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TETRAHEDRON
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Synthesis of rod-shaped compounds: bis(7,7′-heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecanylidene) derivatives

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Abstract

The rod-shaped hydrocarbon molecules **1** and **2** are synthesized from heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]-tetradecane (HCTD) derivatives according to Barton's procedure, where the structures of **1** and the corresponding diketone of **2** belong to D_{2h} and D_{2d} symmetries, respectively. © 1999 Elsevier Science Ltd. All rights reserved.

Sterically hindered olefins such as adamantylideneadamantane (**3**)[1] and derivatives have attracted much attention over the past few years for its usefulness as fulgides,[2] chemiluminescence reagent for biological analysis,[3] and models for theoretical studies.[4] The properties of the derivatives of **3** are often related to the size and bonding geometry of the polycyclic cage structure. In our continuous study on the chemistry of hepta- cyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecane (HCTD),[5] we are interested in synthesizing rod-shaped molecules that possess similar characters. Previous attempts for the preparation of dimeric adduct of HCTD have not been successful,[6] since direct coupling of two units of ketone **6** by low-valent titanium reagents did not yield **9**.[7] Here we report the first synthesis of **1** through Barton's procedure as shown in Scheme 1.[8]

The preparation of diol **4** and some of its derivatives have been reported previously.[9] Treatment of **4** with one molar equiv. of 3,4-dihydro-2*H*-pyran yielded a mixture of **5** (44%) and the doubly protected homologue (23%). After purification, **5** was oxidized with pyridinium chlorochromate (PCC) to yield ketone **6** in 80%. Treatment of **6** with hydrazine hydrate in ethanol gave an azino adduct **7** (HCTD=NN=HCTD) in 90% yield, of which the ^{13}C NMR spectrum showed the appearance of stereoisomers due to the two chiral centers of pyran. Compound **7** was converted to 2,5-di(HCTD-ylidene)-1,3,4-thiadiazole (**8**) in 78% yield by successive reactions with hydrogen sulfide followed by lead tetraacetate. Carbon–carbon coupling was completed by heating **8** with triethyl phosphite in refluxing benzene for 6 h to give **9** in 70% yield. Compound **9** was hydrolyzed in acid to yield a diol

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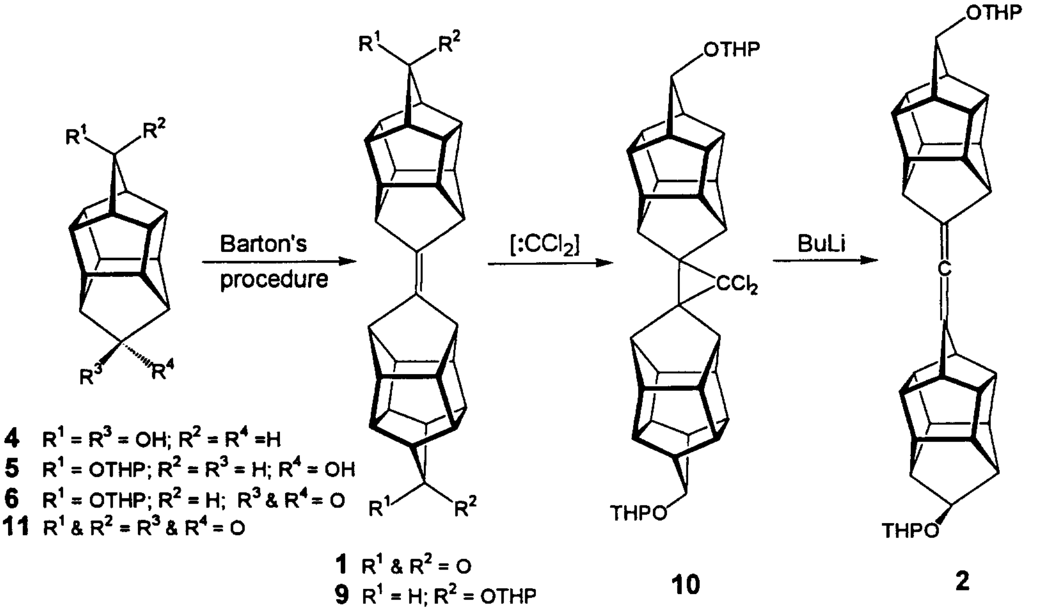

4 R^1 = R^3 = OH; R^2 = R^4 = H
5 R^1 = OTHP; R^2 = R^3 = H; R^4 = OH
6 R^1 = OTHP; R^2 = H; R^3 & R^4 = O
11 R^1 & R^2 = R^3 & R^4 = O

1 R^1 & R^2 = O
9 R^1 = H; R^2 = OTHP

10

2

Scheme 1.

(83%), which was finally oxidized by PCC to give **1** (70%). The spectra of **1** showed the characteristics of D_{2h} symmetry, i.e. it displayed only six absorption signals in the ^{13}C NMR field including the two at δ 139.6 and 217.6 corresponding to the olefinic and carbonyl moieties.[10] The overall yield of **1** from **4** was ca. 10%.

The insertion of a methylene group to the central double bond of **9** was achieved by a reaction with dichlorocarbene to form **10** (55%).[11] Lithium–chloro exchange of **10** with *n*-BuLi followed by rearrangement yielded **2** (47%), whose ^{13}C NMR spectrum showed two olefinic peaks at δ 117.6 and 175.4.[10] Unlike those in **1**, the two HCTD moieties of **2** were oriented 90° with respect to each other. This geometrical change among molecules **1**, **2** and **11** can be utilized as a good model for the analysis of orientation effect in electron/energy transfer processes between the two terminal groups.[12] It has been shown that the two highest occupied molecular orbitals (MO) of **11** are degenerate due to an orthogonal orientation between the *n*-orbitals of >CO.[13] However, the corresponding nonbonding MOs in **1** split to an extend of 0.16 eV predicted by AM1[14] as the result of co-planarity of the >CO groups as well as the central double bond. The magnitude of interaction is remarkable regarding the long distance between the two >CO groups (12 Å) separated by a saturated σ-framework. Orbital analyses for these compounds by photoelectron spectroscopy will be reported in due course.

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10. Selected physical data for **1**: ν_{max}/cm^{-1} (KBr) 1774 (CO); δ_H ($CDCl_3$, 200 MHz) 2.36 (m, 4H), 2.59 (m, 8H), 2.72 (m, 12H); δ_C ($CDCl_3$, 50 MHz, ^{1}H-decoupled) 46.68, 46.98, 52.43, 55.23, 139.56, 217.57; *m/z* (EI, 24 eV) 392 (M^+, 6%), 279 (11), 241 (6). Selected physical data for **2** (a mixture of two diastereomers): ν_{max}/cm^{-1} (KBr) 2359 (C=C=C); δ_H ($CDCl_3$, 200 MHz) 1.45–1.90 (m, 6H), 2.35–2.45 (m, 2H), 2.45–2.51 (m, 2H), 2.51–2.70 (m, 6H), 2.70–2.85 (m, 2H), 3.40–3.55 (m, 1H), 3.82–3.95 (m, 1H), 4.40 (s, 1H), 4.41 (s, 1H); δ_C ($CDCl_3$, 50 MHz, ^{1}H-decoupled) 20.58, 26.24, 31.86, 49.73, 49.86, 52.27, 52.68, 53.09, 53.31, 53.81, 54.34, 55.50, 63.42, 91.19, 98.80, 117.55, 175.41; *m/z* (EI, 24 eV) 577 (M^++1, 80%), 492 (25), 475 (30).
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14. AM1 implanted in PC SPARTAN Pro, which was distributed by Wavefunction, Inc., 1999, Irvine, CA, USA.