## Cycloaddition Reactions of Diarylalkylidenecycloproparenes

Aileen T. McNichols, Peter J. Stang\*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

Brian Halton,\* Andrew J. Kay

Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand

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

The alkylidenecycloproparenes, 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 alkylidenecycloproparenes. 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 methylenecycloproparene 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 cyclobutarenes 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 spirocycloproparene 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).





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 cycloproparenyl  $\sigma$ -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

Reactions of 2 via a formal [2+2] cycloaddition route were also investigated. We chose as our reactants the highly electron deficient acetylenic(phenyl)iodonium triflates. The reaction of 2c with one equivalent of the acetylenic *bis*-iodonium salt  $8^{16}$  proceeded at room temperature in dry acetonitrile. After 7 h., the solvent was removed and the crude product recrystallized (CH<sub>2</sub>Cl<sub>2</sub>/hexane) to give 12c in 60% yield.<sup>11,17</sup> Reaction with the less reactive mono-iodonium salt 11 required an elevated temperature (40 °C) and longer reaction times (>24 h.), which caused considerable decomposition of the starting alkynyliodonium triflate and led to much poorer product yields (<15%).

The mechanism of these reactions is much less obvious. Once again, however, the relief of ring strain appears to be a significant factor. We propose that, in the case of the *bis*-iodonium salt, reaction occurs via a formal [2+2] cycloaddition to give the highly strained, extremely moisture sensitive intermediate 9. Reaction with water upon exposure to air, with concomitant cleavage of the cyclopropane bond and elimination of the mono-iodonium acetylide leads to the enol 10 and alkynyliodonium triflate 11 after proton transfer. Tautomerization then leads to the observed product. In the presence of methanol, the intermediate 9 can be trapped as the methyl enol ether 13 (Scheme 3).





The present results serve to demonstrate that alkylidenecyclopropa[b]naphthalenes react readily by way of cycloaddition across the exocyclic double bond. The principle factor controlling product formation in these reactions is the relief of strain in the spirocyclic cycloproparenyl intermediate, thereby providing either ring-expanded or ring-opened products.

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- 11. All new compounds were fully characterized by elemental analysis, mass spectrometry, infrared and multi-nuclear NMR spectroscopy.
- 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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- 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.

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