

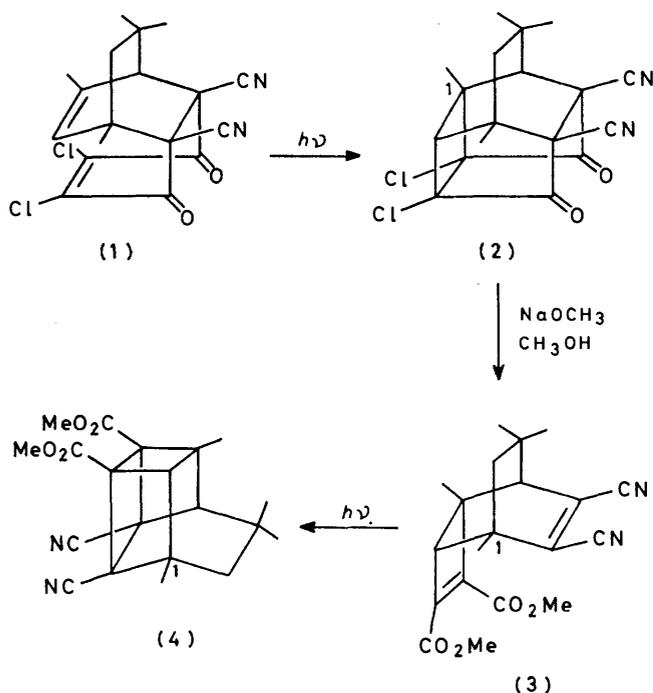
## Cage Compounds. A Ready Synthesis of a Highly Substituted Basketane

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The Diels–Alder adduct, *endo*-2,3-dichloro-4a,8a-dicyano-4a,5,8,8a-tetrahydro-5,7-dimethyl-5,8-(2,2-dimethylethano)-1,4-naphthoquinone (1) undergoes ready intramolecular photocycloaddition to afford 2,7-dichloro-4,5-dicyano-1,9,11,11-tetramethylpentacyclo[6.4.0.0<sup>2,7</sup>.0<sup>4,12</sup>.0<sup>5,9</sup>]dodecane-3,6-dione (2) in 72% yield. Upon treatment with excess of sodium methoxide in refluxing methanol, (2) undergoes a complex sequence of reactions to afford dimethyl 7,8-dicyano-1,5,10,10-tetramethyltricyclo[4.2.2.0<sup>3,5</sup>]deca-3,7-diene-3,4-dicarboxylate (3) in 85% yield. Intramolecular photocycloaddition of (3), affords the basketane, dimethyl 6,7-dicyano-1,3,9,9-tetramethylpentacyclo[4.4.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]decane-4,5-dicarboxylate (4), in 84% yield, thus providing a ready synthesis of a uniquely substituted member of this series.

As a potential source for new, pharmacologically active materials, we have been engaged in the preparation of strained, polyfunctional, polycyclic molecules by thermal and photochemical methods.<sup>1,2</sup> In connection with these studies we report a ready entry into the basketane system.

Recently, Pointer *et al.*<sup>3</sup> reported that the Diels–Alder reaction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 1,3,5,5-tetramethylcyclohexa-1,3-diene affords adduct (1), whose structure was established by



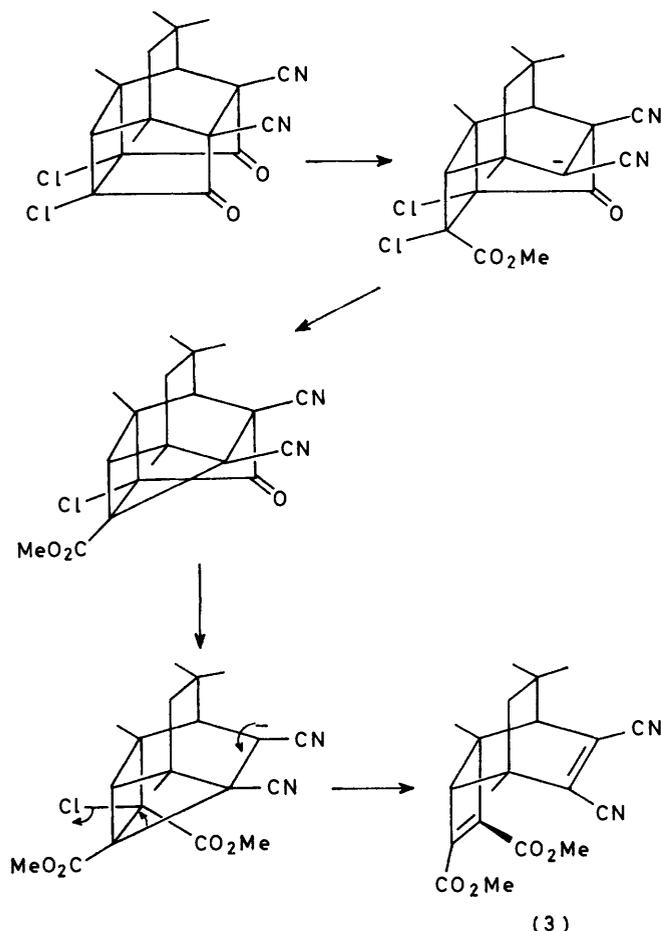
X-ray analysis. This adduct appeared eminently suited for intramolecular photocycloaddition in analogy with the photoreactions established for the cyclopentadiene-1,4-benzoquinone and cyclopentadiene-1,4-naphthoquinone adducts.<sup>4-7</sup> Indeed, photolysis of (1) in acetonitrile proved to be an extremely ready reaction, with (2) precipitating in 72% yield. Spectral and analytical data were in accord with the structural assignment (see Experimental section).

Cage structures related to (2) have been extensively studied recently,<sup>8-10</sup> both as nuclei for chemical modification and as substrates amenable to extensive intramolecular rearrangement. Compound (2) appeared ideally suited for such studies because of its strained skeleton, its high degree of functionalization, and the extremely close juxtaposition of its functional groups. During the course of the study of its chemistry, we discovered that (2), upon treatment with methoxide ion in methanol, underwent an apparent net replacement of its two chloride groups by methoxide groups. Not surprisingly, spectral data suggested that a skeletal rearrangement had also occurred. Based on the accumulated data, we have assigned structure (3) to this product. Its i.r. spectrum ( $\text{CHCl}_3$ ) displayed absorptions at 2220 (conjugated nitrile), 1745 and 1725 (conjugated esters), and 1645  $\text{cm}^{-1}$  (double bond), and its u.v. spectrum showed a shoulder at 247 nm and a peak at 222 nm. By elemental and mass spectral analyses its molecular formula was  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4$ . Of note in the  $^1\text{H}$  n.m.r. spectrum was the presence of two ester methoxy signals at  $\delta$  3.72 and 3.75. The  $^{13}\text{C}$  n.m.r. spectrum ( $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$  internal reference) exhibited two ester carbonyl signals at  $\delta$  161.3 and 160.2 p.p.m. The associated vinyl carbon peaks, C(3) and (4), appeared at  $\delta$  139.8 and 149.3 p.p.m., respectively.<sup>11</sup> Assignments were made by a study of the long range carbon–proton coupling constants. C(3) showed a clear two-bond coupling ( $^2J_{\text{C(3)H(2)}}$ ) of 3.7 Hz, whereas C(4) appeared as a complex multiplet. The remaining vinyl carbons appeared at  $\delta$  133.0 and 129.9 p.p.m. and were assigned to C(7) and (8), respectively. C(7) showed a two-bond coupling ( $^2J_{\text{C(7)H(6)}}$ ) of 5.7 Hz, and C(8) appeared as a multiplet. The nitrile group bound to C(7) ( $^3J_{\text{CH(7)}}$  4.8 Hz) appeared at  $\delta$  114.7 p.p.m. and that bound to C(8), which showed no long-range carbon–hydrogen coupling, at  $\delta$  113.3 p.p.m. In accord with its assigned structure, (3) underwent ready photolysis in acetone to afford the unsymmetrical, highly and uniquely substituted basketane (4) in 84% yield.

No work has been done on the reaction path for the conversion of (2) into (3); however, it is reasonable to assume that the reaction is initiated by attack of methoxide at either of the carbonyl carbons of the  $\alpha$ -cyano-

ketone systems. This results in formation of an ester and a cyano-stabilized anion. Intramolecular displacement of chloride ion gives a highly strained intermediate. A second methoxide addition to the remaining ketone affords a second cyano-stabilized anion. Collapse, as indicated in the Scheme, affords product.

Although the conversion of (1) into (4) involves a complex sequence, the yield of each reaction is good, and substantial quantities of (4) can be readily prepared for



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study. In addition to providing a unique method for the synthesis of a highly substituted basketane, this method illustrates a new use of DDQ as a synthon for the preparation of cage systems. Further work along these lines is in progress.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were obtained with a JEOL C60HL spectrometer. Proton decoupled, single frequency off-resonance decoupled, and gated <sup>1</sup>H coupled <sup>13</sup>C n.m.r. spectra were obtained with a Varian CFT-20 spectrometer. M.p.s are uncorrected.

**2,7-Dichloro-4,5-dicyano-1,9,11,11-tetramethylpentacyclo-[6.4.0.0<sup>2,7</sup>.0<sup>4,12</sup>.0<sup>5,9</sup>]dodecane-3,6-dione (2).**—A solution of (1) (38.5 g, 0.106 mol)<sup>3</sup> in benzene (3 l) was purged with helium for 15 min and then irradiated for 1.25 h with a 450

W Hanovia medium pressure mercury lamp through a Pyrex filter. During the course of the irradiation, the u.v. maximum at 265 nm due to (1) disappeared, and a white precipitate formed. This was filtered, washed with benzene (100 ml) and dried to yield *compound (2)* (27.7 g, 0.076 mol, 72%), m.p. 290–292° (Found: C, 59.2; H, 4.55; Cl, 19.55; N, 7.05%; *M*<sup>+</sup>, 362. C<sub>18</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub> requires C, 59.5; H, 4.45; Cl, 19.5; N, 7.1%; *M*<sup>+</sup>, 362). The <sup>1</sup>H n.m.r. spectrum of (2) taken in [<sup>2</sup>H<sub>6</sub>]DMSO showed two species. The second species was shown to result from hydration of the diketone system due to traces of water present in [<sup>2</sup>H<sub>6</sub>]DMSO. This has already been noted for similar diketones.<sup>4</sup> To simplify the observed spectrum it was run in [<sup>2</sup>H<sub>6</sub>]DMSO-H<sub>2</sub>O to insure complete hydration; thus, the n.m.r. data refer to the bridged hydrate. These observations were confirmed by the <sup>13</sup>C spectral studies on (2); δ([<sup>2</sup>H<sub>6</sub>]DMSO-H<sub>2</sub>O) 1.11, 1.12, 1.25, and 1.33 (12 H, 4 s, 4 × CH<sub>3</sub>), 1.37 (2 H, m, CH<sub>2</sub>), 2.19 (1 H, s, CH), 2.37 (1 H, s, CH), 9.06 (1 H, s, OH), and 9.29 (1 H, s, OH). The <sup>13</sup>C spectrum of (2) run as above, did not show any downfield carbonyl carbons, but displayed resonances at δ 107.1 and 109.5 p.p.m., thus confirming the oxygen-bridged hydrated structure.

**Dimethyl 7,8-Dicyano-1,5,10,10-tetramethyltricyclo[4.2.-2.0<sup>2,5</sup>]deca-3,7-diene-3,4-dicarboxylate (3).**—A solution of (2) (3.63 g, 10.0 mmol) and sodium methoxide (1.08 g, 20.0 mmol) in methanol (100 ml) was refluxed for 2 h and concentrated to dryness at reduced pressure. The residue triturated with water (25 ml), and the resulting insoluble solid was filtered, washed with water (25 ml) and dried at 25° and 1 mmHg to give crude (3) (3.43 g). This was recrystallized from methanol (50 ml) to afford, after drying, pure *product (3)* (3.00 g, 8.47 mmol, 85%), m.p. 165–167°; ν<sub>max</sub> (CHCl<sub>3</sub>) 2 220, 1 745, 1 725, and 1 645 cm<sup>-1</sup>; λ<sub>max</sub> (CH<sub>3</sub>OH) 247sh (ε 7 950) and 222 nm (15 950); δ(CDCl<sub>3</sub>) 0.92, 1.27, and 1.38 (all 3 H, all s, 3 × CH<sub>3</sub>), 1.52 [4 H, s and d, CH<sub>3</sub> and CH (geminal)], 1.62 (1 H, d, *J* 13 Hz), 2.73 (1 H, s, CH), 2.88 (1 H, s, CH), 3.72 (3 H, s, OCH<sub>3</sub>), and 3.75 (3 H, s, OCH<sub>3</sub>) (Found: C, 67.6; H, 6.3; N, 7.55%; *M*<sup>+</sup>, 354. C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub> requires C, 67.8; H, 6.25; N, 7.9%; *M*<sup>+</sup>, 354).

**Dimethyl 6,7-Dicyano-1,3,9,9-tetramethylpentacyclo-[4.4.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]decane-4,5-dicarboxylate (4).**—A solution of (3) 4.00 g, 11.3 mmol in acetone (300 ml) was degassed with nitrogen and irradiated under nitrogen with a 450 W Hanovia medium pressure mercury lamp through a VYCOR® filter for 1 h. The photolysis was followed by t.l.c. [silica gel; ether–light petroleum (1 : 1)] and terminated when no more starting material remained. The solution was concentrated to dryness, flushed with methanol (50 ml) and the residue was recrystallized from methanol (20 ml)–water (8 ml) using activated charcoal (0.2 g) to afford (4) (3.36 g, 9.48 mmol, 84%) as *needles*, m.p. 117–119°; ν<sub>max</sub> (CHCl<sub>3</sub>) 2 240 and 1 740 cm<sup>-1</sup>; δ(CDCl<sub>3</sub>) 0.93 (3 H, s, CH<sub>3</sub>), 1.07 (3 H, s, CH<sub>3</sub>), 1.32 and 1.37 (8 H, s, s, and m, 2 × CH<sub>3</sub> and CH<sub>2</sub>), 2.68br (2 H, s, 2 × CH), and 3.77 and 3.80 (6 H, s, s, 2 × OCH<sub>3</sub>) (Found: C, 67.75; H, 6.1; N, 7.75%; *M*<sup>+</sup>, 354. C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub> requires C, 67.8; H, 6.25; N, 7.9%; *M*<sup>+</sup>, 354).

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