

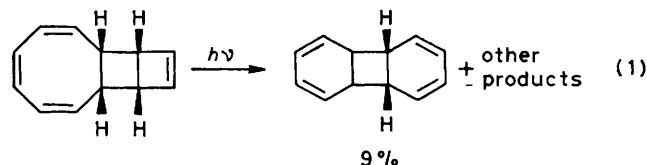
## Syntheses of Cycloadducts of Benzene and Naphthalene

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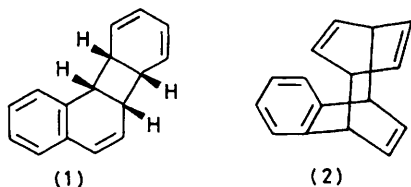
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**Summary** The *oo'*- and *pp'*-cycloadducts between benzene and naphthalene, 6a,6b,10a,10b-tetrahydrobenzo[*a*]-biphenylene (**1**) and 1,4,9,12-tetrahydro-*p*-benzenonaphthalene (**2**) have been synthesized.

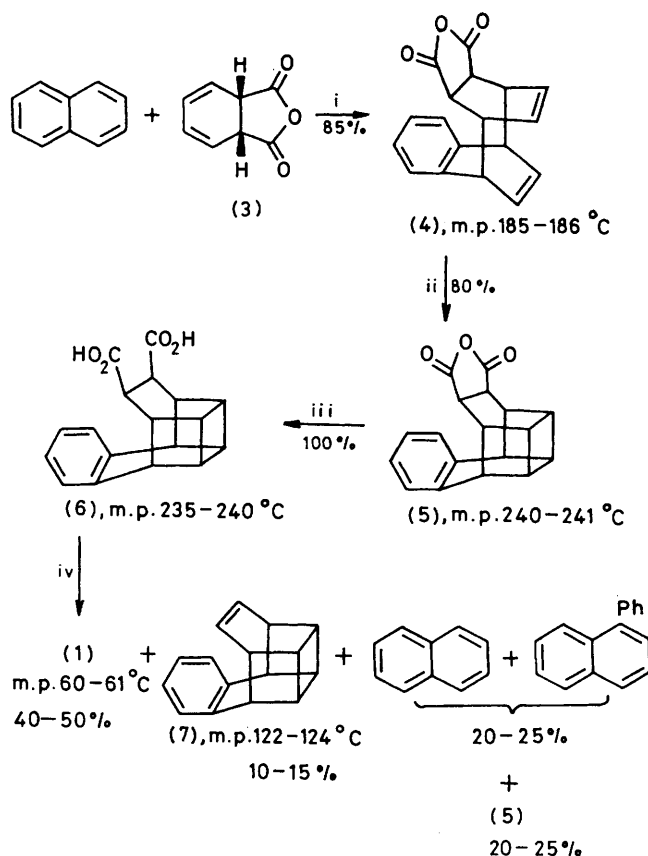
CYCLOADDUCTS of benzenoid hydrocarbons are a group of interesting energy-rich molecules. Their dissociations to aromatic compounds may be treated as retrocycloaddition reactions and are governed by the rule of conservation of orbital symmetry.<sup>1</sup> Although such dissociations are highly exo-energetic, these adducts may be sufficiently stable under



ordinary laboratory conditions if their thermal dissociations cannot proceed *via* a concerted mechanism. Some aromatic compounds, such as anthracenes, and some substituted naphthalenes, undergo photocycloadditions.<sup>2,3</sup> However, for benzene and naphthalene, photocycloaddition does not occur because alternative pathways for the deactivation of their excited states are more favourable. A cycloadduct of benzene was first reported to be formed in very low yield from the photochemical rearrangement of *cis,syn,cis*-tricyclo[8.2.0.0<sup>2,9</sup>]dodeca-3,5,7,11-tetraene (reaction 1),<sup>4</sup> and was prepared later by a directed synthesis.<sup>5</sup> However, no adducts between two different benzenoid hydrocarbons have been reported. We report here the first synthesis of both the *oo'*- (1) and *pp'*-adduct (2) between benzene and naphthalene.†



Cyclohexa-1,3-diene and its derivatives react with many aromatic compounds photochemically to give  $4\pi_s + 4\pi_s$  adducts.<sup>6</sup> Since 1,2-dicarboxylic acids may undergo oxidative bis-decarboxylation to give the corresponding olefin,<sup>7,8</sup> 1,2-dihydrophthalic anhydride (3)<sup>9</sup> may be considered as a 'masked cyclohexa-1,3,5-triene' in organic synthesis. In principle, the photocycloaddition of (3) to an aromatic hydrocarbon followed by hydrolysis and oxidative bis-decarboxylation may yield a cycloadduct of benzene and the aromatic hydrocarbon; therefore, the adduct (4) may be a key intermediate in the synthesis of (1) and (2). However, when the diacid derived from (4) was subjected to oxidative bis-decarboxylation directly under a variety of conditions, it underwent either simple dehydration to give the anhydride (4) or fragmentation to give naphthalene.<sup>10</sup> Compound (2) was not detected among the products. To circumvent this experimental difficulty, (4) was first photocyclized with xanthone as the sensitizer to give the cage product (5) (Scheme 1). When the diacid (6) was treated with lead tetra-acetate under carefully controlled conditions, surprisingly, compound (1) was obtained as the major product, together with the cage



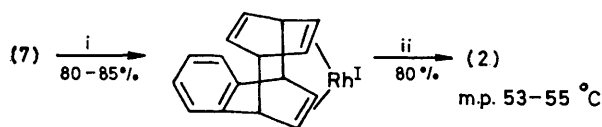
SCHEME 1. Reagents: i,  $h\nu$ , ii,  $h\nu$ , xanthone; iii, 1 M-NaOH; iv,  $\text{Pb}(\text{OAc})_4$ , 72–75 °C, pyridine,  $\text{O}_2$ .

olefin (7), the anhydride (5), and a mixture of naphthalene and 1-phenylnaphthalene. The formation of (1) from (6) may be rationalized by the cleavage of the cage during the bis-decarboxylation followed by a Cope rearrangement, but the exact mechanism is not yet known and is under investigation. Thus, the formation of (1) from naphthalene is achieved in four steps with an overall yield of about 25%. Compound (1) was purified by chromatography on silica gel at 5 °C and the overall yield of the crystalline product from naphthalene is 15%. For the conversion of (5) into (7), the oxidative bis-decarboxylation of (6) with lead tetra-acetate is the method of choice over the electrolytic oxidation of (6)<sup>8</sup> and the direct elimination of  $\text{CO}_2$  and CO from (5) with bis(triphenylphosphine) dicarbonyl nickel.<sup>11</sup>

Compound (2) was synthesized by the method of Halpern, Eaton, *et al.*, who found that a strained cyclobutane may undergo retrocycloaddition with  $\text{Rh}^{\text{I}}$  complexes.<sup>12</sup> When (7) was treated with bis(bicyclo[2.2.1]heptadienyl)rhodium chloride<sup>13</sup> in chloroform, the  $\text{Rh}^{\text{I}}$  complex of (2) was obtained as a yellow precipitate (80–85% yield) from which (2) was regenerated by treatment with triphenyl phosphite (80% yield) (Scheme 2).<sup>14</sup>

Both (1) and (2) are heat-labile compounds and their chemical behaviour is under investigation.

† All new products reported in this communication have been characterized by elemental analysis, and n.m.r., i.r., u.v., and mass spectroscopy.

SCHEME 2. Reagents: i, RhI; ii, (PhO)<sub>3</sub>P.

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- <sup>1</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.
- <sup>2</sup> J. K. McVey, D. Shold, and N. C. Yang, *J. Chem. Phys.*, 1976, **65**, 3375.
- <sup>3</sup> W. H. F. Sasse, T. Teitei, and D. Wells, *Tetrahedron Letters*, 1974, 367 and references therein.
- <sup>4</sup> G. Schröder, W. Martin, and H. Röttele, *Angew. Chem. Internat. Edn.*, 1969, **8**, 69.
- <sup>5</sup> J. A. Berson and R. F. Davis, *J. Amer. Chem. Soc.*, 1972, **94**, 3654.
- <sup>6</sup> N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *J. Amer. Chem. Soc.*, 1975, **97**, 5006; N. C. Yang, C. V. Neywick, and K. Srinivasachar, *Tetrahedron Letters*, 1975, 4313.
- <sup>7</sup> R. A. Sheldon and J. K. Kochi, *Org. Reactions*, 1972, **19**, 279.
- <sup>8</sup> E.g. P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Letters*, 1968, 5117; H. H. Westberg and H. J. Dauben, Jr., *ibid.*, p. 5123.
- <sup>9</sup> R. M. McDonald and C. E. Reinecke, *Org. Synth.*, 1970, **50**, 50.
- <sup>10</sup> K. Srinivasachar, Ph.D. Thesis, University of Chicago, 1975.
- <sup>11</sup> B. M. Trost and F. Chan, *Tetrahedron Letters*, 1971, 2603; W. G. Dauben, G. T. Rivers, R. J. Tweig, and W. T. Zimmerman, *J. Org. Chem.*, 1976, **41**, 887.
- <sup>12</sup> J. Halpern, M. Sohn, and J. Blum, *J. Amer. Chem. Soc.*, 1979, **101**, 2694; L. Cassar, J. Halpern, and P. E. Eaton, *ibid.*, 1970, **92**, 3515.
- <sup>13</sup> G. Wilkinson, E. W. Abel, and M. A. Bennett, *J. Chem. Soc.*, 1959, 3178.
- <sup>14</sup> L. M. Haines, *Inorg. Chem.*, 1970, **9**, 1517.