

## Cycloaddition Reactions of Diarylalkylidenecyclopropenes

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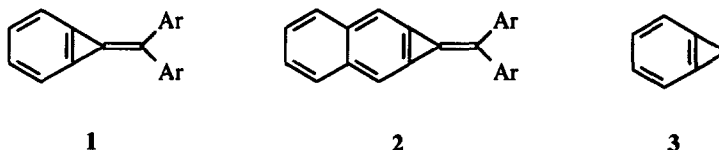
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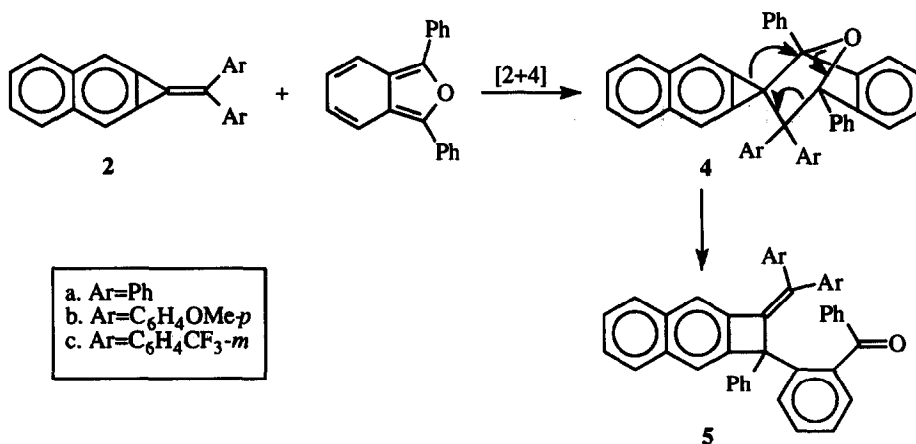
**Abstract:** The reactions of diarylalkylidenecyclopropenes in [2+4] and [2+2] cycloadditions are described.

The alkylidenecyclopropenes, e.g. **1**, **2**, are interesting, highly strained compounds which have attracted considerable current interest.<sup>1-3</sup> They have been thoroughly investigated in regard to their reactions with electrophiles, nucleophiles, oxidizing agents, and organometallic reagents.<sup>4-6</sup> However, there have been no prior reports of cycloaddition reactions employing alkylidenecyclopropenes. This is despite the fact that the analogous cyclopropabenzene **3**, with its HOMO located at the bridge bond,<sup>7</sup> undergoes facile cycloaddition to the internal cyclopropene bond.<sup>8-10</sup> With the high strain present in the methylenecyclopropene system, one might expect both the internal cyclopropene bond and the external double bond to be highly reactive sites. We now wish to report the reactions of **2** in both [2+4] and [2+2] cycloadditions.



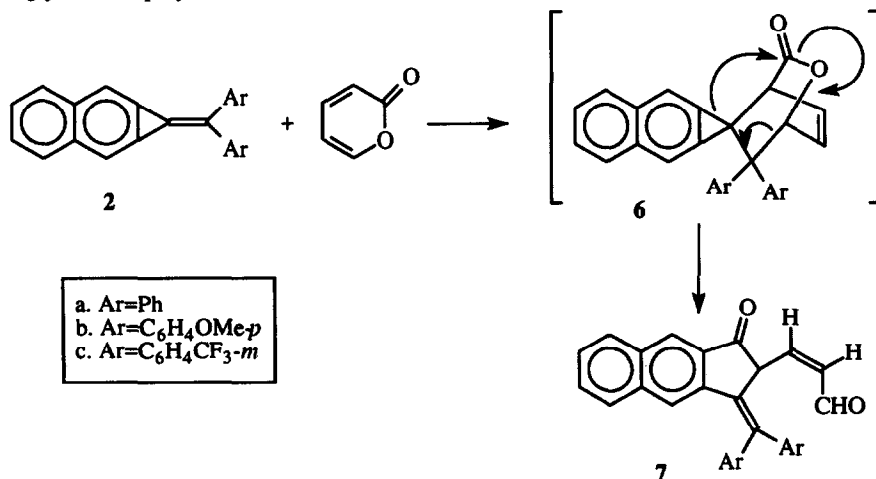
Diarylmethylenecyclopropa[*b*]naphthalene **2** reacts with a variety of dienes. In a typical experiment, the diphenyl derivative **2a** was added to a solution of diphenylisobenzofuran (DPIBF, **2** equivalents) in dry, degassed toluene. The mixture was heated to reflux for several days. After cooling, the solvent was removed, and chromatographic separation gave **5a** in 55% yield. Similarly, **2b,c** and DPIBF provide the cyclobutenes **5b,c** as stable crystalline solids (Scheme 1).<sup>11,12</sup>

The results clearly show that compound **2** resists cycloaddition across the internal bridge bond. Rather, the mechanism likely involves initial [2+4] cycloaddition across the exocyclic double bond to give the highly strained spirocyclopropene **4**. The relief of ring strain appears to dominate here; rearrangement of **4** with concomitant ring expansion provides the observed products (Scheme 1). It is especially notable that the reaction is essentially complete in ~7 h when performed in ethylene glycol. Such a rate increase upon using a hydrophilic solvent has been noted for other inverse electron demand cycloadditions when water is used as the solvent.<sup>13</sup> The yield was affected only slightly (55% to 62% for **2a**).



Scheme 1

The reaction of **2** with  $\alpha$ -pyrone in both toluene and ethylene glycol was also investigated. Typically, **2a** was added to a solution of  $\alpha$ -pyrone (2 equivalents) in the appropriate dry, degassed solvent. The mixture was then heated to 110 °C (several days for toluene, 12 h. for ethylene glycol). After cooling, the solvent was removed, and the crude product chromatographed to yield **7a** (12% in toluene, 50% in ethylene glycol).<sup>11,14</sup> The relief of ring strain also appears to play an important role in the mechanism of formation of **7**. The reaction presumably proceeds via a formal [2+4] cycloaddition to give the highly strained intermediate **6**. This intermediate quickly rearranges (with the migration of the cyclopropenyl  $\sigma$ -bond) to give the cyclopentenone product **7** (Scheme 2). This rearrangement must occur very fast because the customary loss of carbon dioxide common to many pyrone cycloadditions is not observed.<sup>15</sup> Once again, there is a dramatic increase in both the yield and reaction rate when ethylene glycol is employed as the solvent.



Scheme 2



## References and Notes

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11. All new compounds were fully characterized by elemental analysis, mass spectrometry, infrared and multi-nuclear NMR spectroscopy.
12. Selected key spectral data: **5a** (55%) pale yellow crystals, m.p. 124 °C; IR(KBr) 1738 cm<sup>-1</sup> (exocyclic double bond), 1665 cm<sup>-1</sup> (carbonyl); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.1-7.8 (m, aromatic H's); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 198.2 (CO), 163.1, 150.3, 76.1 (3 cyclobutyl C's), and aromatic C's. **5b** (32%) pale orange crystals, m.p. 104 °C; IR 1742 cm<sup>-1</sup>, 1670 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.1-7.9, 3.6 (OMe); <sup>13</sup>C{<sup>1</sup>H} NMR δ 196.3, 161.2, 149.1, 77.2, 53.4 (OMe). **5c** (42%), orange solid, m.p. 98 °C; IR 1737cm<sup>-1</sup>, 1661 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.2-8.0; <sup>13</sup>C{<sup>1</sup>H} NMR δ 199.1, 159.4, 151.3, 79.3.
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14. Results are given for reaction in ethylene glycol. Key spectral data: **7a** (50%) brown solid, m.p. 93 °C; IR (film) 1775 cm<sup>-1</sup>, 1715 cm<sup>-1</sup> (carbonyls); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.48 (CHO), 6.13(d), 6.25(d) (vinyl H and methine H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 193.0 (CHO), 161.3 (CO), 76.7 (sat. ring C) and aromatic C's. **7b** (25%) brown solid, m.p. 101 °C; IR 1773cm<sup>-1</sup>, 1720 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 9.53, 5.98 (d), 5.89 (d), 3.51 (OMe); <sup>13</sup>C{<sup>1</sup>H} NMR δ 189.2, 164.1, 74.6, 51.4 (OMe). **7c** (16%) deep orange solid, m.p. 87-88 °C; IR 1777 cm<sup>-1</sup>, 1718 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 9.71, 6.32 (d), 6.27 (d); <sup>13</sup>C{<sup>1</sup>H} NMR δ 197.3, 159.4, 78.3.
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17. The structure of **12c** was verified by x-ray crystal analysis. Key spectral data: **12a** (53%) white solid, m.p. 125 °C (dec); IR (CCl<sub>4</sub>) 1651 cm<sup>-1</sup> (CO), 1245 cm<sup>-1</sup> (OTf); <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 7.2-8.5 (aromatic), 6.4 (vinyl); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN) δ 195.2 (CO), 52.4 (CH) and aromatic C's. **12b** (39%) pale brown solid, m.p. 97-99 °C (dec); IR 1658 cm<sup>-1</sup>, 1245 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.2-8.5, 6.25; <sup>13</sup>C{<sup>1</sup>H} NMR δ 198.4, 54.5. **12c** (60%) white solid, m.p. 116 °C (dec); IR 1645 cm<sup>-1</sup>, 1245 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.2-8.5, 6.5; <sup>13</sup>C{<sup>1</sup>H} NMR δ 201.0, 57.3.