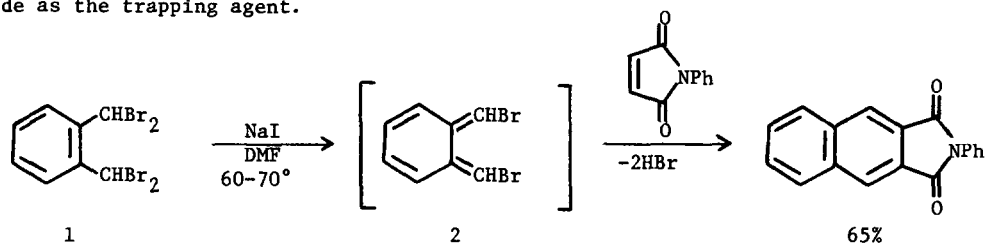


GENERATION AND DIELS-ALDER REACTIONS OF  $\alpha'$ -BROMO-1,2-NAPHTHOQUINODIMETHANE.  
A NEW PHENANTHRENE SYNTHESIS

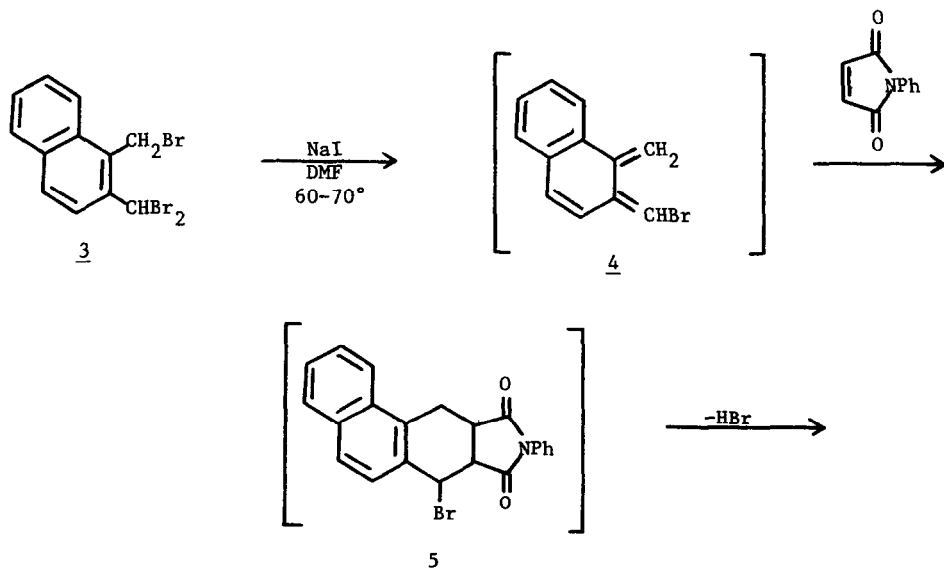
Gordon W. Gribble,<sup>1</sup> Edward J. Holubowitch, and Michael C. Venuti  
Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

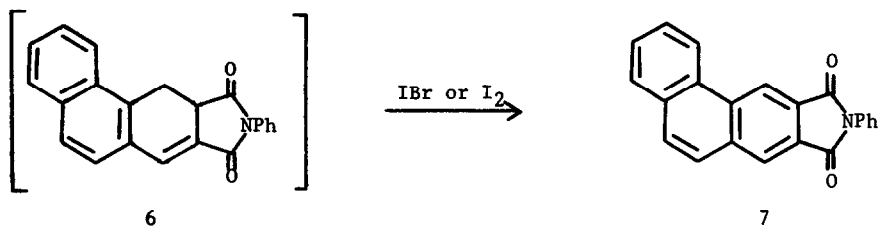
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In 1959 Cava reported<sup>2</sup> that  $\alpha,\alpha'$ -dibromo-*o*-quinodimethane (2), generated by treatment of  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene (1) with NaI in warm DMF, could be trapped by dienophiles to give 2,3-disubstituted naphthalenes. Cava's scheme is shown below with *N*-phenylmaleimide as the trapping agent.



We now describe an extension of Cava's method to the synthesis of phenanthrenes, using not 1,2-bis(dibromomethyl)naphthalene, which apparently cannot easily be prepared, but rather 1-bromomethyl-2-dibromomethylnaphthalene (3).<sup>3</sup> Our results are summarized in the Table. For example, reaction of 3 with NaI/DMF in the presence of *N*-phenylmaleimide leads to *N*-phenyl-2,3-phenanthrenedicarboximide (7) in 75% yield. A plausible reaction sequence is shown below.





The sequence presumably involves generation of  $\alpha'$ -bromo-1,2-naphthoquinodimethane (4), trapping of 4 with a dienophile giving 5, loss of HBr giving 6, and oxidation of 6 (or its double bond isomer) with the IBr (or  $\text{I}_2$ ) that was liberated in the first step. This final oxidation step is the key feature of this sequence: it obviates the need for preparing the bis(dibromomethyl)naphthalene, as in the original Cava scheme,<sup>2</sup> and avoids "wasting" the halogen produced in the first step.

Cava has generated the parent 1,2-naphthoquinodimethane from 1,3-dihydronaphtho[1,2-c]-thiophene 2,2-dioxide, but a separate oxidation step (i.e., Pd/C,  $360^\circ$ ) is necessary to convert the Diels-Alder adduct to a phenanthrene. In this fashion Cava prepared 7 in 16% yield from 1,2-dimethylnaphthalene.<sup>5</sup>

The availability of 3 from either 1,2-dimethylnaphthalene<sup>3</sup> or 2-methylnaphthalene (as shown below) makes this route attractive for the synthesis of 2,3-disubstituted phenanthrenes and phenanthrene-containing polycyclic aromatic quinones illustrated by the examples in the Table.

Finally, we have established that the Ried and Bodem tribromo product is 1-bromomethyl-2-dibromomethylnaphthalene (3), and not 1-dibromomethyl-2-bromomethylnaphthalene, by conversion to 4,5-benzophthalide (8)<sup>4</sup> (mp  $120\text{--}120.5^\circ$ ; lit.<sup>4</sup> mp  $117.5^\circ$ ), and not to 6,7-benzophthalide (lit.<sup>4</sup> mp  $154.5\text{--}155^\circ$ ), as shown below. Presumably, unfavorable interaction with H-8 prevents dibromination of the C-1 methyl group.

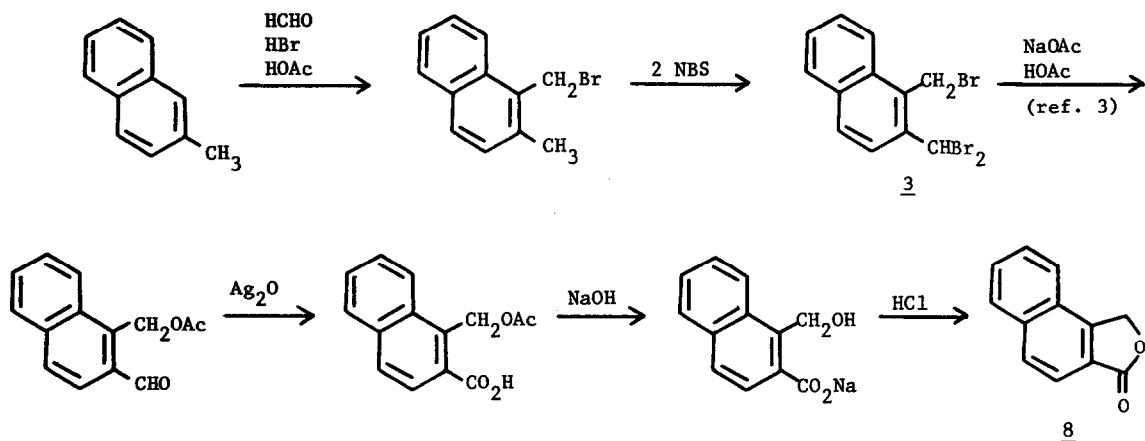
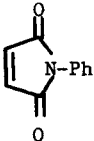

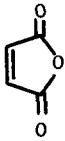
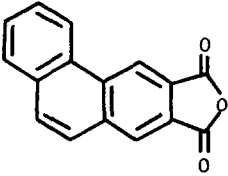
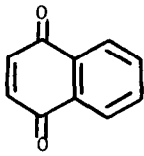
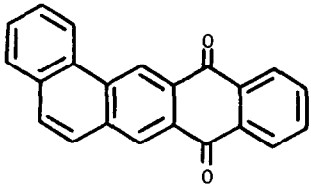
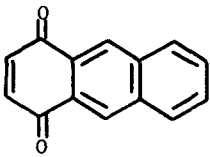
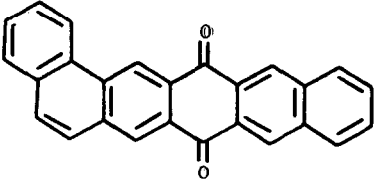
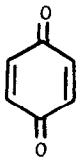
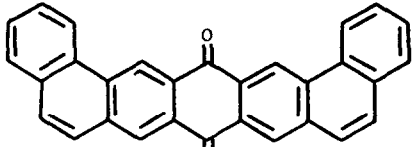
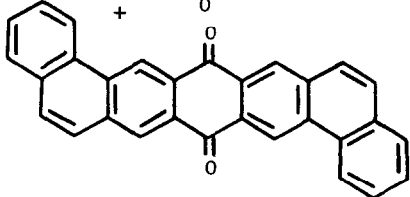


Table. Reactions of 1-Bromomethyl-2-dibromomethylnaphthalene (3) with NaI/DMF/  
60-70° in the Presence of Dienophiles<sup>6</sup>

Dienophile	Product	mp	Yield, % <sup>7</sup>
		257-259° (lit. <sup>5</sup> 259-260°)	75
		275-276° <sup>8</sup>	76
		280° <sup>9</sup> (lit. <sup>10</sup> 272-273°)	47
		341° <sup>11</sup>	60
		378° <sup>12</sup> , >400° <sup>12</sup> (lit. <sup>13</sup> 437-438°)	20
(0.5 equiv.)			

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#### References and Notes

1. To whom inquiries should be directed. Recipient of a Public Health Service Research Career Development Award (1 KO4-23756) from the National Institute of General Medical Sciences, 1971-1976.
2. M.P. Cava, A.A. Deana, and K. Muth, *J. Amer. Chem. Soc.*, **81**, 6458 (1959).
3. W. Ried and H. Bodem, *Ber.*, **89**, 708 (1956). These workers reported that 1,2-bis(bromomethyl)naphthalene with 2 equiv. of NBS gave a tribromo product, mp 136°. We have repeated this reaction and have determined that the product is **3**, mp 132-132.5° (CHCl<sub>3</sub>). Compound **3**: nmr,  $\delta$ (CDCl<sub>3</sub>) 5.1 (s, 2H), 7.2-8.3 ppm (m, 7H). Analysis of **3**: calcd for C<sub>12</sub>H<sub>9</sub>Br<sub>3</sub>: C, 36.68; H, 2.31; found: C, 36.72; H, 2.28; C<sub>12</sub>H<sub>9</sub>Br<sub>3</sub>: m/e calcd 389.82542; m/e found: 389.82546.
4. J.H. Brewster and A.M. Fusco, *J. Org. Chem.*, **28**, 501 (1963). We thank Professor Brewster for infrared spectra of the isomeric benzophthalides.
5. M.P. Cava, R.L. Shirley, and B.W. Erickson, *J. Org. Chem.*, **27**, 755 (1962).
6. Standard reaction conditions: a mixture of **3** (3 mmol), dienophile (3-4 mmol), and NaI (15-20 mmol) in DMF (10 ml) is heated at 60-70° for 20-30 hr. The cooled solution is poured into H<sub>2</sub>O (125 ml), decolorized with aq NaHSO<sub>3</sub>, and the solids collected. Purification is accomplished by sublimation and/or recrystallization.
7. Yield refers to isolated material obtained after sublimation and/or recrystallization of the crude product.
8. The product (2,3-phenanthrenedicarboxylic acid anhydride) was recrystallized from acetic anhydride; this material (ir (KBr) 1830, 1780 cm<sup>-1</sup>) was converted to **7** in 81% yield upon treatment with aniline in boiling xylene.
9. The product (1,2-benzotetracene-6,11-quinone) was recrystallized from acetic acid; C<sub>22</sub>H<sub>12</sub>O<sub>2</sub>: m/e calcd 308.08373; m/e found 308.08582.
10. E. Clar, *Ber.*, **62**, 1574 (1929).
11. The product (1,2-benzopentacene-6,13-quinone) was sublimed and recrystallized from chlorobenzene; C<sub>26</sub>H<sub>14</sub>O<sub>2</sub>: m/e calcd 358.09938; m/e found 358.09956.
12. This is probably a mixture of 1.2,8.9- and 1.2,10.11-dibenzopentacene-6,13-quinone (not separated); C<sub>30</sub>H<sub>16</sub>O<sub>2</sub>: m/e calcd 408.1150; m/e found 408.1180.
13. E. Clar, *Ber.*, **76**, 257 (1943); who prepared only the 1.2,8.9 isomer.