

Photodimerisation of 1,4-Cyclohexadiene-1,2-dicarboxylic Anhydride to Pentacyclo[6.4.0.0<sup>2,7</sup>.0<sup>4,11</sup>.0<sup>5,10</sup>]-dodecane-1,2,5,10-tetracarboxylic Dianhydride\*

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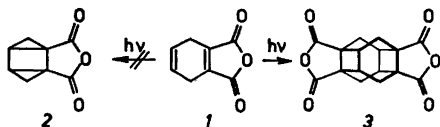
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In the last few years the reactions of interacting but non-conjugated double bonds have been a subject of growing interest. The classical example is the norbornadiene-quadricyclane rearrangement.<sup>1</sup> Although this reaction takes place generally with 3,6-bridged 1,4-cyclohexadienes it does not seem to take place with the corresponding unbridged 1,4-cyclohexadienes.<sup>2</sup>

The rigidity of the norbornadiene system may be the cause of this difference. The UV spectrum indicates that there is considerable interaction between the double bonds of norbornadiene,<sup>3</sup> whereas such interaction is absent in 1,4-cyclohexadiene.<sup>4</sup>



For 1,4-cyclohexadiene-1,2-dicarboxylic anhydride *1* the UV spectrum<sup>5</sup> indicates essentially the same strong interaction as

\* Cycloaddition reactions, part 5. Part 4: Ref. 9.

in the norbornadiene-2,3-dicarboxylic anhydride. On irradiation,<sup>6</sup> however, the compound *1* gave none of the anticipated tricyclohexane *2*. The photolysis product was largely polymeric as in the case of the parent 1,4-cyclohexadiene,<sup>7</sup> but the dimer *3*, m.p. 510°C (decomp., evac capillary) could be isolated in 10% yield. NMR (60 MHz,  $\delta$  TMS, DMSO-*d*<sub>6</sub>): 1.80 m (8H), 2.98 s (4H). IR (cm<sup>-1</sup>): 1847, 1770 (CO, cyclic anhydride). Mass spectrum: small parent peak at *m/e* = 300, base peak at *m/e* = 228, (P<sup>+</sup> - CO<sub>2</sub>, - CO). (Found: C 61.1; H 4.1. Calc. for C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>: C 64.0; H 4.0.)

On esterification, the tetramethylester of the dimer *3* was obtained, m.p. 218–221°C. NMR (Varian HA-100,  $\delta$  TMS, CDCl<sub>3</sub>): the ring system gives a spectrum of the ABX type, 2.13 (4H<sub>A</sub>, CH<sub>2</sub>), 1.86 (4H<sub>B</sub>, CH<sub>2</sub>), 3.16 (4H<sub>X</sub>, CH). *J*<sub>AB</sub> = 14 Hz, *J*<sub>AX</sub>  $\approx$  *J*<sub>BX</sub>  $\approx$  1 Hz; 3.75 s (6H, CH<sub>3</sub>O). IR (cm<sup>-1</sup>): 1710 (CO). Mass spectrum: parent peak at *m/e* = 392, base peak at *m/e* = 196. (Found: C 61.4; H 6.3. Calc. for C<sub>20</sub>H<sub>24</sub>O<sub>8</sub>: C 61.2; H 6.2.)

The tetrahomocubane structure of the compound *3* has been firmly established by single crystal X-ray crystallographic analysis on the corresponding tetracarboxylic acid.<sup>8</sup> The space group is *P*2<sub>1</sub>/*C* and the unit cell dimensions are *a* = 13.83, *b* = 6.54, *c* = 12.90 Å;  $\beta$  = 104.81°.

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