

Synthesis and Photoreaction of 1,2,3,4-Tetra-*t*-butylnaphthalene: A Highly Crowded Naphthalene Derivative and Its Valenceisomers

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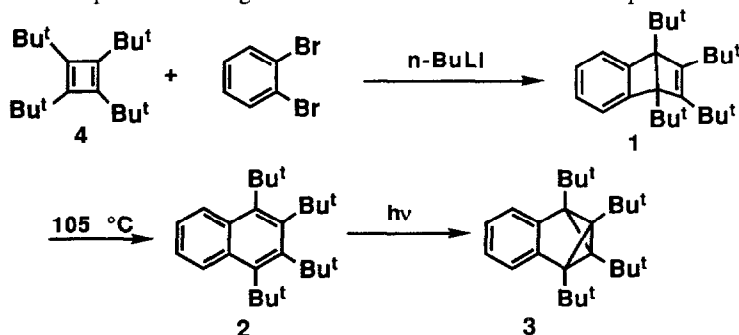
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Abstract: 1,2,3,4-Tetra-*t*-butylnaphthalene (**2**), a highly crowded naphthalene derivative, has been synthesized. Upon irradiation, **2** underwent photovalence isomerization to afford 1,2,5,6-tetra-*t*-butyl-3,4-benzo-3-tricyclo[3.1.0.0^{2,6}]-hexene (**3**). The synthesis of 1,4,5,6-tetra-*t*-butyl-2,3-benzo-2,5-bicyclo[2.2.0]hexadiene (**1**), which was used for the synthesis of **2**, is also described.

Overcrowded aromatic compounds are of considerable interest because they often reveal unique physical and chemical properties.¹ In this paper we wish to report a new example of such molecules: 1,2,3,4-tetra-*t*-butylnaphthalene (**2**), one of the most crowded aromatic molecules. Interestingly, **2** showed a unique photochemical reaction to give 1,2,5,6-tetra-*t*-butyl-3,4-benzo-3-tricyclo[3.1.0.0^{2,6}]hexene (**3**).

Though we already reported the synthesis of 1,2,4-tri-*t*-butylnaphthalene by the Diels-Alder reaction of 2,3,5-tri-*t*-butyl-2,4-cyclopentadien-1-one with benzyne,² this strategy is not applicable to the synthesis of **2**, because 2,3,4,5-tetra-*t*-butyl-2,4-cyclopentadien-1-one is unreactive to benzyne. Alternatively reactive tetra-*t*-butylcyclobutadiene³ (**4**) was chosen and, as shown in Scheme 1, reacted with benzyne generated by treating dibromobenzene with *n*-butyl lithium to afford 1,4,5,6-tetra-*t*-butyl-2,3-benzo-2,5-bicyclo[2.2.0]hexadiene (**1**). In a practical run, **4** obtained by the thermolysis (138 °C, 30 min) of tetra-*t*-butyltetrahedrane³ (**5**) (48 mg) was used without purification. A solution of **4** thus obtained and 4 equiv of 1,2-dibromobenzene in toluene was added a solution of 4 equiv *n*-butyl lithium in hexane. Working up followed by chromatography on silica gel afforded **1** in 49% yield based on **5**. Thermolysis of **1** in methylcyclohexane at 105 °C afforded **2** quantitatively with $t_{1/2}$ = 30 min, and the electronic spectra following the reaction revealed a clear isosbestic point at 218 nm.



Scheme 1.

As shown in Fig. 1, the electronic spectrum of **2** has characteristic naphthalene bands with remarkable red shifts compared with those of 1,2,3,4,6-pentamethylnaphthalene (λ_{\max} 236 nm, 288 nm)⁴ indicating severe deformation of the aromatic ring.

Molecule **2** is anticipated to possess large out-of-plane bending deformation by virtue of the nonbonded repulsive interactions between t-butyl groups and the interactions between the bulky groups at C1 and 4 positions and peri-hydrogens. Consequently, **2** shows quite unique photochemical feature. For example, irradiation ($\lambda > 350$ nm) of **2** in methylcyclohexane afforded valene isomer **3** (Scheme 1), in contrast to naphthalene derivatives with a skew form which are known to give Dewar isomers photochemically.⁵

This fact indicates that naphthalene **2** possesses bending form in which neighboring t-butyl groups take staggered conformation to each other. The photoreaction of **2** is clean, and as shown in Fig. 1 an isosbestic point is observed at 228 nm in the electronic spectra following the photoreaction in methylcyclohexane. Spectroscopic data for **1**, **2** and **3** are reported in footnote.⁶

Further studies including crystallographic analysis of **2** are in progress.

References and Notes

- Greenberg, A.; Liebman, J. F., *Strained Organic Molecules*; Academic Press, New York, 1978 ; Tidwell, T. T., *Tetrahedron*, **1978**, 34, 1855-1868; Sakurai, H.; Ebata, K.; Kabuto, K.; Sekiguchi, A., *J. Am. Chem. Soc.*, **1990**, 112, 1799-1803; Weissensteiner, W.; Schuster, I. I.; Blount, J. F.; Mislow, K., *ibid.*, **1986**, 108, 6664-6668.
- Yoshida, Z.; Kawamoto, F.; Miyoshi, H.; Ogoshi, H., *Jpn Kokai Tokkyo Koho*, **1979**, 138349; Miki, S.; Yoshida, Z., *Kokagaku*, **1987**, 11, 58-61.
- Maier, G.; Pfriem, S.; Schafer, U.; Malsh, K. D.; Matusch, R., *Chem. Ber.*, **1981**, 114, 3965-3987.
- Abadir, B. J.; Cook, J. W.; Gibson, D. T., *J. Chem. Soc.*, **1953**, 8-17.
- Mandella, W. L.; Franck, R. W., *J. Am. Chem. Soc.*, **1973**, 95, 971-972.
- Selected analytical data for **1**, **2** and **3**. **1**; ¹H-NMR (CDCl₃) δ 1.20(s, 18H), 1.34(s, 18H), 6.88-7.18 (AA'BB', 4H); UV(methylcyclohexane) λ_{\max} nm (ϵ) 280 (1100), 288 (1000); Exact Mass: Calcd for C₂₆H₄₀ 352.3132, Found 352.3114. **2**; ¹H-NMR (CDCl₃) δ 1.37(s, 18H), 1.72(bs, 18H), 7.13-8.17 (AA'BB', 4H); UV(methylcyclohexane) λ_{\max} nm (ϵ) 280 (13800), 405 (625); Exact Mass: Calcd for C₂₆H₄₀ 352.3132, Found 352.3152. **3**; ¹H-NMR (CDCl₃) δ 1.36(s, 18H), 1.48(s, 6H), 1.67(s, 12H), 6.78-7.35 (AA'BB', 4H); UV(methylcyclohexane) λ_{\max} nm (ϵ) 244 (1880), 271 (1000), 279(1170); Exact Mass: Calcd for C₂₆H₄₀ 352.3132, Found 352.3114.
In the NMR for **3**, t-butyl groups at C2 and 5 reveal signals at 1.48 and 1.67 ppm with the intensity ratio of 1 : 2 due to the restricted rotation about the bonds, Me₃C-C2 and Me₃C-C5.

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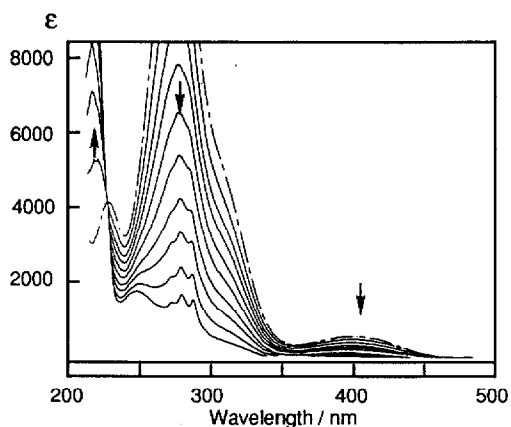


Figure 1. Spectral changes occurring upon irradiation of **2** in methylcyclohexane. Initial curve (— — —) is the spectrum for pure **2**.