

## Decahydro-1,3,5-methenocyclopenta[*cd*]pentalene (Trishomocubane) Framework: Novel Photochemical Synthesis, Acid-catalysed Cycloreversion, and Possible Role as a Solar Energy Storage System

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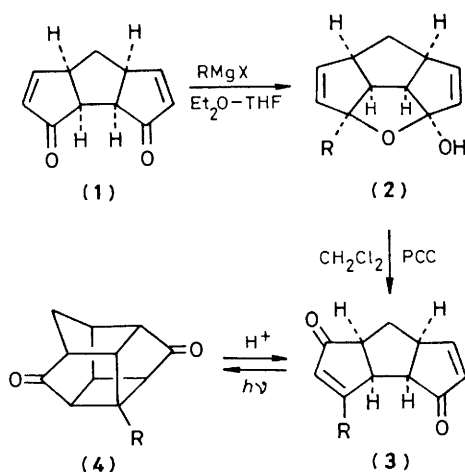
A novel synthetic approach to the decahydro-1,3,5-methenocyclopenta[*c,d*]pentalene skeleton *via* intramolecular photocycloaddition of *cis,syn,cis*-triquinane bis-enones is reported; the facile and efficient acid-induced cycloreversion of these pentacyclic cage compounds to their precursor bis-enones points to the possible role of this system in the reversible storage of light energy.

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Photochemical syntheses of strained, caged, polycyclic molecules and their catalytic cycloreversions have attracted considerable attention in recent years as possible models for light-energy storage systems.<sup>1</sup> We report here a new synthetic

approach to the decahydro-1,3,5-methenocyclopenta[*cd*]pentalene skeleton,<sup>2</sup> a novel trishomocubane system, and describe its mild and efficient acid-catalysed cycloreversion.

The synthesis started with the readily available<sup>3</sup> triquinane-

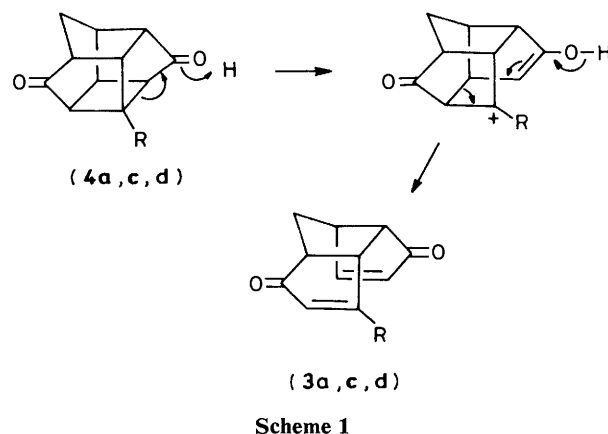


a; R = Me  
 b; R = CH<sub>2</sub>CH=CH<sub>2</sub>  
 c; R = Ph  
 d; R = *p*-MeOC<sub>6</sub>H<sub>4</sub>

based *cis,syn,cis*-bis-enone (1) and involved alkylative enone transposition and intramolecular  $\pi 2_s + \pi 2_s$  photocycloaddition as the two key steps. Controlled addition of appropriate Grignard reagents (1–1.2 molar excess) in Et<sub>2</sub>O-tetrahydrofuran (THF) to (1) resulted in the formation of the intermediate hemiacetals (2a–d), which were directly oxidised with pyridinium chlorochromate (PCC)<sup>4</sup> to furnish the single transposed bis-enones (3a), m.p. 108–110 °C (30%), (3b), m.p. 68 °C (25%), (3c), m.p. 111–112 °C (25%), and (3d), m.p. 134–135 °C (10%). The structures of the bis-enones (3a–d) were assigned on the basis of unambiguous <sup>1</sup>H and <sup>13</sup>C n.m.r. spectral evidence.

Exposure of an ethyl acetate solution of each of the bis-enones (3a–d) to either a 450 W u.v. lamp or sunlight, through a Pyrex filter, resulted in a facile intramolecular  $\pi 2_s + \pi 2_s$  cage cyclisation. The photolyses with the u.v. lamp were complete within 1 h and nearly quantitative chemical yields of the pentacyclic diones (4a–d) were obtained. The quantum yields (potassium ferrioxalate actinometry) for the formation of (4a–d) at *ca.* 360 nm were 0.8, 0.82, 0.92, and 0.48, respectively. The photolyses of (3a–d) in sunlight, as expected, required longer reaction times (2–3 h) but from the preparative point of view were equally efficient. The structures of the cage diones (4a–d) were fully consonant with their spectral data.<sup>†</sup>

Reaction of (4d) with catalytic amounts of toluene-*p*-sulphonic acid in benzene at ambient temperature (30 °C; 2 h) resulted in its smooth cycloreversion to give the bis-enone (3d) in quantitative yield. The use of BF<sub>3</sub>–Et<sub>2</sub>O as the catalyst proved to be even more effective, and (4d) reverted to (3d) almost instantaneously at room temperature and in 100% yield. The phenyl and methyl substituted cage diones (4c) and (4a) similarly also reverted to their precursor bis-enones (3c) and (3a), respectively (Table 1). However, the reaction in case of the methyl substituted compound (4a) was less efficient and there is a clear trend for the propensity towards cycloreversion to decrease with substituent in the order *p*-methoxyphenyl, phenyl, methyl. A plausible mechanism for the facile



Scheme 1

Table 1. Acid-catalysed rearrangement of (4).

Substrate	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H <sup>a</sup>		BF <sub>3</sub> –Et <sub>2</sub> O <sup>b</sup>		Product
	Time; temp.	% Yield	Time; temp.	% Yield	
(4a)	6 h; 110 °C	20	2 h; 80 °C	65	(3a)
(4c)	2 h; 80 °C	100	40 min; 30 °C	100	(3c)
(4d)	2 h; 30 °C	100	< 5 min; 30 °C	100	(3d)

<sup>a</sup> 0.3 mol. equiv. of acid in either benzene or toluene. <sup>b</sup> 0.5 M solution of BF<sub>3</sub>–Et<sub>2</sub>O in benzene (4–5 mol. equiv.).

acid-catalysed rearrangement of the diones (4) to the triquinane bis-enones (3) is in Scheme 1.

The results described here indicate that the system (3) ⇌ (4) may be a possible candidate for the reversible storage of solar energy. At first sight, various properties of the (3) ⇌ (4) system, *e.g.*, large ground-state enthalpy difference,<sup>5</sup> high quantum efficiency (approaching unity), and the good kinetic stability of (4) together with its facile cycloreversion under mild, ambient conditions, comply well with the stringent requirements for the reversible storage of solar energy.<sup>1a</sup>

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<sup>†</sup> (4a): m.p. 200–201 °C; i.r. (KBr): 1760 and 1730 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (100 MHz; CDCl<sub>3</sub>): δ 2.6–3.1 (4H, m), 2.0–2.55 (5H, m), and 1.1 (3H, s); <sup>13</sup>C n.m.r. (25 MHz; CDCl<sub>3</sub>): δ 213.0 (s), 212.9 (s), 57.0 (d), 55.0 (d), 51.1 (d), 49.7 (d), 45.8 (d), 43.7 (t), 42.6 (d), 42.1 (s), 38.6 (d), and 22.0 (q) p.p.m.; (4b): m.p. 69–70 °C; (4c): m.p. 146–147 °C; (4d): m.p. 168–169 °C; i.r. and n.m.r. data for (4b–d) are analogous to data for (4a).