

$^1J_{PC} = 61.5$  Hz,  $PCH_3$ ), 25.6 (d,  $^1J_{PC} = 57.3$  Hz, C-2), 37.6 (d,  $^2J_{PC} = 8.6$  Hz, C-3), 45.3 (d,  $^1J_{PC} = 67.5$  Hz, C-7a), 77.9 (d,  $^2J_{PC} = 10.4$  Hz, C-3a);  $^{31}P$  NMR  $\delta$  73.2.

**Synthesis and Hydrolysis of 1-Bromo-1-methyl-3,4-epoxyphospholanium Bromide.** To a solution of *syn*-1-methyl-3,4-epoxyphospholane (17; 5.0 g, 0.043 mol) in 200 mL of cyclohexane at 0 °C was added a solution of bromine (6.9 g, 0.043 mol) in 100 mL of cyclohexane. The resulting slurry was stirred for 0.5 h and then filtered ( $N_2$ ). The solid was washed with cyclohexane and then added in portions to a slurry of ice in  $NaHCO_3$  solution. The solution was extracted continuously with  $CH_2Cl_2$  for 24 h, and the extract was dried ( $MgSO_4$ ) and stripped to a solid mixture (3.1 g, 55%) of epoxyphospholane oxides 4 (90% by  $^{31}P$  NMR) and 4a (10%). Spectral properties of the latter are included in Table II.

**Synthesis of a Mixture of Epoxyphosphines 17 and 17a.** A 2.0-g sample of the mixed epoxyphospholane oxides 4 (90%) and 4a (10%) prepared in the preceding experiment was reduced with phenylsilane as described for the synthesis of 17. The product was a mixture of phosphines 17 (90%) and 17a (10%; spectral data are given in Table II).

**Quaternization of Epoxyphosphines with Deuteriomethyl Iodide.** A 0.8-g (6.9 mmol) sample of 17 in benzene was treated

with  $CD_3I$  (1.0 g, 6.9 mmol) and the precipitated salt recrystallized from ether-methanol; mp 195–198 °C. Its  $^{13}C$  NMR spectrum ( $CH_3OH$ ) contained a single  $P-CH_3$  signal at  $\delta$  13.9 (d,  $^1J_{PC} = 50$  Hz), a C-2,5 signal at  $\delta$  28.4 (d,  $^1J_{PC} = 54$  Hz), and a C-3,4 signal at  $\delta$  59.5 (d,  $^2J_{PC} = 2$  Hz).

Anal. Calcd for  $C_6H_9D_3IOP$ : C, 27.60; H and D, 5.78; P, 11.86. Found: C, 27.71; H and D, 5.31; P, 11.53.

Similarly, the deuteriomethyl salt was formed from the mixture of isomeric phosphines 18. Its  $^{13}C$  NMR spectrum contained only one  $P-CH_3$  signal,  $\delta$  13.4 (d,  $^1J_{PC} = 50.5$  Hz).

**Registry No.** 3, 930-38-1; 4, 61247-91-4; 4a, 61183-63-9; 5a, 57065-62-0; 5b, 57065-63-1; 6a, 74958-57-9; 6b, 74958-58-0; 7, 65482-10-2; 8, 74925-19-2; 9, 65489-18-1; 10, 74925-20-5; 11, 57065-64-2; 12, 74925-21-6; 13, 74925-22-7; 14, 74925-23-8; 15, 74925-24-9; 16, 74925-25-0; 17, 61183-59-3; 17a, 61217-62-7; 18 ( $\alpha$ -H isomer), 74958-59-1; 18 ( $\beta$ -H isomer), 61183-60-6; 19, 74925-26-1; 20, 61183-61-7; 21, 74925-27-2; 21a, 74925-28-3; 22, 74925-29-4; 23, 74925-30-7; 26, 51015-54-4; 27a, 74925-31-8; 27b, 74958-60-4; 28, 74925-32-9; 29, 74925-33-0; 30a, 74925-34-1; 31a, 74925-35-2; 31b, 74958-61-5; 31c, 74958-62-6; 1-vinylcyclohexene, 2622-21-1; 1-vinylcyclopentene, 28638-58-6; 1,2-dimethylenecyclohexane, 2819-48-9; 1,2-dimethylenecyclopentane, 20968-70-1;  $CH_3PCl_2$ , 676-83-5;  $PCl_3$ , 7719-12-2; pyrrolidine, 123-75-1; cyclohexylamine, 108-91-8.

## Photochemical Reactions of Duroquinone with Cyclic Polyenes. Synthesis of New Cage Compounds

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Photoinduced cycloadditions of duroquinone to cyclic trienes and cyclooctatetraene have been studied. When irradiated in the presence of cycloheptatriene, duroquinone afforded two kinds of 1:1 and 2:1 cage products: pentacyclo[7.4.0.0<sup>2,8</sup>.0<sup>4,12</sup>.0<sup>5,11</sup>]tridec-6-ene-3,13-dione (3) and a more complex cage compound 4, by way of the intermediate [2 + 2] cycloadduct 9. Duroquinone with ethyl bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate produced a 1:1 cage adduct 14 via its valence isomer, a bicyclo[4.3.0]nona-2,5,7-triene derivative. Cyclooctatetraene did not react directly with duroquinone, but a caged dihydrobullvalene (18) was obtained by photolysis with the 76 °C melting dimer of COT. Structural and mechanistic investigations of the formations of these new cage compounds have been carried out.

*p*-Quinones afford cycloadducts upon irradiation in the presence of alkenes and alkynes.<sup>1</sup> Formation of both oxetanes<sup>2</sup> and cyclobutanes<sup>3</sup> has been observed, depending on the substituents present in the quinone. From theoretical and experimental investigations,<sup>4</sup> *p*-benzoquinone is thought to react from a triplet  $n,\pi^*$  excited state to yield exclusively oxetane adducts, while its tetramethyl or tetrachloro derivative, duroquinone or chloranil, whose lowest triplet should be  $\pi,\pi^*$ ,<sup>5</sup> affords only cyclobutanes. These photocyclizations are one of the most convenient methods

for synthesis of cage compounds which are a group of interesting energy-rich molecules.<sup>6</sup>

The photodimerization of certain *p*-quinones occurs to give pentacyclo[6.4.0.0<sup>2,7</sup>.0<sup>4,11</sup>.0<sup>5,10</sup>]dodeca-3,6,9,12-tetraone derivatives either in solution or in the solid phase.<sup>7</sup> The photochemical cyclizations of duroquinones to cyclohexa-1,3-dienes,<sup>3b</sup> bicyclo[2.2.1]hepta-2,5-diene,<sup>3b</sup> and related dienes<sup>8</sup> afford several types of cage adducts via double [2 + 2] cyclizations. Also the endo Diels-Alder adducts of *p*-benzoquinone derivatives with cyclic<sup>9</sup> and acyclic 1,3-dienes<sup>10</sup> are well-known to give cage products

(1) J. M. Bruce in "The Chemistry of the Quinonoid Compounds", S. Patai, Ed., Wiley-Interscience, New York, 1974, Part 1, p 478.

(2) D. Bryce-Smith, G. I. Fray, and A. Gilbert, *Tetrahedron Lett.*, 3471 (1964); H. E. Zimmerman and L. Craft, *ibid.*, 2137 (1964); M. E. Kuehe and H. Linde, *J. Org. Chem.*, 37, 4031 (1972); A. Hassner and D. J. Blythin, *ibid.*, 37, 4209 (1972).

(3) (a) G. O. Schenck, I. Hartman, and W. Metzner, *Tetrahedron Lett.*, 347 (1965); (b) G. Koltzenburg, K. Kraft, and G. O. Schenck, *ibid.*, 353 (1965); (c) C. H. Krauch and S. Fraid, *Chem. Ber.*, 100, 1685 (1967).

(4) N. J. Bunce, J. E. Ridley, and M. C. Zerner, *Theor. Chim. Acta*, 45, 283 (1977).

(5) W. Herre and P. Weis, *Spectrochim. Acta, Part A*, 29, 203 (1973); D. R. Kemp and G. Porter, *Proc. R. Soc. London, Ser. A*, 326, 117 (1971).

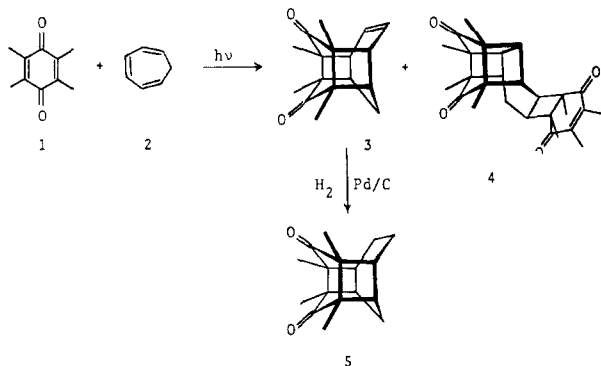
(6) A. Greenberg and J. F. Liebman in "Strained Organic Molecules", Academic Press, New York, 1978, p 228.

(7) W. Flaig, J. C. Salfeld, and A. Llanos, *Angew. Chem.*, 72, 110 (1960); D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 2428 (1964), and references cited therein.

(8) G. Koltzenburg, P. G. Fuss, S.-P. Mannsfeld, and G. O. Schenck, *Tetrahedron Lett.*, 1861 (1966); W. Hartmann H.-G. Heine, and L. Schrader, *ibid.*, 883 (1974).

(9) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964); P. E. Eaton and S. A. Cereface, *J. Chem. Soc. D*, 1494 (1970); J. C. Barboak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, 88, 1328 (1966).

Scheme I



upon photolysis via internal [2 + 2] cycloadditions.

In connection with our studies of different reactivities and regioselectivities in the photochemical reactions of quinone derivatives with various olefinic functions,<sup>11</sup> we were interested in comparing the reactions of duroquinone and conjugated cyclic polyenes with that of *p*-benzoquinone and report a successful synthesis of new cage compounds.<sup>12</sup>

## Results and Discussion

**Photoreactions of Duroquinone with Cyclic Trienes.** The photochemical addition reactions of *p*-benzoquinone and 1,4-naphthoquinone with cyclohepta-1,3,5-triene (2) are known to yield [2 + 6] and/or [2 + 2] carbonyl and ene-cycloadducts.<sup>13</sup> For chloranil, the lowest triplet state may contain both  $n, \pi^*$  and  $\pi, \pi^*$  character, since with *cis*-cyclooctene it yields both the spirooxetane and the biscyclobutane.<sup>3a</sup> However no formation of cycloadducts has been found in the photolysis of chloranil with cycloheptatriene.<sup>13</sup>

The lowest triplet state of duroquinone appears to be entirely of  $\pi, \pi^*$  character, since with a variety of alkenes it yields cyclobutanes exclusively.<sup>3,4</sup> Thus, we used duroquinone for the photoreactions with cyclic trienes.

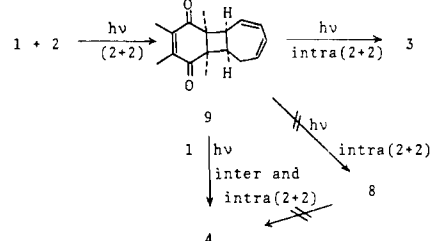
On irradiation of a benzene solution of duroquinone (1) and cyclohepta-1,3,5-triene (2) (air or  $N_2$ , Pyrex filter), two products, 1:1 adduct 3 (colorless needles; mp 155–158 °C;  $C_{17}H_{20}O_2$ ; mass spectrum,  $m/e$  256 ( $M^+$ )) and 2:1 adduct 4 (colorless cubes; mp 288–291 °C;  $C_{27}H_{32}O_4$ ; mass spectrum,  $m/e$  420 ( $M^+$ )) were isolated by silica gel chromatography (Scheme I).

The structure of the photoproduct 3 was suggested by the following partial spectroscopic data: a 1690- $cm^{-1}$  carbonyl IR absorption, a two-proton vinyl hydrogen multiplet centered at  $\delta$  (CDCl<sub>3</sub>) 6.0, and two different carbonyl carbons at  $\delta$  (CDCl<sub>3</sub>) 213.8 and 206.1 in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The <sup>13</sup>C NMR spectrum of 3 consists of only ten peaks for the 17 carbons and the <sup>1</sup>H spectrum also suggested the presence of a plane of symmetry; the structure assigned was 1,2,4,12-tetramethylpentacyclo[7.4.0.0<sup>2,8</sup>.0<sup>4,12</sup>.0<sup>5,11</sup>]trideca-6-ene-3,13-dione (3).

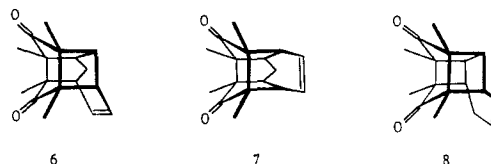
Table I. Photoreaction of Duroquinone (1) with Cyclohepta-1,3,5-triene (2)

molar ratio 1:2	irradiation time, h	products, % yield			
		recovered 1	9	3	4
1:1	72	10	0	10	62
1:2	72	23		24	36
1:10	72	0		36	18
1:10	30	29	15	33	15
1:10	10	56	10	6	5

Scheme II



From these data, the possibilities of structures such as 6–8 were ruled out.



Catalytic hydrogenation of 3 over palladium on charcoal gave pentacyclo[7.4.0.0<sup>2,8</sup>.0<sup>4,12</sup>.0<sup>5,11</sup>]trideca-3,13-dione (5) (colorless needles; mp 104–106 °C; IR  $\nu_{C=O}$  1690 (sh) and 1680  $cm^{-1}$ ) in 95% yield.

The structure of the photoproduct 4 rests in part on IR carbonyl absorptions at 1735, 1690, and 1660  $cm^{-1}$ . The <sup>1</sup>H NMR spectrum, while complex, supports the assigned structure with no vinyl hydrogen signals. The <sup>13</sup>C NMR data also suggest that this material (4) has a five-membered ring, a greater than six-membered carbonyl function ( $\delta$  218.2 and 212.5), and a cyclohexene-1,4-dione chromophore ( $\delta$  200.8, 199.3, 145.7, and 144.8) and indicate the presence of the cage structure. From these data, the caged skeleton of this adduct 4 should be quite different from that of the 1:1 cage product 3. Obviously the 2:1 adduct 4 did not arise from the photoreaction of the photoproduct 3 with duroquinone.

The product ratio of 3:4 was depended upon the initial molar ratio of duroquinone (1) and cycloheptatriene (2) but did not vary with irradiation time. Molar ratios, irradiation times, and yields of the products are summarized in Table I. No thermal reaction of duroquinone with 2 was observed on refluxing the two compounds in benzene for 50 h.

After a short time of irradiation of 1 with 2, and intermediate product could be observed by TLC measurement. Repeated chromatography on a short silica gel column yielded [2 + 2] cycloadduct 9, which was difficult to purify because of its thermal instability. The structure of cycloadduct 9, an unstable pale yellow oil, was indicated by the spectral data: IR carbonyl absorption at 1660  $cm^{-1}$  and a four-proton 1,3-diene hydrogen multiplet at  $\delta$  5.7–6.0. The *cis,cis* structure of 9 is needed for the next intramolecular [2 + 2] cyclization to 3, and this type of adduct formation is known in the photochemical cycloaddition of duroquinone with olefins.<sup>3a,b</sup>

The formation of the photoproduct 3 could be detected by TLC and <sup>1</sup>H NMR measurements after irradiation of

(10) J. R. Scheffer and B. M. Jennings, *J. Chem. Soc., Chem. Commun.*, 609 (1975).

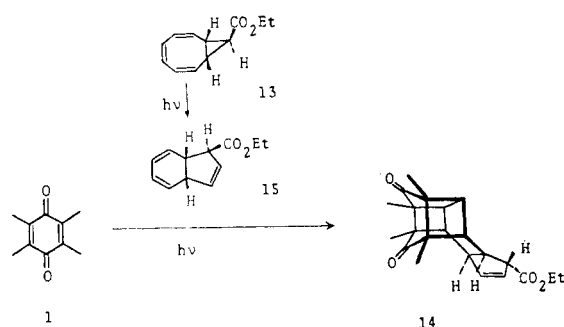
(11) K. Ogino, S. Yamashina, T. Matsumoto, and S. Kozuka, *J. Chem. Soc., Perkin Trans. 1*, 1552 (1979); K. Ogino, T. Matsumoto, and S. Kozuka, *J. Chem. Soc., Chem. Commun.*, 643 (1979); K. Ogino, T. Matsumoto, T. Kawai, and S. Kozuka, *ibid.*, 644 (1979); *J. Org. Chem.*, **44**, 3352 (1979).

(12) K. Ogino, T. Minami, and S. Kozuka, *J. Chem. Soc., Chem. Commun.*, 480 (1980).

(13) A. Mori and H. Takeshita, *Chem. Lett.*, 599 (1975); G. O. Schenck, E. K. von Gustrf, B. Kim, G. v. Bünau, and G. Pfundt, *Angew. Chem., Int. Ed. Engl.*, **1**, 516 (1962).

(14) T. Mukai, T. Tezuka, and Y. Akasaki, *J. Am. Chem. Soc.*, **88**, 5025 (1966); T. Tezuka, A. Akasaki, and T. Mukai, *Tetrahedron Lett.*, 1397, 5003 (1967); A. S. Kende, *J. Am. Chem. Soc.*, **88**, 5026 (1966).

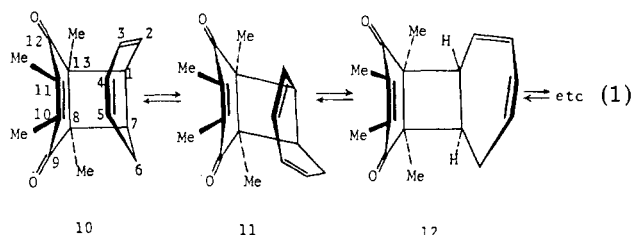
Scheme III



isolated cycloadduct **9** containing some impurities. Also the 1:1 and 2:1 adducts **3** and **4** were isolated after photoreaction of this intermediate adduct **9** with duroquinone. These results suggested that the [2 + 2] cycloadduct **9** should be the common intermediate for the formations of the photoproducts **3** and **4** (Scheme II).

If the photoproduct **4** came from the photocyclization of duroquinone with **9** through the competitive intramolecular [2 + 2] cyclizations of **9** to **3** and **8**, the product ratio of **3**:**4** should be identical in spite of the initial molar ratio of 1:2. However, the competitive intra- and intermolecular photocyclizations of this intermediate **9** were suggested by the change of the product ratio depending upon the initial molar ratio.

The conformational equilibrium ( $10 \rightleftharpoons 11 \rightleftharpoons 12 \rightleftharpoons \text{etc.}$ ) of the intermediate **9** may be expected as shown in eq 1.



As a result, the alternative process of intramolecular [2 + 2] cyclization to give **3**, not **8**, is observed from the intermediate **9** through the overlaps of the proximate and favorably disposed  $\pi$  orbitals on C-4,5 and C-10,11. It seems likely that cage-product formation originates from conformation **10** since the only alternative, conformation **11**, to afford **8** is disfavored by cyclobutane ring twisting.

In a competitive intermolecular process, double [2 + 2] photocycloadditions of duroquinone (**1**) to the cycloheptadiene moiety (C-2,3 and C-4,5 double bonds) of the intermediate adduct **9** should produce the 2:1 cage product **4**, as in the photoreactions of duroquinone with cyclohexa-1,3-diene functions; see later experiments. A more facile steric approach of duroquinone to the diene function should be expected in conformation **12** compared with conformations **10** and **11**.

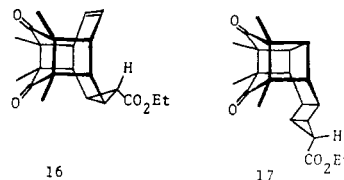
Therefore, the use of a large excess of cycloheptatriene (**2**) should lead to greater amounts of the 1:1 cage product **3**.

The photoreaction of duroquinone with cyclohepta-2,4,6-trienone (tropone) was tried, but only formation of dimers of tropone and recovery of duroquinone was observed.

The next approach to a cyclic triene was done with ethyl bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate (**13**).<sup>15</sup> On irradiation of duroquinone **1** with **13** under similar con-

ditions, the 1:1 adduct **14** (colorless needles; mp 88–91 °C) was obtained in 85% yield (Scheme III).

The photoadduct **14** showed ester and carbonyl functions at 1730 and 1690  $\text{cm}^{-1}$  in its IR spectrum. The spectral data of **14** indicate an asymmetrical structure, not **16** or **17**, and suggest the absence of a cyclopropane ring system.



The  $^1\text{H}$  NMR spectrum of **14** shows resonance signals at  $\delta(\text{CDCl}_3)$  1.13 (Me, s), 1.15 (Me, s), 1.21 (2 Me, s), 1.26 (Me, t,  $J = 7.5$  Hz), 2.5–2.9 (6 H, m), 3.1–3.4 (1 H, m), 4.14 ( $\text{CH}_2$ , q,  $J = 7.5$  Hz), and 5.4–5.8 (2 H, m). The  $^{13}\text{C}$  NMR indicates two carbonyl functions at  $\delta$  218.0 (s, five-membered  $\text{C}=\text{O}$ ) and 208.7 (s, greater than six-membered  $\text{C}=\text{O}$ ), an ester carbonyl at 173.6 (s), and olefinic carbons at 135.3 (d) and 128.6 (d). The  $^{13}\text{C}$  NMR carbonyl and other signals are quite similar to those of **4** and **18**, shown later, and suggest the presence of a cage structure in **14**.

The cage structure and the disappearance of the cyclopropane moiety in **14** suggested that double [2 + 2] photocycloaddition of duroquinone and a photochemical and/or thermal isomerization of the cyclopropane ring had occurred in the formation of the adduct **14**. The photochemical and thermal isomerizations of bicyclo[6.1.0]nona-2,4,6-triene derivatives are known to give tricyclo[4.3.0.0<sup>7,9</sup>]nona-2,4-diene,<sup>16</sup> cyclonona-1,3,5,7-tetraene,<sup>17</sup> bicyclo[4.3.0]nona-2,4,7-triene,<sup>18</sup> bicyclo[5.2.0]nona-2,4,8-triene,<sup>17</sup> and bicyclo[4.2.1]nona-2,4,6-triene isomers.<sup>19</sup> The photoisomerization of **13** to ethyl bicyclo[4.3.0]nona-2,4,7-triene-9-carboxylate (**15**)<sup>18</sup> was found after an irradiation of a benzene solution of **13** under similar conditions for 30 h. Isomerized triene **15** was irradiated in the presence of duroquinone (**1**) to afford the same photoadduct **14** in good yield, as was obtained by the photoreaction of **1** with **13**. Therefore, the first step for this photoreaction of duroquinone with **13** should be a photoinduced valence isomerization of **13** to **15**, and then double [2 + 2] photocycloaddition of duroquinone to **15** should produce the adduct **14**, like the photoreaction of duroquinone with cyclohexa-1,3-diene derivatives.<sup>3b</sup> Thus only the assigned structure is reasonable for the product **14** of this reaction.

**Photoreaction of Duroquinone with Cyclooctatetraene.** We extended our interest in the photoreaction of duroquinone with cyclic trienes to that with tetraenes. It is known that the laser-initiated photoreaction of *p*-benzoquinone with cyclooctatetraene (COT) leads to the formation of a 1:1 [2 + 4] carbocycloadduct.<sup>20</sup>

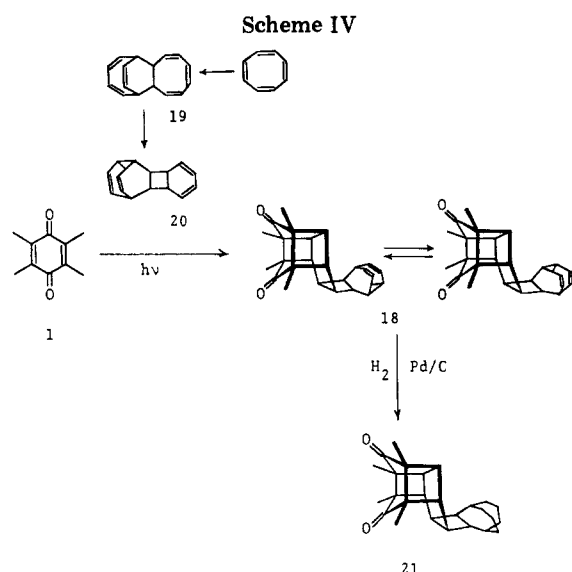
(16) W. H. Okamura and T. W. Osborn, *J. Am. Chem. Soc.*, **92**, 1061 (1970); C. S. Baxter and P. J. Carratt, *ibid.*, **92**, 1062 (1970); G. Scholes, C. R. Graham, and M. Brookhart, *ibid.*, **96**, 5665 (1974).

(17) A. G. Anastassiou and R. C. Griffith, *J. Am. Chem. Soc.*, **93**, 3083 (1971); L. A. Paquette and M. J. Epstein, *ibid.*, **93**, 5936 (1971); **95**, 6717 (1973); G. Boche, H. Weber, and J. Benz, *Angew. Chem., Int. Ed. Engl.*, **13**, 207 (1974); J. E. Baldwin and D. B. Bryan, *J. Am. Chem. Soc.*, **96**, 319 (1974).

(18) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963); G. J. Fonken and W. Moran, *Chem. Ind. (London)*, 1841 (1963); K. F. Bangert and V. Boekelheide, *ibid.*, 1121 (1963); *J. Am. Chem. Soc.*, **86**, 905 (1964); A. G. Anastassiou and R. C. Griffith, *ibid.*, **95**, 2379 (1973).

(19) E. Cignek, *J. Am. Chem. Soc.*, **88**, 1979 (1966); A. G. Anastassiou, R. P. Cellura, and E. Ciganec, *Tetrahedron Lett.*, 5267 (1970); D. Schöleber, *Chem. Ber.*, **102**, 1789 (1969); J. M. Brown and M. M. Ogilvy, *J. Am. Chem. Soc.*, **96**, 292 (1974); F.-G. Klärner and M. Wette, *Chem. Ber.*, **111**, 282 (1978).

(15) S. Akiyoshi and T. Matsuda, *J. Am. Chem. Soc.*, **77**, 2476 (1955); D. D. Philips, *ibid.*, **77**, 5179 (1955).



A solution of duroquinone and COT in benzene was irradiated under similar conditions for 72 h. Chromatography on a short silica gel column yielded a single product (18) in low yield (3–5%). Elemental analysis and mass spectrum  $m/e$  372 ( $M^+$ ), indicate that the 18 should be a 1:2 adduct between duroquinone and COT. A quite low conversion suggested that the photoreaction of duroquinone with COT should be different from that of *p*-benzoquinone with COT<sup>20</sup> or duroquinone with cycloheptatriene.

The possibility of the photochemical isomerization of COT<sup>21</sup> could be ruled out because of the low triplet level of duroquinone (53 kcal/mol).<sup>1</sup> After a benzene solution of duroquinone and COT was refluxed for 20 h, the mixture was irradiated to give the same adduct 18 in a slightly higher yield (5–8%). COT is known to be thermally dimerized to afford tricyclo[8.4.2.0<sup>2,9</sup>]hexadeca-3,5,7,11,13,15-hexaene (53 °C melting dimer) (19) and/or pentacyclo[8.4.2.0<sup>2,9</sup>.0<sup>3,8</sup>.0<sup>11,14</sup>]hexadeca-4,6,12,15-tetraene (76 °C melting dimer) (20),<sup>22</sup> and these COT dimers are reactive species with some unsaturated compounds.<sup>23</sup> Thus COT dimers should be possible reactive materials for the photocyclization with duroquinone.

Indeed duroquinone 1 reacted photochemically with pentacyclo[8.4.2.0<sup>2,9</sup>.0<sup>3,8</sup>.0<sup>11,14</sup>]hexadeca-4,6,12,15-tetraene (20) to afford the same photoproduct 18 under similar conditions in 63% yield, but not with 19 (Scheme IV).

This photoproduct 18 has mp 193–195 °C; IR, two carbonyl absorptions at 1750 and 1695  $\text{cm}^{-1}$ . The <sup>1</sup>H NMR spectra of this adduct 18 at various temperatures confirmed the dihydrobullvalene structure. Namely, the adduct 18 showed temperature-dependent NMR spectra<sup>12</sup> similar to 20<sup>22b</sup> and to other compounds containing the dihydrobullvalene moiety.<sup>24</sup> The <sup>13</sup>C NMR spectrum of 18 consists of only 13 peaks for the 26 carbons at room

temperature: two carbonyl carbons at  $\delta$  ( $\text{CDCl}_3$ ) 218.6 and 208.5, and olefinic carbon at  $\delta$  126.6, and a broad peak at  $\delta$  75.3. These data indicate the presence of the cage structure in 18 and suggest that the Cope rearrangement of 18 occurs very rapidly at this temperature.

The dihydrobullvalene function of 18 was also supported by its hydrogenation.<sup>22a</sup> Catalytic reduction of 18 over Pd–C gave the cage derivative 21: mp 192–193 °C; IR  $\nu_{\text{C=O}}$  1730 and 1690  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.06 (2 Me, s), 1.20 (2 Me, s), 1.4–1.7 (8 H, m), and 1.8–2.8 (14 H, m).

These data were consistent with a caged dihydrobullvalene structure of the photoproduct 18 formed via the photochemical cyclization of duroquinone with the 76 °C melting dimer 20 of COT via double [2 + 2] cycloaddition, similar to that of duroquinone with bicyclo[4.3.0]nona-2,4,7-triene derivative 15 or cyclohexa-1,3-dienes.<sup>3,8</sup>

Although *p*-benzoquinone<sup>20</sup> and thiobenzophenone<sup>25</sup> are known to react photochemically with COT, in this case COT did not react directly with duroquinone. At this time we have no reasonable explanation for the difference in reactivity observed in cycloadditions of duroquinone to cycloheptatriene (2), bicyclo[6.1.0]nona-2,4,6-triene (13), and COT; however, the different electron densities and/or the electronic characters of the double bonds should affect these photocycloaddition reactions.

## Experimental Section

**Materials.** Commercial duroquinone was used without further purification. Cyclohepta-1,3,5-triene and COT were purified by distillation. Ethyl bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate (13),<sup>15</sup> ethyl bicyclo[4.3.0]nona-2,4,7-triene-9-carboxylate (15),<sup>18</sup> tricyclo[8.4.2.0<sup>2,9</sup>]hexadeca-3,5,7,11,13,15-hexaene (19),<sup>22a</sup> and pentacyclo[8.4.2.0<sup>2,9</sup>.0<sup>3,8</sup>.0<sup>11,14</sup>]hexadeca-4,6,12,15-tetraene (20)<sup>22a</sup> were prepared by literature procedures. Solvents used were distilled by usual methods.

**Photoreaction of Duroquinone with Cyclohepta-1,3,5-triene (2).** A nondegassed solution of duroquinone (492 mg, 3 mmol) and cycloheptatriene (552 mg, 6 mmol) in 25 mL of benzene was irradiated with a 150-W high-pressure Hg lamp through a Pyrex filter for 72 h. Removal of solvent in vacuo gave a partially oily residue which was chromatographed on a silica gel column (Wakogel C-200). Elution with chloroform afforded cycloheptatriene from the first fraction and duroquinone (111 mg, 23% recovery) from the second. From the third, 1,2,4,12-tetramethylpentacyclo[7.4.0.0<sup>2,8</sup>.0<sup>4,12</sup>.0<sup>5,11</sup>]tridec-6-ene-3,13-dione (3; 185 mg, 24% yield) was obtained as colorless needles: mp 155–158 °C (recrystallized from *n*-hexane, sublimed over 100 °C); IR (KBr disk) 1690  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  256 ( $M^+$ ), 228, 119, 91; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.28 (4 Me, s), 1.60–1.90 (2 H, m), 2.56 (2 H, m), 3.12–3.35 (2 H, m), 5.88–6.12 (2 H, m); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  213.8 (s), 206.1 (s), 132.2 (d), 61.8 (s), 48.4 (s), 43.9 (d), 43.5 (d), 24.5 (t), 19.3 (q), 18.4 (q). Anal. Calcd for  $\text{C}_{17}\text{H}_{20}\text{O}_2$ : C, 79.69; H, 7.86. Found: C, 79.66; H, 7.64.

Further elution gave the photoadduct 4 (232 mg, 36% yield) as slightly yellow cubes from the last fraction: mp 288–391 °C (recrystallized from ether–light petroleum); IR 1735, 1690, 1660  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  420 ( $M^+$ ), 283, 255, 166; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  0.92 (Me, s), 1.03 (Me, s), 1.12 (Me, s), 1.20 (Me, s), 1.20 (1 H, m), 1.21 (Me, s), 1.23 (Me, s), 1.32 (Me, s), 1.62 (2 H, m), 1.90 (1 H, m), 1.98 (2 Me, s), 2.7–3.1 (4 H, m); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  218.2, 212.5, 200.8, 199.3, 145.7, 144.8, 68.6, 66.7, 55.1, 54.0, 52.5, 51.8, 48.2, 46.2, 45.9, 45.2, 44.5, 42.6, 26.8, 20.7, 17.0, 16.2, 13.6, 12.7, 12.6, (2 C), 11.6. Anal. Calcd for  $\text{C}_{27}\text{H}_{32}\text{O}_4$ : C, 77.11; H, 7.67. Found: C, 77.23; H, 7.83.

The change of the initial molar ratio of duroquinone (2 mmol) and cycloheptatriene (2–20 mmol) was examined under similar conditions and the products and yields are presented in Table I. The difference between a nondegassed and nitrogen-purged condition did not affect the ratios of the products or the yields of 3 and 4.

(20) R. M. Wilson, E. J. Garder, R. C. Elder, R. H. Squire, and L. R. Florian, *J. Am. Chem. Soc.*, **96**, 2955 (1974).

(21) H. E. Zimmerman and H. Iwamura, *J. Am. Chem. Soc.*, **90**, 4763 (1968); **92**, 2015 (1970).

(22) (a) G. Schröder, *Chem. Ber.*, **97**, 3131, 3140 (1964); (b) R. Merényi, J. F. M. Oth, and G. Schröder, *ibid.*, **97**, 3150 (1964).

(23) J. Daub, U. Erhardt, and V. Trauz, *Chem. Ber.*, **109**, 2197 (1976); D. M. Bratby, J. C. Chadwick, G. I. Fray, and R. G. Saxton, *Tetrahedron*, **33**, 1527 (1977); K. N. Houk and L. J. Luskus, *J. Org. Chem.*, **42**, 4151 (1977).

(24) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); A. Busch and H. M. R. Hoffmann, *Tetrahedron Lett.*, 2379 (1976); G. R. Krow, J. Reilly, D. M. Fan, J. Marakowski, and K. C. Ramay, *J. Am. Chem. Soc.*, **98**, 3636 (1976).

(25) T. S. Cantrell, *J. Org. Chem.*, **39**, 853 (1974).

**Isolation of Transient Intermediate 9.** After a shorter irradiation (30 h) of 25 mL of a benzene solution of duroquinone (492 mg, 3 mmol) and cycloheptatriene (2.76 g, 30 mmol), five spots were observed at the  $R_f$  values 1.0 (cycloheptatriene), 0.6 (duroquinone), 0.5 (transient intermediate), 0.3 (product 3), and 0.15 (product 4) by TLC analysis, using chloroform as eluent. After removal of the solvent, the oily residue was chromatographed on a Lobar column (LiChroprep Si 60, Merck). Elution with *n*-hexane-chloroform (1:1) afforded cycloheptatriene and duroquinone (388 mg, recovery) from fractions 1 and 2. Further elution gave the transient intermediate *cis,cis* [2 + 2] cycloadduct **9** (173 mg, 15% yield) as an oil: IR 1660  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.25 (Me, s), 1.35 (Me, s), 2.02 (2 Me, s), 1.9–2.1 (1 H, m), 2.2–2.5 (3 H, m), 5.7–6.0 (4 H, m). However, complete purification of **9** failed because of its thermal instability; many minor spots were observed by TLC analysis after repeated chromatographies on a short silica gel column.

The photoinduced isomerization of the isolated adduct **9** (containing some impurities) to **3** was monitored by  $^1\text{H}$  NMR and TLC analyses. During irradiation, the methyl signals corresponding to the starting adduct **9** and the cage product **3** were observed, and after 5 h of irradiation the signals matched those of **3** with impurities. Also the chloroform-*d* solution of duroquinone and the isolated adduct **9** was irradiated in a NMR tube for 5 h to show the methyl signals due to two photoadducts **3** and **4**.

**Catalytic Hydrogenation of 1:1 Photoadduct 3.** To a suspension of 40 mg of 5% Pd/C in 10 mL of absolute ethanol was added the 1:1 photoadduct **3** (60 mg) under hydrogen at atmospheric pressure. After standing for 3 h, the mixture was filtered and concentrated in vacuo, leaving 57 mg (95% yield) of colorless needles which were recrystallized from *n*-hexane. 1,2,4,12-Tetramethylpentacyclo[7.4.0.0<sup>2,8</sup>.0<sup>4,12</sup>.0<sup>5,11</sup>]trideca-3,13-dione **5**: mp 104–106 °C; IR 1690 (sh) and 1680  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.22 (2 Me, s), 1.24 (2 Me, s), 1.87 (6 H, br s), 2.82 (4 H, br s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  214.3 (s), 210.7 (s), 58.2 (s), 48.3 (s), 47.6 (d), 42.6 (d), 24.7 (t), 22.5 (t), 19.3 (q), 18.2 (q). Anal. Calcd for  $\text{C}_{17}\text{H}_{22}\text{O}_2$ : C, 79.03; H, 8.58. Found: C, 79.04; H, 8.54.

**Irradiation of Duroquinone with Cyclohepta-2,4,6-triene.** A solution of duroquinone (328 mg, 2 mmol) and tropone (2.12 g, 20 mmol) in benzene (25 mL) was irradiated under similar conditions for 30 h. The solvent was removed to leave a solid, which was chromatographed on silica gel. Chloroform eluted duroquinone (308 mg, 94% recovery) and a mixture of the dimers of tropone; the IR and  $^1\text{H}$  NMR spectra of the mixture were similar to those of the 117–118 and 137 °C melting dimers reported in the literature.<sup>14</sup>

**Irradiation of Duroquinone with Ethyl Bicyclo[6.1.0]-nona-2,4,6-triene-9-carboxylate (13).** A solution of duroquinone (164 mg, 1 mmol) and bicyclopentatriene **13** (380 mg, 2 mmol) was irradiated for 24 h and then concentrated to give an oily residue. Chromatography on silica gel gave a colorless solid **14**: mp 88–91 °C; IR 1730 and 1690  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.13 (Me, s), 1.15 (Me, s), 1.21 (2 Me, s), 1.26 (Me, t,  $J = 7.5$  Hz), 2.5–2.9 (6 H, m), 3.1–3.4 (1 H, m), 4.14 (2 H, q,  $J = 7.5$  Hz), 5.45–5.8 (2 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  218.0 (s), 208.7 (s), 173.6 (s), 135.3 (d), 128.6 (d), 63.7 (s), 63.5 (s), 60.9 (t), 56.8 (d), 52.8 (s, 2 C), 43.9 (d), 41.0 (d, 2 C), 35.5 (d), 35.0 (d), 34.3 (d), 16.2 (q), 16.0 (q), 14.3 (q), 12.4 (q, 2 C); mass spectrum,  $m/e$  354 ( $\text{M}^+$ ), 326, 298, 281, 166, 117. Anal. Calcd for  $\text{C}_{22}\text{H}_{26}\text{O}_4$ : C, 74.55; H, 7.39. Found: C, 74.64; H, 7.62.

**Irradiation of Duroquinone with Ethyl Bicyclo[4.3.0]-nona-2,4,7-triene-9-carboxylate (15).** The photoinduced cy-

cloaddition of duroquinone (40 mg) and ethyl bicyclo[4.3.0]-nona-2,4,7-triene (**15**; 38 mg) in 0.5 mL of chloroform-*d* was monitored by  $^1\text{H}$  NMR and TLC analyses. During irradiation, the signals corresponding to **1**, **15**, and the cage product **14** were observed, and after 5 h of irradiation the signals matched those of the product **14** and duroquinone.

**Photoreaction of Duroquinone with Cycloocta-1,3,5,7-tetraene.** A solution of duroquinone (328 mg, 2 mmol) and freshly distilled COT (416 mg, 4 mmol) in 25 mL of benzene was irradiated for 72 h. The usual workup and column chromatographic separation yielded the caged dihydrobullvalene **18** (11 mg, 3% yield): colorless cubes (recrystallized from ether-light petroleum); mp 193–195 °C; IR 1730 and 1690  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  373 ( $\text{M}^+$ ), 344, 207, 165, 129;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , room temperature)  $\delta$  1.06 (2 Me, s), 1.19 (2 Me, s), 1.7–1.9 (2 H, m), 2.2–2.3 (2 H, m), 2.5–2.6 (4 H, m), 2.7–2.8 (2 H, m), 3.6–3.9 (4 H, m), 5.6–6.0 (2 H, m);  $\delta$  NMR ( $\text{CS}_2$ , –110 °C) 0.96 (2 Me, s), 1.12 (2 Me, s), 1.56 (4 H, br s), 1.9–2.1 (2 H, m), 2.5–2.8 (6 H, m), 5.44 (2 H, br s), 5.72 (2 H, br s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , room temperature)  $\delta$  218.6, 208.5, 126.6, 75.3 (br), 64.1, 52.4, 41.8, 36.2, 35.3, 33.5, 27.2, 15.9, 12.4. Anal. Calcd for  $\text{C}_{26}\text{H}_{28}\text{O}_2$ : C, 83.87; H, 7.53. Found: C, 83.92; H, 7.63.

When commercial COT (after a filtration of stabilizer hydroquinone) was used under similar conditions, the same product **18** (19 mg, 5% yield) was obtained. When a solution of **1** and COT which had been refluxed for 20 h was irradiated, **18** was obtained in 8% yield.

**Irradiation of Duroquinone with Tricyclo[8.4.2.0<sup>2,9</sup>]hexadeca-3,5,7,11,13,15-hexaene (19).** A solution of duroquinone (82 mg, 0.5 mmol) and **19** (104 mg, 0.5 mmol) in 25 mL of benzene was irradiated for 20 h to afford some polymeric materials on the surface of the vessel, and a spot due to the product **18** could not be found by TLC analysis.

**Irradiation of Duroquinone with Pentacyclo[8.4.2.0<sup>2,9</sup>.0<sup>3,8</sup>.0<sup>11,14</sup>]hexadeca-4,6,12,15-tetraene (20).** A solution of duroquinone (82 mg, 0.5 mmol) and **20** (104 mg, 0.5 mmol) in 25 mL of benzene was irradiated for 3 h under similar conditions. After usual treatment, chromatography on a short silica gel column yielded the caged dihydrobullvalene **18** (118 mg, 63% yield). Its melting point and other spectroscopic data were identical with those of the product **18** of the reaction of duroquinone with COT.

**Catalytic Hydrogenation of Caged Dihydrobullvalene 18.** To a suspension of 20 mg of 5% Pd/C in 10 mL of absolute ethanol was added the caged dihydrobullvalene **18** (30 mg) and the mixture was allowed to stand for 5 h under hydrogen at atmospheric pressure. The mixture was filtered and concentrated in vacuo to give a solid. Chromatography on a short silica gel column yielded colorless needles (28 mg, 90% yield) of the caged compound **21**: mp 192–193 °C (recrystallized from light petroleum); IR 1730 and 1690  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  378 ( $\text{M}^+$ ), 350, 268, 136, 121;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.06 (2 Me, s), 1.20 (2 Me, s), 1.4–1.7 (8 H, m), 1.8–2.8 (14 H, m). Anal. Calcd for  $\text{C}_{26}\text{H}_{34}\text{O}_2$ : C, 82.49; H, 9.05. Found: C, 82.55; H, 9.26.

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**Registry No.** 1, 527-17-3; 2, 544-25-2; 3, 74824-38-7; 4, 74824-39-8; 5, 74824-40-1; 9, 74824-41-2; 13, 13380-77-3; 14, 74824-42-3; 15, 55660-87-2; 18 (isomer 1), 74824-43-4; 18 (isomer 2), 74867-96-2; 19, 1082-18-4; 20, 74824-44-5; 21, 74824-45-6; tropone, 539-80-0; cycloocta-1,3,5,7-tetraene, 629-20-9.