

The First Synthesis of Norbornadiene Tetramers

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Norbornadiene tetramers

exo-trans-exo-trans-exo-endo-dodecacyclo[14.9.1.1^{4,13}.1^{7,10}.0^{2,15}.0^{3,14}.0^{5,12}.0^{6,11}.0^{17,25}.0^{18,23}.0^{19,21}.0^{20,24}]octacos-8-ene **2** and *exo-trans-exo-trans-exo-exo*-dodecacyclo[14.9.1.1^{4,13}.1^{7,10}.0^{2,15}.0^{3,14}.0^{5,12}.0^{6,11}.0^{17,25}.0^{18,23}.0^{19,21}.0^{20,24}]octacos-8-ene **3** have been synthesized in 32% total yield, *via* Pd complex catalysed cyclodimerization of a known norbornadiene trimer *exo-trans-exo-trans-exo*-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]hencosa-5,14-diene **1** with quadricyclane,

Dimers and trimers of norbornadiene (NBD) can be prepared by homo- and co-dimerization of NBD, assisted by metal complex catalysts.¹ These and more complicated molecules are of interest as providing specific molecular geometries in the design of new materials. The preparation of norbornadiene tetramers is, therefore, of importance. Before our research, there were no references in the literature concerning the problem of tetramer synthesis.

We are the first group to succeed in synthesizing norbornadiene tetramers *via* cyclocodimerization of a known NBD trimer **1**² with an NBD isomer quadricyclane **4** in the presence of Pd catalysts (Scheme 1). The resultant tetramers **2** and **3** are represented as two stereoisomeric C₂₈ dodecacyclic hydrocarbons of *exo-trans-exo-trans-exo-endo*- and *exo-trans-exo-trans-exo-exo*-dodecacyclo[14.9.1.1^{4,13}.1^{7,10}.0^{2,15}.0^{3,14}.0^{5,12}.0^{6,11}.0^{17,25}.0^{18,23}.0^{19,21}.0^{20,24}]octacos-8-enes, respectively.

The total yield of the isomers **2** and **3** is essentially dependent on the nature of the catalyst, its ligand environment and on the nature of the solvent. With the most active catalyst Pd(PPh₃)₄, the yield of tetramers reaches 32% in a ratio **2**:**3** = 3:1 in toluene at 80 °C after 5 h.

The tetramers **2** and **3** are almost insoluble in organic solvents except for boiling chloroform, and can be easily sublimated, hence the impossibility of their individual isolation. The structures of the tetramers were assigned by their

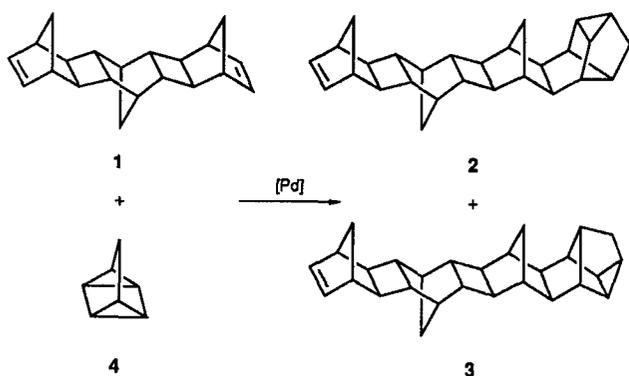
¹H and ¹³C NMR, IR and mass spectroscopic data and also by comparison of these characteristics with those of known NBD dimers and trimers.^{†3} Thus, the minor isomer **3**, showing a

[†] ¹H NMR spectra were recorded on a Tesla BS-567 instrument (100 MHz, CDCl₃, SiMe₄ as an internal standard). ¹³C NMR spectra were registered on a Jeol-FX-90Q instrument (22.5 MHz, CDCl₃, SiMe₄). IR spectroscopy was performed on a UR-20 device (KBr). Mass spectra were taken on an MX-1306 spectrometer at 70 eV (50 °C). GLC analysis was carried out on a Chrom-5 instrument (helium as gas-carrier, 1.2 × 0.003 m columns with 5% SE-30 on chromaton N-AW).

Spectroscopic data: IR ν/cm⁻¹ 690, 730 (*cis*, —C=C—), 815, 830, 3060 (cyclopropane ring), 790, 850, 870, 900, 1340, 1390, 3010; ¹H NMR δ 5.92 (2H, —CH=CH—), 0.74–0.90 (cyclopropane ring), 1.11–1.89, 2.40–2.57 (complex resonance of the norbornane structure); MS *m/z* 368 (M⁺).

For **2**: ¹³C NMR δ 40.55 (d, C₁, C₁₆), 44.22 (d, C₂, C₃, C₁₄, C₁₅), 41.88 (d, C₄, C₁₃), 40.70 (d, C₅, C₆, C₁₁, C₁₂), 43.56 (d, C₇, C₁₀), 135.26 (d, C₈, C₉), 47.31 (d, C₁₇, C₂₅), 47.05 (d, C₁₈, C₂₄), 12.92 (d, C₁₉, C₂₀), 17.35 (d, C₂₁), 27.90 (t, C₂₂), 43.33 (d, C₂₃), 29.20 (t, C₂₆), 29.03 (t, C₂₇), 41.67 (t, C₂₈).

For **3**: ¹³C NMR δ 40.60 (d, C₁, C₁₆), 42.72 (d, C₂, C₃, C₁₄, C₁₅), 41.80 (d, C₄, C₁₃), 40.80 (d, C₅, C₆, C₁₁, C₁₂), 43.50 (d, C₇, C₁₀), 135.31 (d, C₈, C₉), 50.95 (C₁₇, C₂₅), 46.74 (d, C₁₈, C₂₄), 16.80 (d, C₁₅, C₂₀), 11.50 (d, C₂₁), 33.50 (t, C₂₂), 39.20 (d, C₂₃), 30.24 (t, C₂₆), 29.03 (t, C₂₇), 42.72 (t, C₂₈).



Scheme 1

resonance series at δ 46.47, 39.20, 33.50, 16.80, 11.50 (this being inherent to a tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane structure of *exo*-configuration) was assigned to the *exo-exo*-species, whereas the major isomer 2 was ascribed to the *exo-endo*-species by its resonances at δ 47.05, 43.32, 27.90, 17.35, 12.92.³

The starting compounds 1 and 4 were prepared according to the procedures reported by Jennings *et al.*² and Smith,⁴

respectively. The complex Pd(PPh₃)₄ was obtained as described in the literature.^{‡5}

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‡ *General codimerization procedure.* A solution of the NBD trimer (1.2 g, 4.34 mmol) and quadricyclane 4 (0.2 g, 2.17 mmol) in toluene (4 ml) was poured into a microautoclave. Then the complex Pd(PPh₃)₄ (0.02 mmol) and PPh₃ (0.02 mmol) were added in an inert atmosphere. The mixture was heated at 80 °C for 5 h, after which the solvent was evaporated and the resultant precipitate was dissolved in boiling chloroform (5–10 ml). Then the solution was diluted with a 10-fold excess of pentane and filtered. The residue was dried and sublimated in vacuum. In case of impurities in the trimers, the sublimated tetramer was recrystallized from chloroform-pentane (1:10). The total yield of octacos-8-enes 2 and 3 was 32% as calculated for the amount of reacted 4.