

# Antiaromatic Peripheral Systems. Synthesis and Chemistry of Pyracloquinone<sup>1</sup>

Barry M. Trost<sup>2</sup>

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received October 3, 1968

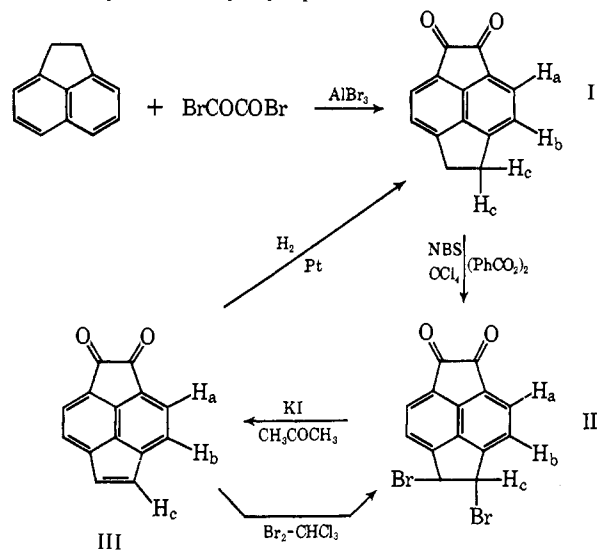
**Abstract:** Diketopyracene has been prepared from acenaphthene by Friedel–Crafts acylation with oxalyl bromide. This compound does not tautomerize under acid or basic conditions to dihydroxypyracylene or a derivative thereof. Bromination with *N*-bromosuccinimide followed by debromination with iodide ion produced pyracloquinone. All attempts to reduce the quinone to a derivative of the pyracylene system either produced diketopyracene or unidentifiable mixtures. The quinone undergoes Diels–Alder reactions with both cyclopentadiene and 2,6-diphenyl-3,4-benzofuran. In the latter case, a mixture of *exo* and *endo* isomers is produced. This result is discussed in light of recent theories of the Diels–Alder reaction. Irradiation of pyracloquinone produces either acenaphthene-5,6-dicarboxylic anhydride or acenaphthylene-5,6-dicarboxylic anhydride depending on reaction conditions. All of these results as well as the spectral properties of the quinone are discussed in terms of the periphery electronic model defining this system as an antiaromatic.

The question of the energy associated with increased electron delocalization is one of fundamental and practical concern that has occupied the attention of many investigators. Theoretical considerations suggest that  $4n$  systems are antiaromatic; that is, associated with increased electron delocalization is a destabilization of the system.<sup>3a</sup> Studies of this phenomenon in simple monocyclic systems is frustrated by the lack of planarity of the molecules. We, therefore, focussed our attention on polycyclic systems in which the molecules are constrained to be planar. We further limited our studies to those molecules possessing  $4n$  peripheries and vinyl cross-links.<sup>3b</sup> Whereas first-order perturbation theory predicts these systems to be antiaromatic, some of these molecules fulfill the requirements of Craig's rules for aromaticity. In order to test the validity of the concept of antiaromaticity in these types of systems and to compare the periphery electronic model to that of Craig's model, we first examined the pyracylene system. In this paper we wish to report the synthesis of the first simple derivative of pyracylene, its quinone, and the relationship of the quinone and some of its derivatives to the parent system.

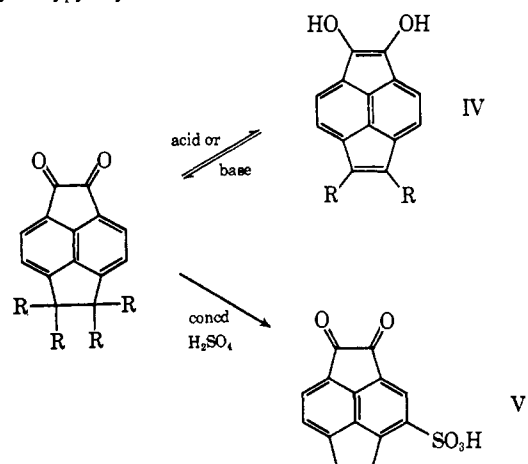
## Results

Bis acylation of acenaphthene with oxalyl bromide produces 1,2-diketopyracene (I, Scheme I) in 17% yield. This compound is the keto form of dihydroxypyracylene (IV, Scheme II). If aromaticity is to be associated with the pyraclyl system, an equilibrium between I and IV should be established. To examine this possibility, 1,2-diketopyracene-5,5,6,6-*d*<sub>4</sub> was prepared from ace-

Scheme I. Synthesis of Pyracloquinone



Scheme II. Tautomeric Relationship of Diketopyracene and Dihydroxypyracylene



(1) This paper forms part VII in our series on pyracylenes. A preliminary report of a portion of this work has appeared: B. M. Trost, *J. Am. Chem. Soc.*, **88**, 853 (1966).

(2) Alfred P. Sloan Foundation Fellow.

(3) (a) For leading references see R. Breslow, J. Brown, and J. J. Gajewski, *J. Am. Chem. Soc.*, **89**, 4383 (1967); R. Breslow and M. Douek, *ibid.*, **90**, 2698 (1968); (b) B. M. Trost and G. M. Bright, *ibid.*, **89**, 4244 (1967).

naphthene-1,1,2,2-*d*<sub>4</sub>. Treatment of this deuterated compound with potassium *t*-butoxide-*t*-butyl alcohol in *t*-butyl alcohol or dimethyl sulfoxide, tritylsodium in 1,2-dimethoxyethane or dimethyl sulfoxide, dimethylsodium in dimethyl sulfoxide, or lithium diethylamide-diethylamine in 1,2-dimethoxyethane or dimethyl sulfoxide led only to recovered diketopyracene with no loss of deuterium. If high temperatures were employed, only decomposition of I was observed. Treatment of I-*d*<sub>4</sub> with trifluoroacetic acid at reflux for 7 days or at room temperature for 7 months revealed no proton incorporation at the saturated methylenes. With concentrated sulfuric acid at room temperature no loss of deuterium occurred. At 40°, diketopyracene undergoes slow change in concentrated sulfuric acid to produce the *meta* sulfonic acid V.

Treatment of a suspension of diketopyracene in carbon tetrachloride with N-bromosuccinimide converted it to 5,6-dibromo-1,2-diketopyracene (II). The stereochemistry of the bromines is presumed to be *trans* analogous to the stereochemistry of bromination of acenaphthene to *trans*-1,2-dibromoacenaphthene.<sup>4</sup> Furthermore, addition of bromine to pyracloquinone (III) produces the same dibromide. Reductive vicinal elimination with potassium iodide converted II to the quinone III in 90–95% yields. The spectral properties are in complete accord with the structure. Its infrared spectrum shows a pair of peaks at 1735 and 1685 cm<sup>-1</sup> attributable to the diketone moiety. The energy separation between these peaks is about 30 cm<sup>-1</sup> (about 90 cal) less than any of the diketopyracene derivatives (see Experimental Section). This decreased coupling is associated with the increased strain in the diketo bridge. Its ultraviolet spectrum (see Table I)

Table I. Ultraviolet Spectrum of Pyracloquinone

| Experimental |       | SCF calculation |                     |
|--------------|-------|-----------------|---------------------|
| Max, mμ      | Log ε | Max, mμ         | Oscillator strength |
| 230          | 4.47  | 234             | 0.745               |
| 247          | 4.19  | 252             | 0.014               |
|              |       | 264             | 0.002               |
| 307          | 4.25  | 288             | 0.061               |
|              |       | 289             | 0.244               |
| 314          | 4.23  | 315             | 0.107               |
| 346          | 3.85  | 348             | 0.022               |

shows a hypsochromic shift compared to diketopyracene. This spectrum agrees remarkably well with the ultraviolet spectrum calculated using the Pople-Pariser-Parr SCF method.<sup>5</sup> The mass spectrum exhibits a molecular ion at *m/e* 206 and very abundant ions for the consecutive loss of two molecules of carbon monoxide. Chemical verification was provided by the addition of bromine to re-form II and catalytic hydrogenation to diketopyracene.

(4) (a) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956); (b) A. G. Anderson, Jr., and R. G. Anderson, *ibid.*, **77**, 6610 (1955); (c) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **80**, 4327 (1958); (d) F. D. Greene, W. A. Remers, and J. W. Wilson, Jr., *ibid.*, **79**, 1416 (1957).

(5) We are indebted to Dr. Howard E. Simmons for this calculation.

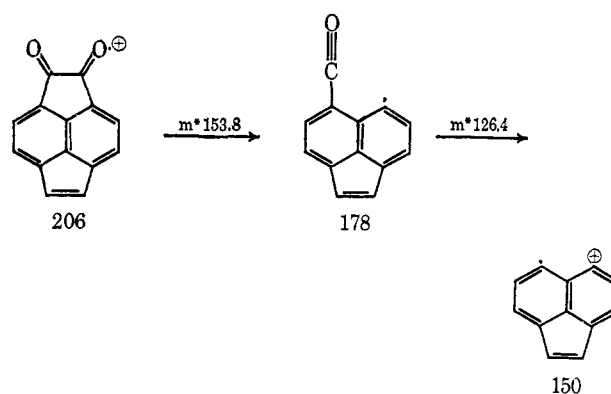


Table II summarizes the nmr spectral data for the quinone and several related compounds. Most striking is the abnormally low chemical shift of proton B of pyracloquinone. Using the other compounds in the table, proton B appears about 0.4 ppm at lower field than would be anticipated. We attribute the extra deshielding to the fact that higher positive charge density exists at position 4 of III than at corresponding positions of the model quinones. Theoretical calculations indeed predict a higher positive charge density at position 4 than at 3 or 5 (see Table III), a fact that

Table II. Nmr Spectra<sup>a</sup> of Acenaphthalene Derivatives

| Compd                | H <sub>A</sub> | H <sub>B</sub> | H <sub>C</sub> | H <sub>D</sub> | J <sub>A,B</sub> | J <sub>B,C</sub> | J <sub>A,C</sub> |
|----------------------|----------------|----------------|----------------|----------------|------------------|------------------|------------------|
| III <sup>b,e</sup>   | 8.26           | 8.26           | 7.69           |                |                  |                  |                  |
| I <sup>e,f</sup>     | 8.12           | 7.72           | 3.76           |                | 8.0              |                  |                  |
| II <sup>e,g</sup>    | 8.25           | 7.91           | 6.09           |                | 7.5              |                  |                  |
| VI <sup>d,f,i</sup>  | 7.95           | 7.12           | 7.75           |                | 7.5              | 7.0              | 1.0              |
| VII <sup>d,e,h</sup> | 7.90           | 7.58           | 7.79           | 7.15           | 7.5              | 7.5              | 1.0              |

<sup>a</sup> Chemical shifts are in parts per million (ppm) relative to TMS as an internal standard. <sup>b</sup> The naphthalene ring protons collapsed to an A<sub>2</sub> system. <sup>c</sup> AB spectrum. <sup>d</sup> ABC spectrum. <sup>e</sup> DMSO-*d*<sub>6</sub> solvent. <sup>f</sup> CF<sub>3</sub>CO<sub>2</sub>H solvent. <sup>g</sup> CDCl<sub>3</sub> solvent. <sup>h</sup> See structure VII. <sup>i</sup> See structure VI.

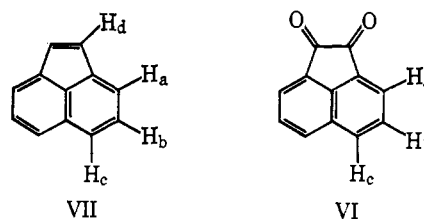
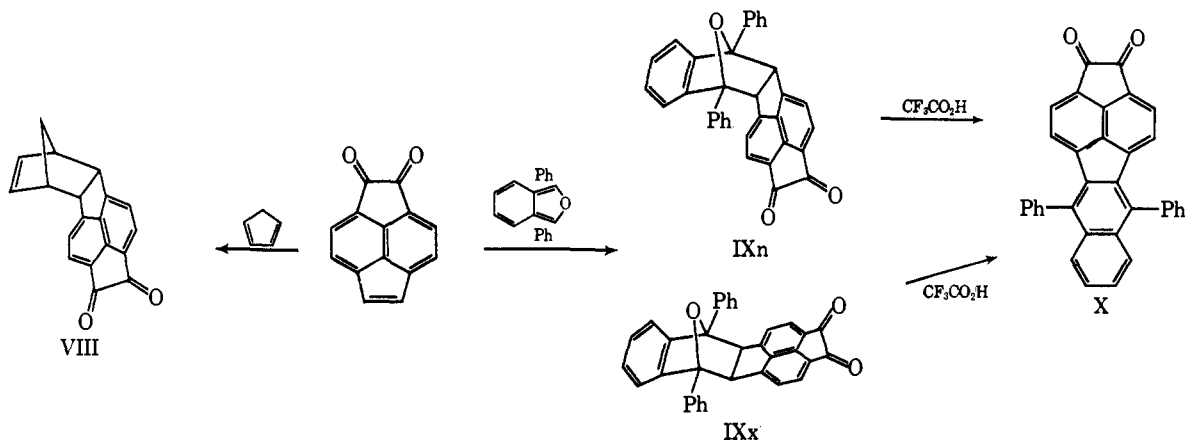


Table III. Charge Densities of Pyracloquinone

| Position | Hückel | PPP-SCF |
|----------|--------|---------|
| 3        | 0.958  | 0.960   |
| 4        | 0.937  | 0.930   |
| 5        | 1.032  | 1.015   |

would not be anticipated on the basis of resonance theory.

Attempts to reduce pyracloquinone chemically to a derivative of the pyracylene system all failed. Among the methods examined were trimethyl phosphite, zinc in acetic acid, zinc in acetic anhydride, and sodium and lithium in liquid ammonia followed by acetylation or alkylation with methyl iodide. Polarographic reduction shows two one-electron waves at -0.738 and -1.305 V. Controlled potential electrolysis at



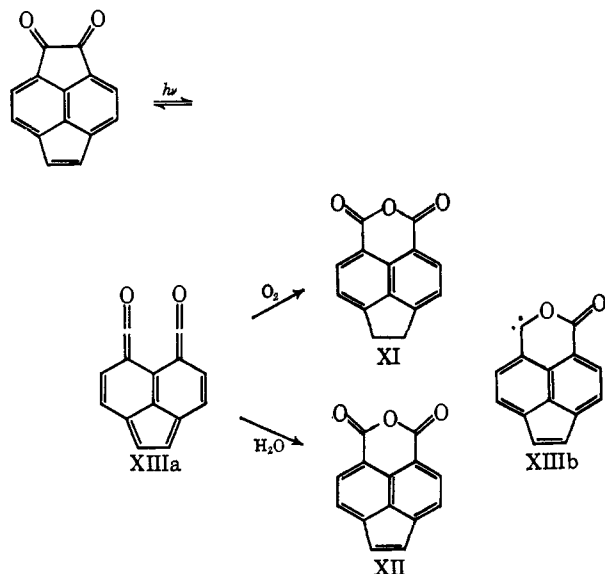
−0.8 V produces the radical anion which has been characterized by its electron spin resonance spectrum.<sup>6</sup> Controlled potential electrolysis at −1.4 V to generate the dianion followed by quenching with water produced diketopyracene which was identified by the characteristic esr spectrum of its radical anion produced upon further reduction. If the electrolysis was carried out in the presence of ethyl bromide, only intractable tars were produced.

Pyracyloquinone behaves as a fair dienophile. Reaction with cyclopentadiene in refluxing benzene produces exclusively the *endo* adduct VIII (Scheme III). Stereochemistry is assigned on the basis of the nmr spectrum which shows a doublet,  $J = 3.2$  cps, for the benzylic protons.<sup>7</sup> Diphenylisobenzofuran reacts with pyracycloquinone to give isomeric adducts, each of which is converted to 5,6-(1',4'-diphenyl-2',3'-naphthaleno)pyracycloquinone upon dissolving in trifluoro-

acetic acid. On this basis, the compounds are assigned the *exo* and *endo* configurations IXx and IXn. The major product is tentatively assigned the *endo* configuration based on the abnormally high-field absorptions of the quinone ring protons. Similar results are found in the pyracylene adducts.<sup>8</sup> The two adducts do not interconvert under the conditions of their formation.

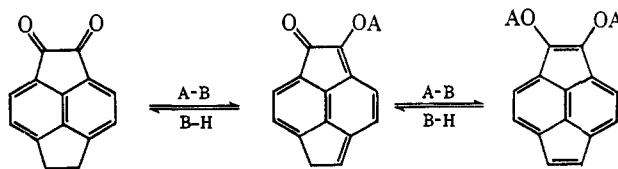
Unlike acenaphthylene derivatives, pyracycloquinone does not undergo photochemical dimerization.<sup>9</sup> Irradiation of a solution in moist dimethoxyethane at 360 m $\mu$  produces a transient deep red color. The product isolated is the saturated anhydride XI, identified by infrared and mass spectral comparisons with an authentic sample. Irradiation in carefully dried dimethoxyethane again produces a transient red color. The product isolated was identified as the unsaturated anhydride XII by infrared and mass spectral comparison with an authentic sample (Scheme IV).

Scheme IV. Photolysis of Pyracycloquinone



## Discussion

The failure to observe any detectable tautomerism as depicted in Scheme II does not suggest that unusual stability is to be associated with pyracylene. Tautomerism might be thought of as proceeding in two steps. The lack of any deuterium loss indicates that neither step is occurring to any detectable extent. The results



suggest that diketopyracene is less acidic than toluene.<sup>10</sup> This failure is also quite surprising in light of the facile dehydration of 5-( $\alpha$ -hydroxybenzyl)acenaphthene to 5-benzylacenaphthylene.<sup>11</sup> The increased reluctance to undergo the initial proton abstraction may be associated with the increased strain energy when addi-

(6) S. F. Nelsen, B. M. Trost, and D. H. Evans, *J. Am. Chem. Soc.*, **89**, 3034 (1967).

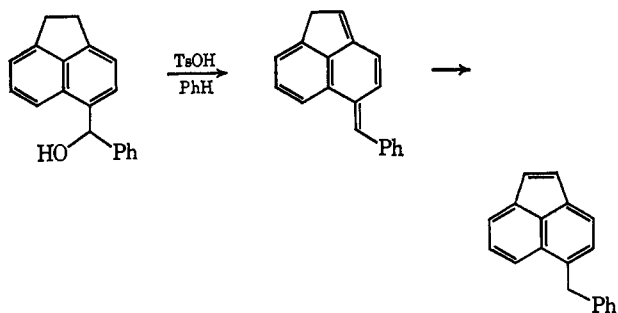
(7) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2625 (1965).

(8) B. M. Trost and G. M. Bright, to be published.

(9) D. O. Cowan and R. L. Drisko, *Tetrahedron Letters*, 1255 (1967).

(10) For leading references see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 1-45.

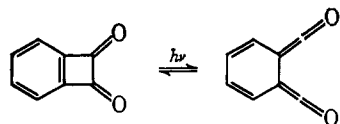
(11) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3059 (1965).



tional  $sp^2$  centers are introduced into the diketopyracene system.

Nevertheless, strong supporting evidence refuting any aromaticity associated with the pyracylene system arises from reduction experiments. In no case was reduction of the quinoid grouping observed. Furthermore, protonation of the dianion occurred exclusively at carbon. These results in combination with our previous results in this series<sup>6,12</sup> are in best accord with the periphery electronic model defining pyracloquinone as cyclododecapentaenoquinone with a vinyl cross-link.

The photolytic behavior agrees with this interpretation and parallels the reactivity of a derivative of cyclobutadienoquinone. Benzocyclobutadienoquinone has been reported to undergo ring opening to the



diketene.<sup>13</sup> Such behavior is in direct contrast to the photolytic behavior of quinones derived from aromatic systems<sup>14</sup> in which the bond between the carbonyl groups remains intact. Thus, Scheme IV represents a reasonable interpretation of the experimental results. The transient red color may arise from a disrotatory ring opening to yield the diketene intermediate XIIIa. However, attempts to detect the diketene by following the irradiation by infrared spectroscopy failed. Hydration of XIIIa produces the saturated anhydride XI, whereas oxidation (*via* XIIIb?) produces the unsaturated anhydride XII. Thus, these results agree with the hypothesis that pyracloquinone resembles a perturbed cyclododecapentaene-quinone.

The first half-wave potential represents a measure of this destabilization. The half-wave potential is related to the amount of work required to convert a molecule to its radical anion. Thus, to a large degree, it represents the stability of the radical anion compared to its precursor. If electronic stabilization is associated with the pyracylene system, the first half-wave potential of its quinone would lie between that of 1,2-naphthoquinone<sup>5</sup> ( $E_{1/2} = -0.463$  V) and 9,10-phenanthroquinone<sup>6</sup> ( $E_{1/2} = -0.545$  V) since the de-

localization energy of the pyracylene system should be between that of the naphthalene and phenanthrene systems. We attribute its substantially higher half-wave potential ( $E_{1/2} = -0.738$  V) to electronic destabilization accompanying the formation of the antiaromatic derivative pyracloquinone anion.

In the Diels-Alder reaction, pyracloquinone reacts somewhat more sluggishly than 1,4- or 1,2-benzoquinone. The stereochemistry of the adducts provide some insight into the mechanism of this reaction.

Recent theoretical discussion<sup>15</sup> of the Diels-Alder reaction attribute the preferred *endo* addition to secondary interactions between atoms not bonded in the adduct. These secondary forces are functions of the difference in energy between the highest occupied molecular orbital of the diene and the lowest antibonding molecular orbital of the dienophile and of the symmetry of these two orbitals. If such factors are important in determining adduct stereochemistry, pyracloquinone should exhibit very high *endo* preference. The fact that the *endo:exo* ratio for the diphenylisobenzofuran adduct is about 3:1 does not support this contention. Recently, Herndon and Hall<sup>16</sup> have offered an alternative explanation based on the geometrical overlap relationship of the  $\pi$  orbitals at the reacting centers in which the greater efficiency of overlap in the *endo* transition state leads to a greater stabilization of this transition state compared to the *exo* case. Our results do not refute this argument.

The Platt<sup>17</sup> model has proved to be extremely useful in understanding the properties of many aromatic systems. In our previous paper, we provided a theoretical foundation for extending this periphery electronic model to antiaromatic systems. The accumulated experimental evidence in the pyracylene system attests to the validity of this hypothesis.

## Experimental Section<sup>18</sup>

**Preparation of Diketopyracene.** The following procedure is quite similar to that of Richter and Stocker;<sup>19</sup> however, we were able to obtain quite reproducible results. A solution of 17.60 g (0.114 mol) of acenaphthene (Eastman Kodak recrystallized material) in 1500 ml of carbon disulfide was prepared under nitrogen. After cooling in an ice-salt bath at  $-5^\circ$ , 25.00 g (0.116 mol) of freshly distilled oxalyl bromide (Aldrich Chemical Co.) was added. Then 62.50 g (0.234 mol) of powdered aluminum bromide was added over a period of 10-15 min with vigorous stirring during the addition. A black gum slowly formed. After about 30-40 min stirring became impossible and was discontinued. The mixture

(15) (a) L. Salem, *J. Am. Chem. Soc.*, **90**, 543, 553 (1968); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388 (1965); (c) W. C. Herndon and L. H. Hall, *Theoret. Chim. Acta*, **7**, 4 (1967).

(16) W. L. Herndon and L. H. Hall, *Tetrahedron Letters*, 3095 (1967).

(17) J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954).

(18) Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometer. Nmr. spectra were determined on a Varian Associates Model A-60 spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million (ppm) relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C and AEI MS-902 mass spectrometer fitted with an electron multiplier at an ionizing current of 40 ma and ionizing voltage of 70 V. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent. Elemental analyses were determined by Spang and Micro-Tech Analytical Laboratories.

(19) H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 366 (1959).

(12) B. M. Trost, S. F. Nelsen, and D. R. Brittelli, *Tetrahedron Letters*, 3959 (1967), and references therein.

(13) (a) H. A. Staab and J. J. Ipaktschi, *Angew. Chem.*, **78**, 308 (1966); (b) R. F. C. Brown and R. F. K. Solly, *Tetrahedron Letters*, 169 (1966).

(14) For leading references see M. B. Rubin and R. A. Reith, *Chem. Commun.*, 431 (1966).

stood overnight (about 15 hr) during which time it was allowed to warm to room temperature. The mixture was warmed with a 35° bath for 30 min and the carbon disulfide decanted. The black gum was treated with 1 l. of cold 10% aqueous hydrochloric acid. The dark brown solid was filtered and thoroughly washed with water. The solid was mixed with 7.5 g of Norit and 7.5 g of Supercel. This mixture was suspended in 500 ml of 4% aqueous sodium bisulfite and heated to 80° for 1 hr. While hot, it was filtered. The filtrate was warmed to 80° and acidified to pH 1 with concentrated hydrochloric acid. A fluffy yellow solid formed and it was collected. This extraction process was repeated five times on the dark brown Norit-Supercel mixture to yield a total of 4.16 g (17.5% yield), mp 288–290° dec. After recrystallization from DMF, there was obtained 4.06 g (17% yield) of beautiful yellow needles, mp 305–306° (lit.<sup>19</sup> 302–305°). Infrared analysis<sup>20</sup> shows carbonyl absorptions at 1660 and 1735 cm<sup>-1</sup> and C–H stretching absorptions at 2925 and 3050 cm<sup>-1</sup>. The ultraviolet spectrum<sup>21</sup> shows absorptions at ( $m\mu$  ( $\epsilon$ )) 213 (4300), 238 (52,500), 246 (48,200), 318 (sh, 4950), 332 (6400), 354 (6700), and 364 (sh, 5600). Nmr data is listed in Table II. Its mass spectrum shows a molecular ion at  $m/e$  208 and abundant peaks 180 (base peak,  $M^+ - CO$ ), 152 ( $M^+ - 2CO$ ), 151 ( $M^+ - 2CO - H$ ), 150 ( $M^+ - 2CO - 2H$ ). These peaks account for over 50% of the total ion current.

Anal. Calcd for C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>: C, 80.76; H, 3.87. Found: C, 80.51; H, 3.90.

5,5,6,6-Tetradeuteriodiketopyracene was prepared as described above from 1,1,2,2-tetradeuterioacenaphthene.<sup>22</sup> Its infrared spectrum<sup>20</sup> lacked the absorption at 2925 cm<sup>-1</sup> and its nmr lacked the singlet at 3.76 ppm. Mass spectral analysis indicated it was 84%  $d_4$ , 14%  $d_3$ , 1%  $d_2$ , 1%  $d_1$ .

**Attempted Deuterium Exchange of Diketopyracene. General Basic Procedure.** Diketopyracene- $d_4$  (21.2 mg, 0.1 mmol) was suspended (dissolved) in a degassed 1 *M* solution of base under an atmosphere of nitrogen. Stirring was continued between room temperature and not greater than 50° for 1 week and the mixture poured into cold dilute aqueous hydrochloric acid. The solid was filtered and dried. The deuterium content was determined by mass spectral and nmr analysis. In each case examined, potassium *t*-butoxide-*t*-butyl alcohol in *t*-butyl alcohol and dimethyl sulfoxide, tritylsodium-triphenylmethane in 1,2-dimethoxyethane and dimethyl sulfoxide, dimethylsodium in dimethyl sulfoxide, and lithium diethylamide-diethylamine in 1,2-dimethoxyethane and dimethyl sulfoxide, only diketopyracene with the original deuterium content was found. If temperatures in excess of 50° were employed, the mixtures invariably turned black and no diketopyracene could be recovered.

**Acid Exchange.** Diketopyracene- $d_4$  (21.2 mg, 0.1 mmol) was dissolved in trifluoroacetic acid and the solution refluxed for 1 week. Nmr analysis revealed no proton incorporation. After subsequent standing for 7 months in trifluoroacetic still no incorporation could be detected. Dissolution of 21.2 mg (0.1 mmol) of diketopyracene in concentrated sulfuric acid and examination by nmr initially showed the AB quartet at  $\delta$  8.28 and 7.84 and the methylene protons at 3.76. This spectrum slowly changed and after 16.0 hr became a singlet (1 H) at  $\delta$  8.63, a doublet (1 H,  $J = 8$  cps) at 8.54, a doublet (1 H,  $J = 8$  cps) at 8.09, and a very broad absorption (4 H) centered at 4.00. The ultraviolet spectrum in concentrated sulfuric acid shows ( $m\mu$  ( $\epsilon$ )) absorption at 432 (6500), 323 (6000), 262 (sh, 21,600), and 245 (58,300). Pouring onto ice gave a yellow orange solid, mp >300°, tentatively assigned the sulfonic acid structure V.

Anal. Calcd for C<sub>14</sub>H<sub>8</sub>SO<sub>3</sub>: C, 58.3; H, 2.8. Found: C, 58.0; H, 3.0.

Repetition with diketopyracene- $d_4$  produced the same changes in the aromatic region of the nmr spectrum but did not show any absorptions in the  $\delta$  3–4 region.

**Preparation of 5,6-Dibromo-1,2-diketopyracene.** In 100 ml of carbon tetrachloride, 1.00 g (4.8 mmol) of 1,2-diketopyracene was refluxed 30 min under nitrogen. To the hot solution, 2.60 g (15.0 mmol) of *N*-bromosuccinimide and 100 mg of dibenzoyl peroxide was added and the mixture refluxed 5 hr. It was filtered hot and the solid washed with 25 ml of additional hot carbon tetrachloride. The resultant solid was swirled with 50 ml of methanol to remove the succinimide. The yellow solid that remained was unreacted 1,2-

diketopyracene (350 mg, 35% recovery). Evaporation of the carbon tetrachloride solution produced a yellow solid. This material was washed with methanol. Recrystallization from a small volume of chloroform produced yellow flakes (936 mg, 55% yield) with mp 189–191° dec. Its infrared spectrum<sup>22</sup> shows carbonyl absorptions at 1740 and 1660 cm<sup>-1</sup>. Its ultraviolet spectrum<sup>21</sup> exhibits maxima at ( $m\mu$  ( $\epsilon$ )) 225 (33,200), 231 (34,200), 243 (sh, 18,600), 324 (7700), and 332 (7800). Nmr data are listed in Table II.

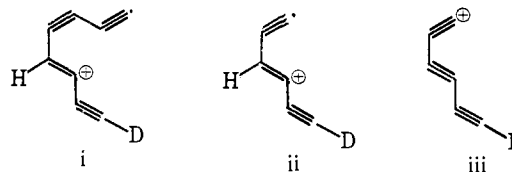
Anal. Calcd for C<sub>14</sub>H<sub>8</sub>Br<sub>2</sub>O<sub>2</sub>: C, 45.94; H, 1.65; Br, 43.67. Found: C, 45.77; H, 1.82; Br, 43.64.

5,6-Dideuterio-5,6-dibromo-1,2-diketopyracene was prepared in an identical fashion in 60% yield from 5,5,6,6-tetradeuterio-1,2-diketopyracene. Its nmr spectrum<sup>24</sup> lacked the singlet at  $\delta$  6.09.

**Preparation of Pyracloquinone.** In a nitrogen atmosphere, 2.50 g (68.4 mmol) of 5,6-dibromo-1,2-diketopyracene dissolved in 175 ml of acetone was treated with 15 g (0.91 mol) of anhydrous potassium iodide. After 4 hr of refluxing, the acetone solution became deep purple. The mixture was cooled and poured into cold aqueous sodium thiosulfate. The aqueous mixture was extracted with a large volume of chloroform. Drying and subsequent evaporation produced a red solid. Recrystallization from ethanol gave 1.39 g (99% yield) of orange flakes, mp >350°. Its infrared spectrum<sup>23</sup> shows carbonyl absorptions at 1735 and 1685 cm<sup>-1</sup>. Its ultraviolet<sup>21</sup> and nmr spectral data are recorded in Tables I and II. Its mass spectrum exhibits intense peaks at  $m/e$  206 ( $M^+$ ), 178 ( $M^+ - CO$ ), and 150 ( $M^+ - 2CO$ , base peak) and moderate peaks at 98, 75, and 74.

Anal. Calcd for C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>: C, 81.5; H, 2.9. Found: C, 81.2; H, 3.0.

5,6-Dideuteriopyracyloquinone was prepared in an identical fashion from 5,6-dideuterio-5,6-dibromo-1,2-diketopyracene. Its nmr spectrum<sup>24</sup> lacked the singlet at  $\delta$  7.69. Mass spectral analysis indicates 97%  $d_2$ , 3%  $d_1$ . It shows intense peaks at  $m/e$  208 ( $M^+$ ), 180 ( $M^+ - CO$ ), and 152 ( $M^+ - 2CO$ , base peak) and moderate peaks at 99, 76, and 75. This shift in the moderately intense peaks suggest structures i, ii, and iii for the corresponding fragments.



**Bromination of Pyracloquinone.** To a suspension of 10.3 mg (0.05 mmol) of pyracloquinone in 5 ml of chloroform under a N<sub>2</sub> atmosphere was added 16.0 mg (0.10 mmol) of bromine. A deep orange solution formed very rapidly. It was stirred 1 hr at 25° and diluted with 10 ml of chloroform. The solution was washed with dilute aqueous sodium thiosulfate and then water. Drying followed by evaporation produced 15.2 mg (83% yield) after recrystallization from ethanol-chloroform. It was identical in melting point and infrared spectrum with *trans*-5,6-dibromo-1,2-diketopyracene.

**Hydrogenation of Pyracloquinone.** Into 10 ml of absolute ethanol was dissolved 10.3 mg (0.05 mmol) of pyracloquinone. After addition of a trace of Adam's catalyst, hydrogenation at 1.0 atm and room temperature proceeded rapidly. After uptake of 10 ml, further hydrogen uptake ceased. Removal of the catalyst by filtration through Supercel and evaporation of the solvent produced a yellow powder, mp 300–305°, whose infrared spectrum was identical with 1,2-diketopyracene.

**Electrolytic Reduction of Pyracloquinone.** Electrolytic reductions were carried out utilizing 0.001 *M* solutions of pyracloquinone in dimethyl sulfoxide containing 0.1 *M* tetrabutylammonium iodide as a supporting electrolyte. The Varian electrolytic cell was utilized for these reductions.

The half-wave potentials were determined using a Sargent Model XV polarograph converted to a three-electrode system. The

(20) Determined as a KBr disk.

(21) Determined as a solution in ethanol.

(22) B. M. Trost, *J. Am. Chem. Soc.*, **89**, 1847 (1967).

(23) Determined as a solution in chloroform.

(24) Determined as a solution in deuteriochloroform.

polarographic cell was a water-jacketed all glass assembly. The anode was a platinum spiral. The reference electrode capillary tip was within 1 cm of the mercury drop. The reference electrode bridge was filled with supporting electrolyte and separated from the aqueous SCE compartment by a fine-porosity sintered-glass disk, a renewable electrolyte bridge containing 0.1 M tetrabutylammonium iodide in DMSO, and a second sintered-glass disk. The reported half-wave potentials are averages of cathodic and anodic scans and include the liquid junction potential between the aqueous and DMSO solutions.

**Reaction of Pyracloquinone with Cyclopentadiene.** Into 5 ml of benzene was placed 100 mg (0.485 mmol) of pyracloquinone and 264 mg (4.0 mmol) of freshly cracked cyclopentadiene. Refluxing under nitrogen proceeded until all suspended solid went into solution (24 hr). Upon cooling, a precipitate formed. Filtration and subsequent washing of the solid with benzene left 32 mg (32% recovery) of orange material which was identical with pyracloquinone. The combined benzene layers were evaporated to yield 75 mg (56% yield) of yellow needles, mp 175–179°, after recrystallization from ethanol. Nmr analysis<sup>24</sup> showed an AB pattern ( $J_{AB} = 7.3$  cps) with  $H_A$  at  $\delta$  7.92 and  $H_B$  at 7.58 (naphthalene ring protons), a 2 H triplet ( $J = 2.0$  cps) at  $\delta$  5.50 (vinyl protons), a 2 H doublet ( $J = 3.2$  cps) at 4.41 (benzylic protons), a 2 H multiplet at 3.42 (bridgehead protons), and a 2 H triplet ( $J = 1.3$  cps) at 1.85 (bridge protons). The coupling constant of the benzylic protons demonstrate their *exo* position. Examination of the crude material by nmr showed an essentially identical spectrum. A small sample for elemental analysis was prepared by passing a solution in benzene through a column of silica gel and recrystallizing from ethanol, mp 189–191°.

*Anal.* Calcd for  $C_{19}H_{12}O_2$ : C, 83.8; H, 4.4. Found: C, 83.7; H, 4.5.

The infrared spectrum showed carbonyl stretching bands at 1735 and 1650  $cm^{-1}$ . Its ultraviolet spectrum<sup>21</sup> exhibited maxima ( $m\mu$  ( $\epsilon$ )) at 232 (40,350), 244 (22,200), and 327 (10,100). The mass spectrum showed peaks at  $m/e$  272 ( $M^+$ ), 244 ( $M^+ - CO$ ), 215 ( $M^+ - 2CO - H$ ), 206 ( $M^+ - C_3H_6$ ), 178 ( $M^+ - C_3H_6 - CO$ , base peak), and 150 ( $M^+ - C_3H_6 - 2CO$ ).

**Reaction of Pyracloquinone with 2,5-Diphenyl-3,4-benzofuran.** A suspension of 103 mg (0.5 mmol) of pyracloquinone in 6 ml of benzene under nitrogen was stirred with 135 mg (0.5 mmol) of 2,5-diphenyl-3,4-benzofuran for 15 hr at 25°. The suspended solid was removed by filtration. One recrystallization from benzene gave 59 mg (25% yield) of chromatographically (silica gel PF-254 with benzene as solvent,  $R_f$  0.13 after two developments) homogeneous material as yellow flakes, mp 290–290.5°. Evaporation of the benzene produced a second compound. Recrystallization from cyclohexane yielded 172 mg (72% yield) of chromatographically (silica gel PF254 with benzene as solvent,  $R_f$  0.26 after two developments) homogeneous material as yellow flakes, mp 285–286°. The slower moving spot (IXx) showed carbonyl absorptions at 1740 and 1665  $cm^{-1}$  in its infrared spectrum.<sup>13</sup> Its mass

spectrum does not show a molecular ion but shows fragment ions at  $m/e$  270 (2,5-diphenyl-3,4-benzofuran), 241, 240, 239, 206 ( $III^+$ ), 178 ( $III^+ - CO$ ), and 150 ( $III^+ - 2CO$ ).

*Anal.* Calcd for  $C_{34}H_{20}O_3$ : C, 85.7; H, 4.2. Found: C, 85.7; H, 4.4.

The faster moving spot (IXn) showed an infrared spectrum<sup>23</sup> very similar to IXx, the only differences being visible in the fingerprint region. The mass spectrum was virtually superimposable. The nmr spectrum<sup>24</sup> shows complex aromatic absorptions between  $\delta$  7.4 and 8.1 (18 H), an AB pattern ( $J = 9$  cps) with  $H_A$  at 6.60 and  $H_B$  at 6.52 (naphthalene ring protons), and a singlet (2 H) at 5.42 (benzylic protons).

*Anal.* Calcd for  $C_{34}H_{20}O_3$ : C, 85.7; H, 4.2. Found: C, 85.7; H, 4.3.

**Preparation of 5,6-(1,4-Diphenyl-2,3-naphthaleno)pyracloquinone.** Addition of 70 mg (0.15 mmol) of either IXx or IXn to 2 ml of trifluoroacetic acid under  $N_2$  at 25° produced a clear solution after stirring 10 min. After 1 hr nmr indicated the absence of starting material. Evaporation of solvent yielded 65 mg (95% yield) of red solid. Recrystallization from a large volume of ethanol gave beautiful red needles, mp >350°. Its infrared spectrum<sup>23</sup> showed carbonyl absorptions at 1740 and 1675  $cm^{-1}$ . Its nmr spectrum<sup>24</sup> showed an AB pattern ( $J = 7.5$  cps) with  $H_A$  at  $\delta$  7.85 and  $H_B$  at 6.85 and a complex multiplet centered at 7.67. The protons *meta* to the diketone moiety experience a large shielding effect from the phenyl groups whose planes must be almost perpendicular to the molecular plane.

*Anal.* Calcd for  $C_{34}H_{18}O_2$ : C, 89.1; H, 4.0. Found: C, 88.9; H, 4.0.

**Photolysis of Pyracloquinone.** A solution of 5 mg (0.024 mmol) of quinone in 10 ml of unpurified 1,2-dimethoxyethane was irradiated at 360  $m\mu$  utilizing a Bausch and Lomb Model 33-86-07 monochromator fitted with a mercury light source. After 30 min, ultraviolet analysis revealed the absence of starting material. Evaporation to dryness yielded a solid with infrared absorptions<sup>20</sup> at 1780 and 1740  $cm^{-1}$ . Its mass spectrum indicated a molecular weight of 224 and showed abundant peaks at  $m/e$  180 ( $M^+ - CO_2$ ), 152 ( $M^+ - CO_2 - CO$ ), 151, and 150 ( $M^+ - CO_2 - CO - 2H$ ). These spectra were identical with those of an authentic sample of 5,6-acenaphthenedicarboxylic anhydride.

Repetition of this photolysis in 1,2-dimethoxyethane purified by distillation from lithium aluminum hydride, then sodium-potassium alloy, and finally lithium aluminum hydride produced a red powder with infrared<sup>20</sup> bands at 1780 and 1740  $cm^{-1}$ . Its mass spectrum showed a molecular ion at  $m/e$  222 and abundant peaks at 178 ( $M^+ - CO_2$ ) and 150 ( $M^+ - CO_2 - CO$ ). These spectra were identical with those of an authentic sample of 5,6-acenaphthylenedicarboxylic anhydride.

**Acknowledgment.** We wish to thank the Petroleum Research Fund for generous support of this work.