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A NOVEL PHOTOCHEMICAL REACTION OF [3]DENDRALENE DERIVATIVES

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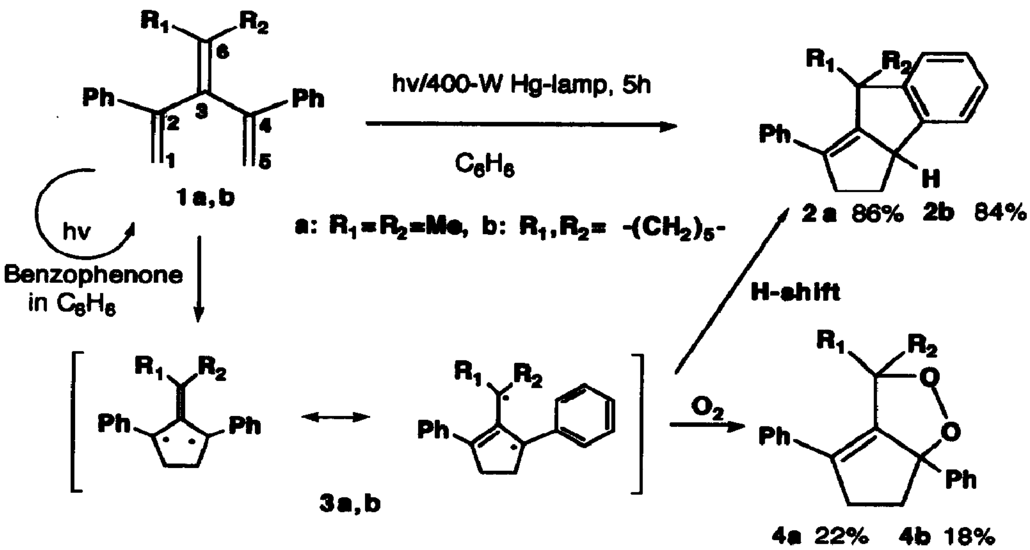
Abstract: Direct irradiation of a benzene solution of [3]dendralene derivative **1a** or **1b** under a nitrogen atmosphere gave a cyclized product **2a** or **2b** in high yield. The conceivable trimethylenemethane intermediate was successfully trapped by molecular oxygen.

In contrast to the photochemical reactions of linearly conjugated trienes,[1] the excited state behavior of acyclic cross conjugated trienes has poorly been understood. 3-Methylene-1,4-pentadiene ([3]dendralene) is a typical example and the photochemistry of it or its derivatives has not been reported.[2] Several interesting photochemical features can be expected for this compound provided that the probable polymerization is prohibited by suitable substituents, e.g., i) [2+2] reaction in the butadiene moiety leading to vinyl-cyclobutane or -bicyclobutane, ii) C_2-C_4 bridging or iii) C_1-C_5 bridging giving trimethylenemethane (TMM) diradical; a reverse reaction of the known thermal reaction of TMM to [3]dendralene.[3] We report a novel photochemical reaction (path iii) of 6,6-dialkyl-2,4-diphenyl[3]dendralenes.

Although synthesis of 3-methylene-1,4-pentadiene has been reported,[4] general synthetic method applicable for its derivatives has not been reported. We synthesized 6,6-dialkyl-2,4-diphenyl[3]dendralenes **1a** and **1b** (50-56% in both cases) through Pd(0)-mediated cross coupling reaction of 1,1-dibromoethylene derivatives with the excess amount of α-styrylmagnesium bromide or α-styrylzinc chloride.

Direct irradiation of a benzene solution of **1a** (1.5×10^{-4} M) with a 400 W high-pressure Hg-lamp for 5 h under a nitrogen atmosphere resulted in a clean reaction and cyclized product **2a** was obtained as a single product in 86% yield. Similarly, **2b** was produced in 84% yield from **1b** [**2a**: colorless oil, MS (EI) *m/e* 260 $[M]^+$; ^{1}H NMR (270 MHz, $CDCl_3$) δ=7.34-7.10 (m, 9H), 4.46 (t-like (broad), J=7-9 Hz, 1H), 3.06-2.95 (m, 1H), 2.94-2.85 (dd-like, J=15.4, 9.4 Hz, 1H), 2.56-2.48 (m, 1H), 1.90-1.78 (m, 1H), 1.45 (s, 3H), 1.19 (s, 3H); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ=154.75, 153.38, 143.98, 138.47, 133.40, 128.64, 127.87, 126.83, 126.76, 126.66, 123.18, 122.16, 55.96, 43.22, 41.14, 31.13, 29.73, 24.65; **2b**, colorless oil, MS (FI) *m/e* 300 $[M]^+$; ^{1}H NMR δ=7.60-7.10 (m, 9H), 4.41 (t-like (broad), J=7-9 Hz, 1H), 3.11-2.96 (m, 1H), 2.71 (dd-like, J=15.2, 8.9 Hz, 1H), 2.54-2.42 (m, 1H), 1.90-1.00 (m, 11H); ^{13}C-NMR δ=154.03, 152.65, 144.92, 139.94, 132.83, 128.71, 127.94, 126.56 (two carbons), 126.13, 124.49, 123.27, 55.63, 47.58, 43.47, 37.63, 32.02, 30.84, 25.86, 22.61, 22.57]. Sensitized irradiation in the presence of excess amount of benzophenone did not produce the cyclized product,[5] indicating the singlet state as a reactive excited state. The product **2** is reasonably interpreted by ring closure at C_1 and C_5-terminals giving TMM intermediate **3**. The conversion of **3** to **2** involves radical attack of aromatic ring followed by 1,3-hydrogen shift in aromatization step.



The intermediate **3** was successfully trapped by oxygen; irradiation of **1a** or **1b** under an oxygen atmosphere produced the expected oxygenated product **4a** (22%) or **4b** (18%) along with several unidentified oxygenated products [**4a**; mp163-164 °C, MS (FAB) *m/e* 293[M+H]$^+$; ^{1}H NMR δ=7.60-7.25 (m, 10H), 3.40-3.20 (m, 2H), 2.50 (ddd, *J*=12.2, 9.6. 9.6 Hz, 1H), 2.02 (ddd, *J*=12.2, 5.0, 1.7 Hz, 1H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C-NMR δ=154.52, 143.25, 136.03, 135.40, 128.57, 128.52, 128.28, 127.83, 127.26, 124.78, 102.46, 82.34, 41.24, 37.36, 25.82, 25.57; **4b**; mp 140-141°C, MS (FAB) *m/e* 333 [M+H]$^+$;^{1}H NMR δ=7.60-7.25 (m, 10H), 3.40-3.15 (m, 2H), 2.49 (ddd, *J*=12.2, 9.9, 9.9 Hz, 1H), 1.99 (ddd, *J*=12.2, 4.6, 2.3 Hz, 1H), 1.90-0.90 (m, 10H); ^{13}C-NMR δ=154.89, 143.43, 136.13, 135.90, 128.46 (two carbons), 128.14, 127.98, 127.19, 124.85, 101.87, 83.63, 42.23, 37.52, 35.81, 33.08, 24.87, 22.64, 22.30]. Further studies are in progress.

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5. Controlled shorter direct irradiation (1.5 h with 100 W high-pressure Hg-lamp through a Pyrex filter) of **1a** gave **2a** in 25% yield with 64% recovery of **1a**. Under the same conditions except for the presence of 10 equiv. of benzophenone, **2a** was not detected (NMR) and the starting **1a** was recovered in 84% yield.

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