90 | 5 |
| 2 | 97 | 17 | 81 | 2 |
| 3 | 98 | 28 | 71 | 1 |
| 4 | 97 | 40 | 59 | 1 |

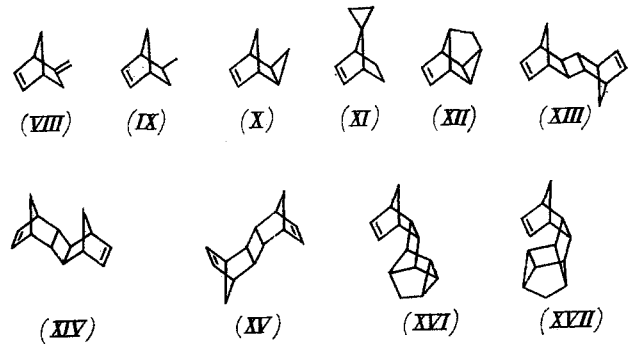
*Calculated on the basis of reacted QC, whose conversion reached ~100%.
†100% NB.

reaction rate (determined from the consumption of QC) decreases fivefold, and the isomeric composition of (I) and (II) and (V)-(VII) remains unchanged. At a $PPh_3$:Pd(0) ratio of 2:1 the conversion of QC reaches ~100%. Increasing the codimerization temperature to 60°C shortens the reaction time to 2 h. Changing the solvent (toluene, benzene, THF, $CHCl_3$) has almost no effect on the process. The selectivity of the reaction with respect to codimers increases with an increase in the NB concentration, reaching 40% at a NB:QC ratio of 4:1 (Table 1).

It should be noted that addition of MeCN or DMSO to the catalyst results in selective isomerization of QC to NBD. Addition of $P(OPh)_3$ and duroquinone almost completely deactivates the catalyst.

As seen from Table 1, an increase in the NB concentration leads primarily to the formation of codimers (I) and (II). At a fourfold excess of NB over QC, the overall yield of hydrocarbons (I) and (II) is 40%.

Next we studied under optimal conditions the codimerization of QC with 5-methylenenorbornene-2 (VIII), 5-methylnorbornene-2 (IX), exo-tricyclo[3.2.1.$0^{2,4}$]octene-6 (X), 7-spirocyclopropanenorbornene-2 (XI), tetracyclo[4.2.0.$0^{2,4}$.$0^{3,7}$]nonene-8 (XII), and penta- and hexacyclic norbornene dimers (III), (IV), and (XIII)-(XVII) (Table 2).



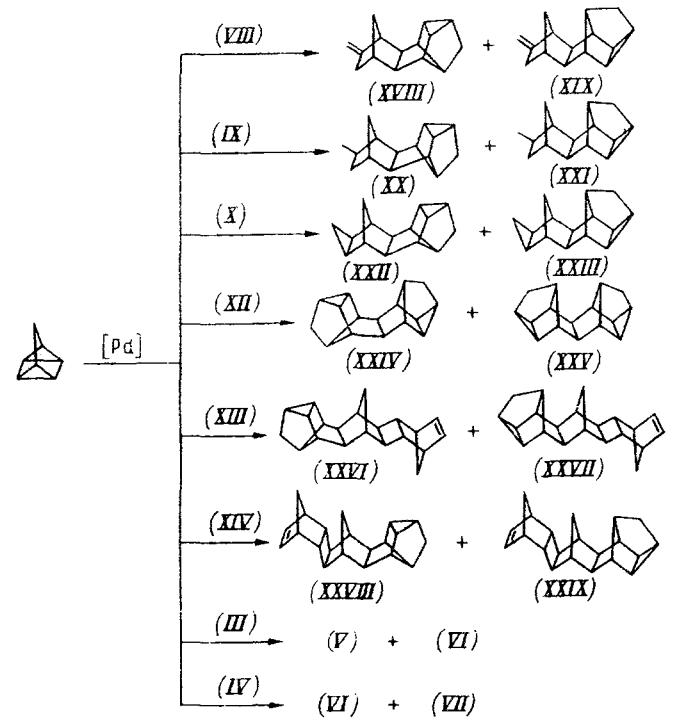

Compounds (XI) and (XV)-(XVII) with bulky exo and endo substituents are almost inert in the codimerization reaction with QC. The inertness of compound (XI) is readily explained by steric hindrance of the 7-spirocyclopropane group during exo attack on the norbornene double bond. The reason for the low reactivity of compounds (XV)-(XVII) (they form codimers only in trace amounts), whose endo substituents are sufficiently removed from the double bond, is as yet unclear. The high reactivity of the norbornene bond and its availability for attack in chemical reactions only from the exo direction is due to nonplanar deformation of the olefin bond, as a result of which the olefin protons are bent by 6° out of the plane of the double bond [2]. Apparently, the bulky 5,6-endo substituents of norbornenes hinder such proton deflection from a distance, which decreases the activity of the norbornene double bond in the basic state and increases the activation energy in the transition complex.

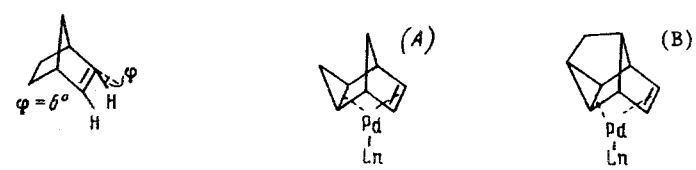
TABLE 2. Codimerization of Norbornene Compounds with Quadricyclane (QC)

| Norbornene substrate (NBS) | NBS conversion*, % | Codimer yield and composition,* % | Yield, % | | |
|---|---|---|---|---|---|
| | | | NBD | (III)+(IV)† | (V)+(VII) |
| (VIII) | 28 | (XVIII), 14; (XIX), 10 | 4 | 69 | 3 |
| (IX) | 37 | (XX), 18; (XXI), 15 | 3 | 62 | 2 |
| (X) (60°, 5 h) | 62 | (XXII), 32; (XXIII), 26 | 1 | 41 | – |
| (X) (6°, 1 h) | 51 | (XXII), 29; (XXIII), 21 | – | 31 | – |
| (XII) (60°, 0.5 h) | 55 | (XXIV), 30; (XXV), 22 | 3 | 38 | 3 |
| (XII) (6°, 1 h) | 49 | (XXIV), 29; (XXV), 18 | 4 | 20 | 3 |
| (XIII) ‡ | 38 | (XXVI), 18; (XXVII), 15 | 3 | 63 | 1 |
| (XIV) ‡ | 26 | (XXVIII), 16; (XXIX), 8 | 3 | 64 | 4 |
| (III) ‡ | – | (V), 23; (VI), 7 | 4 | 61(III) | 1(VII) |
| (IV) ‡ | – | (VI), 6; (VII), 26 | 4 | 59(IV) | 2(VI) |

*Conversion of QC was 100% in all experiments; the codimer yield is calculated per reacted QC.
†The ratio (III):(IV) = 56.44.
‡The experiments were carried out at 60°C (2 h) in toluene.

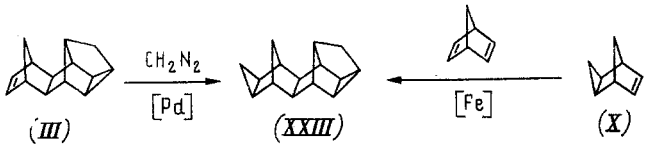
On the other hand, compounds (X) and (XII), which have a cyclopropane ring in conjugation with the double bond, were very active in codimerization with QC. These olefins readily participate in codimerization with QC even at 6°C, forming codimers (XXII)-(XXV), whereas monomers (VIII), (IX), (XIII), and (XIV) react with QC only at a higher temperature (60°C).




The presence of a double bond and a cyclopropane fragment in compounds (X) and (XII) increases their coordination capacity at the central catalyst atom. This leads to the formation of chelate complexes A or B during the course of cyclocodimerization, which actively participate in the reaction with QC.

The structure of the synthesized compounds was determined by physicochemical methods and also by comparing their characteristics with those of known samples prepared according to the methods described in [1, 3-5]. The structure of compound (XXIII) was verified by countersynthesis according to two methods: 1) cyclopropanation of NBD dimer (III) with $CH_2N_2$ in the presence of $Pd(OAc)_2$, and 2) codimerization of (X) with NBD in the presence of $Fe(acac)_3$–$(Ph_2PCH_2–)_2$–$AlEt_2Cl$ [3]. Both reactions are stereospecific and occur as exo additions.




Thus, codimerization of QC with norbornene hydrocarbons in the presence of palladium complexes is a fairly simple method for obtaining new types of hexa- to nonacyclic strained hydrocarbons with diverse structures.

## EXPERIMENTAL

$^1H$ and $^{13}C$ NMR spectra were recorded on Tesla BS-467 ($CCl_4$, TMS standard) and Jeol-FX-90Q (22.5 MHz, $CDCl_3$, relative to TMS) spectrometers. IR spectra were recorded on a UR-20 instrument (in a thin layer). GLC analysis was carried out on a Khrom-4 chromatograph with a flame-ionizing detector; 3.7 × 0.003 m (with 15% PEG-6000) and 2.4 × 0.003 m (with 5% SE-30) columns on Chromaton N-AW-HMDS; helium carrier gas (47 ml/min); vaporizer temperature, 275°C; temperature programmed from 50 to 210°C (to 300°C for trimers). The isomers were isolated by preparative HPLC, with phase inversion, on a ZhKh-1304 chromatograph equipped with a Varian Aerograf refractometric detector and a Zorbax ODS column, 21 × 250 mm; eluent, methanol (10 ml/min); 24°C.

Compounds (III), (IV), and (VIII)-(XVII) were obtained according to [6-10].

Codimerization of Quadricyclane with Norbornenes (general method). A 0.92-g (10 mmoles) portion of QC and 10-40 mmoles of norbornene compound were added to 0.112 g (0.108 mmole) $Pd_2(DBA)_3 \cdot CHCl_3$ [11] and 0.028 g (0.108 mmole) $PPh_3$ [or 0.108 mmole DMSO, duroquinone, acetonitrile, or $P(OPh)_3$] in toluene (benzene), and the mixture was heated for 0.5-5 h at 20-60°C. At the end of the reaction the solution was filtered through $Al_2O_3$ and eluted with hexane. The codimers were isolated by fractionation and high-performance LC.

12-Methylene-exo-endo-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane (XVIII); yield 14%; bp 108°C (1 mm). PMR spectrum (δ, ppm): 0.73-1.25 (4H), 1.53-2.08 (8H), 2.14 s (3H), 2.44 s (1H), 4.48 (1H), 4.79 (1H). IR spectrum (ν, $cm^{-1}$): 765, 790, 815, 890, 1300, 1665, 3040, 3065.

12-Methylene-exo-exo-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane (XIX); yield 10%; bp 109°C (1 mm). PMR spectrum (δ, ppm): 0.66-1.16 m (4H), 1.46 s (2H), 1.66-2.00 m (7H), 2.10 s (2H), 2.43 s (1H), 4.43 s (1H), 4.70 s (1H). IR spectrum (ν, $cm^{-1}$): 770, 795, 810, 880, 1295, 1665, 3015, 3040, 3070.

12-Methyl-exo-endo-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane (XX); yield 18%; bp 112°C (1 mm). PMR spectrum (δ, ppm): 0.67-1.14 m (5H), 1.25-1.91 m (14H), 2.21 s (1H). IR spectrum (ν, $cm^{-1}$): 1030, 1460, 805, 822, 3065.

12-Methyl-exo-exo-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane (XXI); yield 15%; bp 112°C (1 mm). PMR spectrum (δ, pm): 0.71-1.20 (5H), 1.33-2.01 (14H), 2.09 (1H). IR spectrum (ν, $cm^{-1}$): 805, 820, 1020, 1475, 3055.

Exo-exo-endo-heptacyclo[9.3.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,14}$]pentadecane (XXII); yield 29%; mp 59-59.5°C. $^{13}C$ NMR spectrum (δ, ppm): 50.41 d ($C^2$, $C^{10}$), 46.10 d ($C^3$, $C^9$), 44.58 d ($C^8$), 36.93 d ($C^1$, $C^{11}$), 27.98 t ($C^7$), 21.52 t ($C^{15}$), 18.16 d ($C^6$), 17.68 d ($C^{12}$, $C^{14}$), 13.07 d ($C^4$, $C^5$), 4.53 t ($C^{13}$). PMR spectrum (δ, ppm): 0.48-0.94 m (7H), 1.38 s (2H), 1.85-2.30 m (9H). IR spectrum (ν, $cm^{-1}$): 720, 810, 1015, 1033, 1310, 1465, 2800-3000, 3015, 3065.

Exo-exo-exo-heptacyclo[9.3.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,14}$]pentadecane (XXIII); yield 21%; bp 96.5°C (1.5 mm); mp 12-13°C; $n_D^{20}$ 1.5525. IR spectrum (ν, $cm^{-1}$); 805, 815, 1005, 1040, 1290, 1310, 1500, 2870, 2900-3000, 3020, 3060. PMR spectrum (δ, ppm): 0.25-0.83 m (7H), 1.08 s (1H), 1.37 s (2H), 1.71 s (2H), 1.83-2.05 m (6H). $^{13}C$ NMR spectrum (δ, ppm): 2.82 t ($C^{13}$),

12.35 d ($C^6$), 16.12 d ($C^4$, $C^5$), 17.38 d ($C^{12}$, $C^{14}$), 22.80 t ($C^{15}$), 33.74 t ($C^7$), 39.18 d ($C^1$, $C^{11}$), 39.57 d ($C^8$), 45.30 d ($C^3$, $C^9$), 54.05 d ($C^2$, $C^{10}$).

Exo-endo-octacyclo[7.7.0.$0^{2,7}$.$0^{3,5}$.$0^{4,8}$.$0^{11,13}$.$0^{12,16}$]hexadecane (XXIV); yield 30%; mp 39.5-40.5°C (from $C_2H_5OH$). IR spectrum ($\nu$, $cm^{-1}$): 810, 815, 3070 (nortricyclane), 1070, 1303, 1390, 1470, 2880, 2950, 2980. PMR spectrum ($\delta$, ppm): 0.78 (2H, $H^3$, $H^4$), 0.80 (2H, $H^{11}$, $H^{12}$), 1.05 (1H, $H^{13}$), 1.20 (1H, $H^5$), 1.35 (2H, $H^2$, $H^8$), 2.31 (2H, $H^1$, $H^9$), 2.43 (1H, $H^{15}$). $^{13}C$ NMR spectrum ($\delta$, ppm): 13.27 d ($C^3$, $C^4$), 14.90 d ($C^{13}$), 16.79 d ($C^5$), 17.83 ($C^{11}$, $C^{12}$), 29.27 t ($C^6$), 33.05 t ($C^{14}$), 38.46 d ($C^{15}$), 44.03 d ($C^7$), 44.35 d ($C^2$, $C^8$), 48.16 d ($C^1$, $C^9$). Mass spectrum: 210 ($M^+$).

Exo-trans-exo-endo-nonacyclo[9.8.1.$1^{14,17}$.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,19}$.$0^{13,18}$]heneicosene-15 (XXVI); yield 18% (93% pure). IR spectrum ($\nu$, $cm^{-1}$): 723, 1570, 1623, 3020 (CH=CH), 812, 820, 3060 (nortricyclane). PMR spectrum ($\delta$, ppm): 0.74-0.90 (3H), 1.23-1.40 (5H), 1.52-2.58 (14H), 5.91 (2H). $^{13}C$ NMR spectrum ($\delta$, ppm): 12.80 d ($C^4$, $C^5$), 17.55 d ($C^6$), 27.67 t ($C^7$), 29.03 t ($C^{21}$), 39.05 d ($C^1$, $C^{11}$), 40.83 d ($C^{13}$, $C^{18}$), 41.80 d ($C^{12}$, $C^{19}$), 41.85 t ($C^{20}$), 44.80 d ($C^{14}$, $C^{17}$), 44.48 d ($C^8$), 46.90 d ($C^3$, $C^9$), 50.73 d ($C^2$, $C^{10}$), 135.38 d ($C^{10}$, $C^{16}$). Mass spectrum: 286 ($M^+$).

Endo-trans-exo-endo-nonacyclo[9.8.1.$1^{14,17}$.$0^{2,10}$.$0^{3,9}$.$0^{4,6}$.$0^{5,9}$.$0^{12,19}$.$0^{13,18}$]heneicosene-15 (XXVIII); yield 16%. IR spectrum ($\nu$, $cm^{-1}$): 728, 1578, 1631, 3020 (CH=CH), 810, 819, 3059, 3077 (nortricyclane). PMR spectrum ($\delta$, ppm): 0.68-0.90 (3H), 1.22 (4H), 1.52-2.75 (14H), 2.60-2.75 (2H), 6.30 (2H). $^{13}C$ NMR spectrum ($\delta$, ppm): 12.82 d ($C^4$, $C^5$), 17.71 d ($C^6$), 28.13 t ($C^7$), 29.25 t ($C^{21}$), 39.20 d ($C^1$, $C^{11}$), 40.85 d ($C^{12}$, $C^{19}$), 41.02 d ($C^{13}$, $C^{18}$), 44.52 d ($C^8$), 45.11 d ($C^{14}$, $C^{17}$), 46.92 d ($C^3$, $C^9$), 50.82 d ($C^2$, $C^{10}$), 53.30 t ($C^{20}$), 135.91 d ($C^{15}$, $C^{16}$). Mass spectrum: 276 ($M^+$).

The characteristics of compounds (V)-(VII), (XXV), (XXVII), and (XXIX) were in accord with those described in the literature [1, 3-5].

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