

Synthesis of Dibenzo[4.4.2.2]buttaflanes†

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The synthesis of [4.4.2.2]buttaflanes (**6**) and (**7**), which possess two fused benzene rings facing each other, is reported.

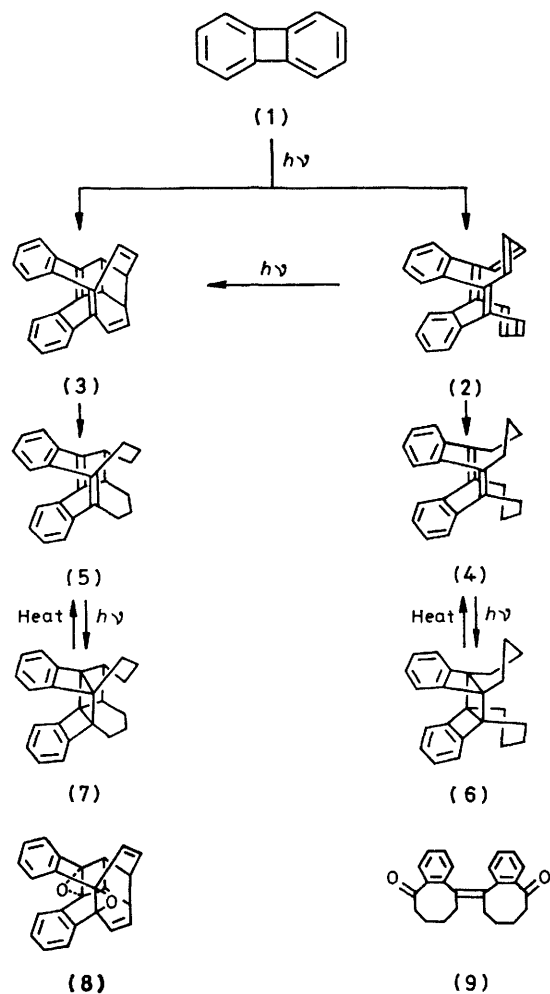
Buttaflane systems, comprising two propellane moieties with a cyclobutane ring in common, are of chemical and synthetic interest.¹ We now report the synthesis of the little known

dibenzo[4.4.2.2]buttaflane system by a novel route, *via* the photodimerization of biphenylene (see Scheme 1).

Irradiation ($\lambda > 290$ nm) of biphenylene (**1**) in n-hexane yielded the *syn*-photodimer (**2**);² m.p. 247—252 °C (decomp.), along with the pentacyclic compound (**3**),‡ the photoproduct

† Trivial name proposed by Greenberg *et al.*, *cf.* A. Greenberg and J. F. Liebman, 'Strained Organic Molecules,' Academic Press, New York, San Francisco, London, 1978. [4.4.2.2]Buttaflane = pentacyclo[6.4.2.2^{2,7}.0^{1,8}.0^{2,7}]hexadecane.

‡ All new compounds gave satisfactory spectral and elemental analyses.



Scheme 1

of (2); m.p. 178–179 °C (decomp.); m/e 304 (M^+); λ_{\max} (MeCN) 276 nm (ϵ 1094); ^1H n.m.r. (CDCl_3) δ 3.32–3.52 (2H, m), 3.68–3.80 (2H, m), 5.20–5.54 (2H, m), 6.45 (2H, d), and 6.92–7.20 (8H, m); ^{13}C n.m.r. (CDCl_3) δ 38.7 (d), 45.7 (d), 124.1 (d), 126.5 (d), 126.9 (d), 127.6 (d), 137.5 (s), 137.7 (s), 138.5 (d), 146.4 (s), and 151.8 (s) p.p.m. In the photo-stationary state, the ratio of (1), (2), and (3) was 5:1:3. Epoxidation of (3) with *m*-chloroperbenzoic acid took place preferentially at the two bridgehead double bonds to give the

diepoxide (8); m.p. 234–236 °C (decomp.). Catalytic hydrogenation of the four peripheral double bonds in (2) with palladium on carbon in ethyl acetate gave virtually quantitatively the octahydro-dimer³ (4); yield 88%, m.p. 182.5–183.5 °C (decomp.). Ozonolysis of (4) gave the diketone (9); yield 72%, m.p. 171–172 °C. In a similar reaction sequence with (3), however, reductive cleavage of one bond of the cyclobutane ring took place concurrently to provide the tetracyclic compound (5); yield 78%, m.p. 162–166 °C (decomp.); m/e 310 (M^+); λ_{\max} (MeCN) 273 nm (ϵ 679); ^1H n.m.r. (CDCl_3) δ 1.85–2.47 (6H, m), 2.55–3.15 (6H, m), 3.63–3.78 (2H, m), and 6.75–7.10 (8H, m); ^{13}C n.m.r. (CDCl_3) δ 33.1 (t), 34.6 (t), 39.5 (t), 48.3 (d), 126.1 (d), 126.2 (d), 130.0 (d), 138.1 (s), 139.2 (s), 143.3 (s), and 144.9 (s) p.p.m.

Intramolecular [2 + 2] photocycloaddition of (4) and (5) respectively in benzene afforded the desired buttaflanes: the dibenzo[4.4.2.2]buttaflane (6); yield 100%, m.p. 179–183 °C (decomp.); m/e 312 (M^+); λ_{\max} (MeCN) 278 nm (ϵ 3203); ^1H n.m.r. (CDCl_3) δ 1.35–1.64 (8H, m), 1.96–2.25 (8H, m), and 6.44–6.76 (8H, m), and the cage-like dibenzo[4.4.2.2]-buttaflane (7); yield 80%, m.p. 240–208 °C (decomp.); m/e 310 (M^+); λ_{\max} (MeCN) 276 nm (ϵ 1040); ^1H n.m.r. (CDCl_3) δ 1.24 (2H, d), 1.84–3.40 (10H, m), 3.44–3.56 (2H, m), and 6.52–6.96 (8H, m); ^{13}C n.m.r. (CDCl_3) δ 24.9 (t), 25.5 (t), 30.5 (t), 41.6 (s), 42.4 (d), 50.8 (s), 124.8 (d), 124.9 (d), 126.3 (d), 126.9 (d), 140.3 (s), and 144.2 (s) p.p.m., respectively. The ^{13}C n.m.r. spectrum of (6) in CDCl_3 attested to its C_{2v} symmetry, consisting of only six peaks: δ 22.2 (t), 25.0 (t), 49.3 (s), 121.2 (d), 126.5 (d), and 150.1 (s) p.p.m.

Interestingly, (6) readily cycloreversed to (4) with a catalytic amount of $[\text{Rh}(\text{norborene})\text{Cl}]_2$ or on heating at ≥ 150 °C. The thermal conversion of (7) into (5) above 170 °C was also quite efficient.

In the ^1H n.m.r. and the electronic spectra of (6) and (7) high field shifts of some aromatic protons and bathochromic and hypsochromic shifts were observed, in comparison with *o*-xylene. This may be attributed to transannular π - π interactions between the two benzene rings.

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