Unexpected formation of 9,10-dibenzoylphenanthrene

Alan P. Marchand,*[a] **Gadthula Srinivas**,[a] **and William H. Watson**,*[b]

[a]*Department of Chemistry, University of North Texas, Denton, Texas 76203-5070 USA*
[b]*Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129-8860 USA*

E-mail: marchand@unt.edu (organic synthesis, compound characterization)
w.watson@tcu.edu (X-ray crystallography)

Dedicated to Professor Sukh Dev on the occasion of his 80th anniversary.
SATAMANAM BHAVATI SATAYU

(received 09 Oct 02; accepted 04 Nov 02; published on the web 21 Nov 02)

Abstract

When heated in the presence of atmospheric oxygen, either in diffuse room light or in the dark, phencyclone (**1**) undergoes autoxidation to afford 9,10-dibenzoylphenanthrene (**3**). The structure of **3** was elucidated via application of single crystal X-ray crystallographic techniques. A mechanism is suggested to account for the formation of **3** via (i) stepwise 1,4-addition of $^3O_2$ to the 1,3-diene system in the cyclopentadiene moiety of **1** to form endoperoxide **5** followed by (ii) cheletropic extrusion of carbon monoxide from **5**. The structure of **3** is described: $P2_1/C$, a = 12.116(2), b = 9.6850(2), c = 16.839(3) Å, β = 100.331(3)°.

Keywords: Phencyclone, oxidative degradation, Diels-Alder reaction, X-ray crystal structure

---

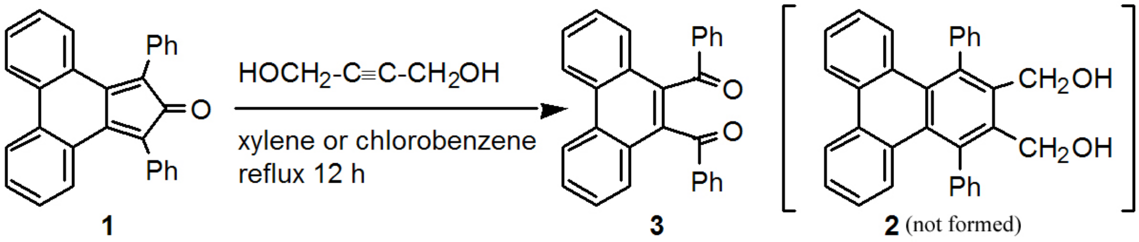
Introduction

As part of a continuing program that involves the study of cage-annulated crown ethers,[1] it was of interest to introduce a fluorescent moiety into the macrocyclic polyether backbone. As a first step toward the preparation of a fluorescent ligand, we attempted to perform Diels-Alder cycloaddition of 2-butyne-1,4-diol to 1,3-diphenyl-2*H*-cyclopenta[I]phenanthrene-2-one (i.e., phencyclone, **1**, Scheme 1).

In view of the fact that 2-butyne-1,4-diol contains a relatively electron-rich carbon-carbon triple bond, this compound was not expected to function as an avid dienophile toward diene **1**. Accordingly, the reaction of interest was performed at relatively high temperature, i.e., in refluxing xylene or in refluxing chlorobenzene (see the Experimental Section). Under these conditions, the desired [4 + 2] cycloaddition reaction to form **2** failed to take place. Instead, oxidative degradation of the cyclopentadienone ring in **1** occurred, thereby affording **3** in 40% yield. Compound **3** was characterized via analysis of its ^{1}H and ^{13}C nmr spectra (see the Experimental Section) and also via single crystal X-ray structural analysis (*vide infra*).

When **1** was refluxed in xylene in the absence of 2-butyne-1,4-diol, the deep black-green color associated with **1** gradually faded to a pale greenish-yellow solution. Workup of the reaction mixture afforded pure **3** in 72% yield. The IR, ^{1}H nmr, and ^{13}C nmr spectra of the material thereby obtained were identical with the corresponding spectra obtained for **3** that had been obtained previously via attempted high temperature Diels-Alder cycloaddition of 2-butyne-1,4-diol to **1** (*vide supra*).

It is well known that tetracyclones of the type **1** undergo both thermal[2] and photochemical[3] oxidative degradation in the presence of atmospheric O_2 to afford compounds of the type **3**. Presumably, the thermal process proceeds via reaction of phencyclone with ground state (triplet) dioxygen ($^3O_2$). However, it should be recognized that compounds of the type **1** might function as photosensitizers and thus potentially could promote formation of singlet dioxygen ($^1O_2$), which then becomes the reactive oxidizing species.[3]



Scheme 1

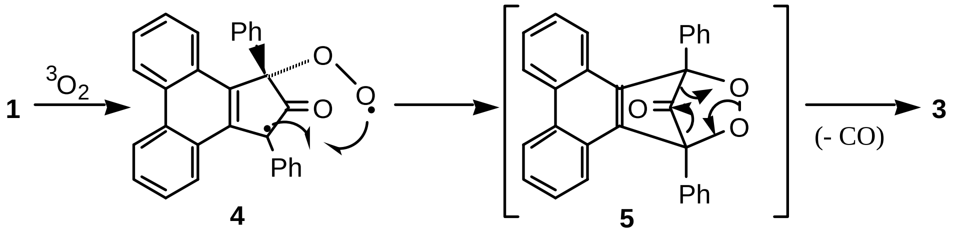
In our hands, thermal autoxidation of phencyclone was performed in diffuse room light and in the presence of atmospheric O_2. In order to investigate the potential role that photoactivation of $^3O_2$ to $^1O_2$ might play in the autoxidation of **1**, a control experiment was performed in which a solution of **1** in xylene was refluxed with stirring overnight in the dark in the presence of atmospheric O_2. Under these conditions, **3** was formed in 65% yield; this result suggests that autoxidation of **1** is promoted by $^3O_2$.

Results and Discussion

Chemistry

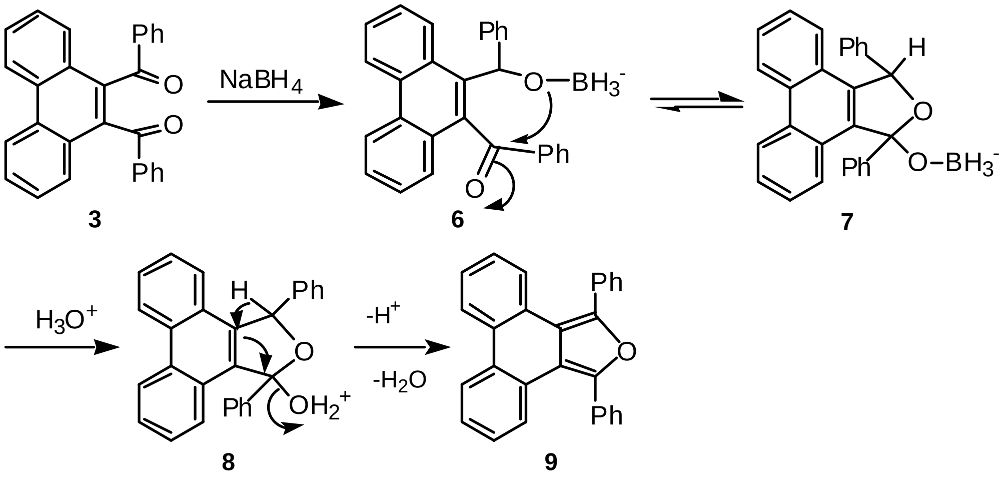
Reactions of $^1O_2$ with cyclic or *cisoid* acyclic 1,3-dienes frequently afford endoperoxides via Diels-Alder [4 + 2] cycloaddition.[4] However, the corresponding concerted reaction that employs $^3O_2$ as dienophile is spin-forbidden.[5] For this reason, the mechanism suggested in Scheme 2 invokes stepwise endoperoxide formation with initial formation of a diradical, **4**, which subsequently suffers rapid spin-inversion and concomitant ring closure to afford **5**. Thermal cycloreversion of **5**, a spin-allowed process that proceeds via cheletropic extrusion of carbon monoxide, then leads to the formation of the observed reaction product, **3**.

A potential competing process might involve thermally spin-allowed retro-Diels-Alder extrusion of dioxygen from intermediate **5**. If this occurs, the starting material, i.e., **1**, would be regenerated, along with $^1O_2$.[6]



Scheme 2

In a separate experiment, $NaBH_4$ promoted reduction of diketone **3** followed by aqueous acidic workup led to the formation of the corresponding 2,3-annulated furan (**9**). A mechanism that accounts for the formation of **9** in this reaction is shown in Scheme 3.



Scheme 3

X-ray crystallography

An X-ray structure drawing of **3** is shown in Figure 1. The phenanthrene moiety is planar; the two *trans* phenyl rings reside at dihedral angles of 79.1(2)° and 80.8(2)°, respectively, relative to the plane of the phenanthrene rings. The two *trans* carbonyl groups are twisted slightly out of the phenyl planes [O(1)-C(15)-C(16)-C(17) = 165.5(3)° and O(2)-C(22)-C(23)-C(24) = -172.9(3)°].

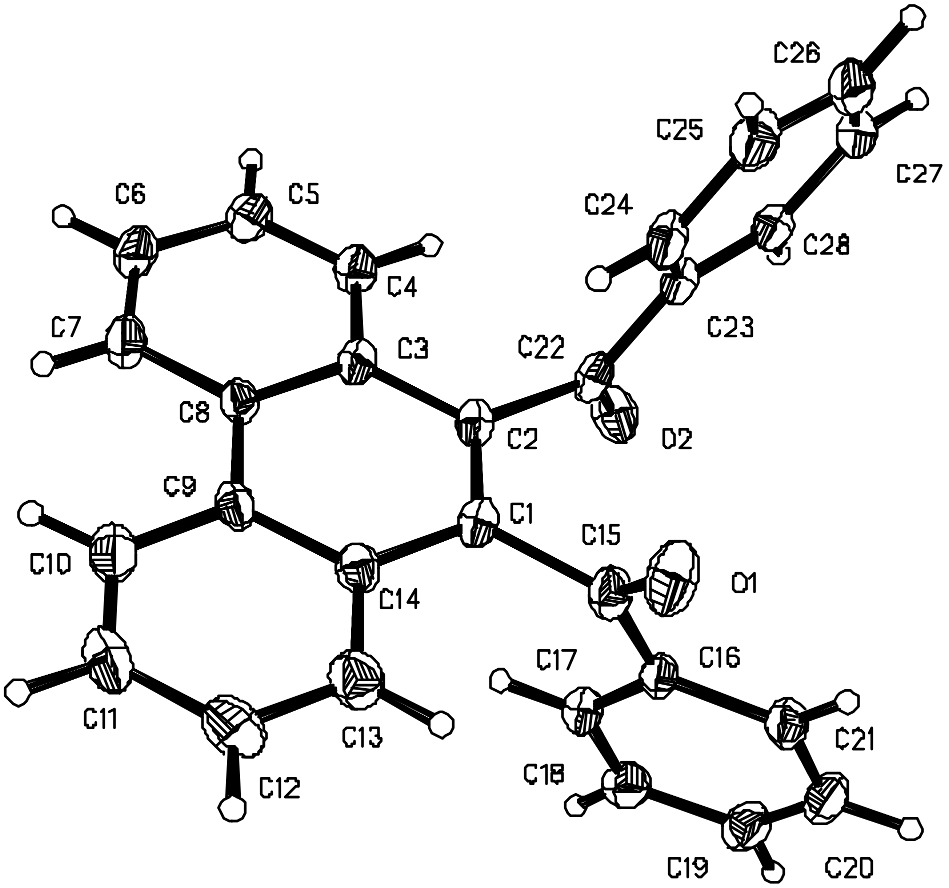


Figure 1. ORTEP-style thermal ellipsoid X-ray structure drawing of **3**.

The corresponding crystal packing diagram (Figure 2) shows the orientations of the three planar groups in the structure. The shortest intermolecular distance is a weak interaction between a carbonyl oxygen and two phenyl hydrogen atoms on adjacent molecules.

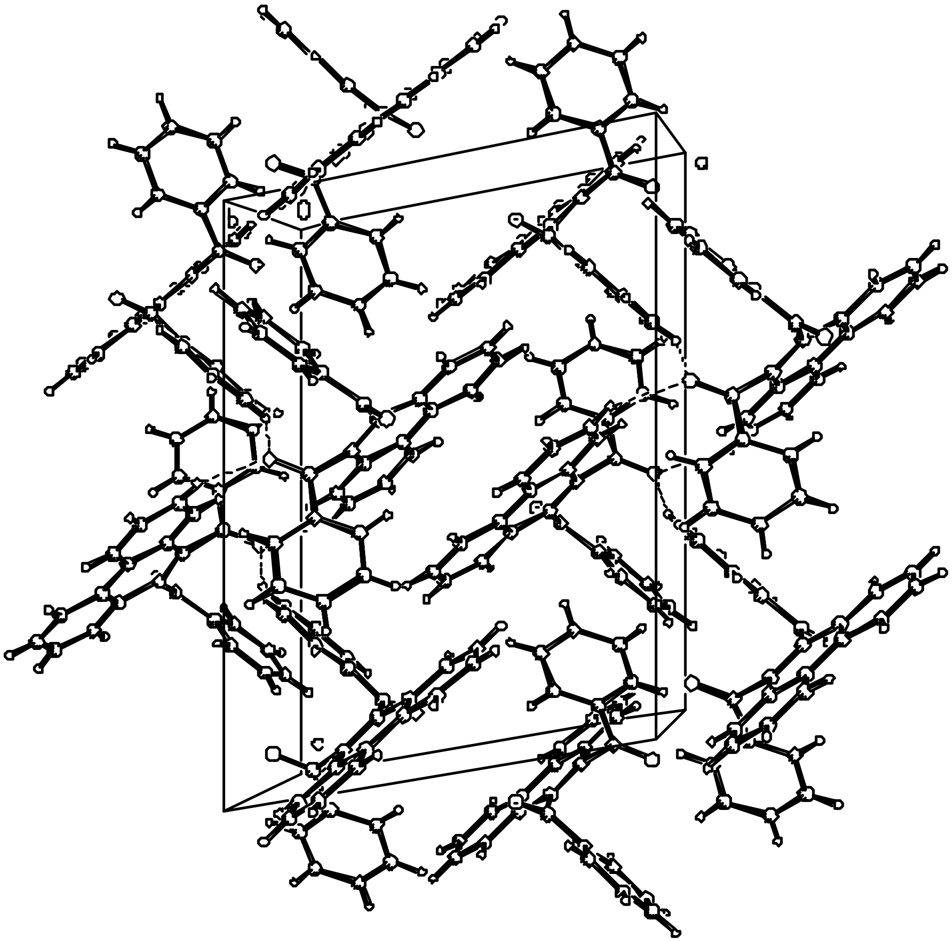


Figure 2. X-ray crystal packing diagram for **3**.

Conclusions

9,10-Dibenzoylphanthrene (**3**) was prepared via thermal autoxidation of phencyclone (**1**) in the presence of atmospheric O_2. The structure of **3** was elucidated via single crystal X-ray structural analysis. A mechanism is suggested in Scheme 2 to account for the formation of **3**. It is believed that stepwise 1,4-addition of $^3O_2$ to the 1,3-diene system in the cyclopentadiene moiety of **1** occurs to form endoperoxide **5**. Subequent cheletropic extrusion of carbon monoxide from **5** then leads to the formation of the observed autoxidation product, **3**.

Experimental Section

General Procedures. Melting points were obtained on a Thomas Hoover Uni-Melt melting point capillary apparatus and are uncorrected, IR spectra were obtained by using a Midac Corp. Model 101025 infrared spectrophotometer. Proton nmr spectra (obtained at 200 MHz) and ^{13}C nmr spectra (obtained at 50.3 MHz) were run on a Varian Gemini 200 nuclear magnetic resonance spectrometer.

1,3-Diphenyl-2*H*-cyclopenta[l]phenanthrene-2-one (Phencyclone, 1). Phencyclone was prepared by using a modification of a published procedure.[7] Thus, to a mixture of phenanthrene-9,10-quinone (2.08 g, 10 mmol) and 1,3-diphenylacetone (2.31 g, 11 mmol) in EtOH (40 mL) was added dropwise with stirring at ambient temperature 20% ethanolic KOH (4 mL, 14 mmol). The initial yellow suspension gradually darkened to a black solution. This solution was cooled to 0-5 °C via application of an external ice-water bath, whereupon a precipitate formed gradually. This precipitate was collected via suction filtration, and the residue was washed with cold EtOH (15 mL). Pure **1** (1.85 g, 48%) was thereby obtained as a black microcrystalline solid: mp 243-245 °C (lit. mp 226 °C,[2] mp 243-246 °C[7]); IR (KBr) 3062 (w), 1697 (s), 1443 (m), 1100 (m), 750 (s), 729 (s), 695 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 6.88-6.98 (m, 2 H), 7.21-7.28 (m, 2 H), 7.34-7.45 (m, 10 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.79 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 123.1 (s), 124.4 (d), 128.2 (d), 128.3 (d), 128.5 (s), 128.6 (d), 129.0 (d), 130.0 (d), 131.4 (d), 132.3 (s),133.5 (s), 148.2 (s), 199.7 (s). This material was used as obtained in the next step, without additional purification.

9,10-Dibenzoylphenanthrene (3). Method A. A solution of **1** (200 mg, 0.52 mmol) in either xylene (20 mL) or chlorobenzene (20 mL) was refluxed with stirring during 4 h. No special precautions were taken to exclude atmospheric oxygen. The reaction mixture was allowed to cool gradually to ambient temperature and then was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 2% EtOAc-hexane. Pure **3** (140 mg, 72%) was thereby obtained as a colorless microcrystalline solid: mp 206-207 °C (lit.[8] mp 206 °C); IR (KBr) 3057 (s), 1663 (s), 1447 (s), 1231 (s), 760 (s), 708 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.30-7.42 (m, 4 H), 7.48-7.60 (m, 4 H), 7.66-7.90 (m, 8 H), 8.81 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 123.5 (d), 127.75 (d), 127.79 (d), 127.9 (d), 128.5 (d), 128.9 (s), 130.6 (d), 131.0 (s), 134.3 (d), 135.8 (s), 138.1 (s), 198.7 (s).

9,10-Dibenzoylphenanthrene (3). Method B. A solution of **1** (135 mg, 0.35 mmol) in xylene (10 mL) was refluxed overnight in the dark during 12 h. No precautions were taken to exclude atmospheric O_2. After the reflux period had concluded, the reaction mixture was allowed to cool gradually to ambient temperature and then was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 2% EtOAc-hexane. Pure **3** (88 mg, 65%) was thereby obtained as a colorless microcrystalline solid: mp 206-207 °C. The IR, ^{1}H

nmr, and ^{13}C nmr spectral data for this material were essentially identical to the corresponding spectra obtained for **3** that had been prepared previously by using Method A (*vide supra*).

Sodium Borohydride Promoted Reduction of 3. To a solution of **3** (150 mg, 0.39 mmol) in MeOH (15 mL) under argon at ambient temperature was added portionwise with stirring $NaBH_4$ (38 mg, 1.0 mmol). After all of the reducing agent had been added, the reaction mixture was stirred at ambient temperature during 8 h and then was quenched via careful dropwise addition of 10% aqueous HCl (15 mL, excess). The resulting mixture was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic extracts were washed sequentially with water (20 mL) and brine (15 mL), dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Pure **9** (122 mg, 85%) was thereby obtained as a spongy white solid: mp 178-179 °C (lit.[2] mp 185 °C); IR (KBr) 3054 (s), 1484 (m), 1432 (m), 950 (m) 745 (s), 692 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.22-7.31 (m, 2H), 7.38-7.57 (m, 8H), 7.82 (dd, J_1 = 7.7 Hz, J_2 = 0.7 Hz, 4 H), 8.17 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 2H), 8.35 (dd, J_1 = 8.1 Hz, J_2 = 0.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 117.3 (s), 123.8 (d), 124.1 (d), 126.9 (d), 127.0 (s), 127.1 (d), 128.7 (d), 128.8 (d), 129.3 (d), 130.6 (s), 132.6 (s), 147.1 (s).

X-ray Structure Determination of 3. X-ray data were collected on a Bruker SMART^{TM} 1000 CCD-based diffractometer. The frames were integrated with the *SAINT* software package[9] by using a narrow frame algorithm, and the structre was solved and refined using the *SHELXTL* program package.[10] The structure was checked with *PLATON*.[11] Crystal data, collection parameters, and refinement criteria for compound **3** are presented in Table 1.

Table 1. Crystal data and structure refinement for compound **3**

Compound	**3**		
Formula	$C_{28}H_{18}O_2$	D_{calc} (g-cm^{-3})	1.320
Size (mm)	0.18 _ 0.16 _ 0.16	μ (mm^{-1})	0.082
Space Group	$P2_1/C$	T (K)	213(2)
a (Å)	12.116(2)	2θ range (°)	1.71 to 20.81
b (Å)	9.6850(2)	Total reflections	6639
c (Å)	16.839(3)	Independent reflections	2037
α (°)	90	R_{int}	0.0609
β (°)	100.331(3)	Data/restraints/ parameters	2037/0/272
γ (°)	90	R, R(all)	0.0461, 0.0808
V (Å^3)	1943.9(5)	GOF	1.007
Z-value	4	Extinction correction	0.0016(7)

Acknowledgments

We thank the Robert A. Welch Foundation [Grants B-0963 (A. P. M) and P-0074 (W. H. W.)] for financial support of this study. In addition, we thank the Texas Advanced Technology Program [Grant 003659-0206-1999 (A. P. M.)] and the U. S. Department of Energy [Grant DE-FG07-98ER14936 (A. P. M.)] for additional financial support of the work reported herein.

References and Notes

1. For leading references, see: Marchand, A. P.; Kumar, K. A.; McKim, A. S.; Alihodzic, S.; Chong, H.-S.; Krishnudu, K.; Takhi, M.; Mlinaric-Majerski, K.; Kragol, G.; Sumanovac, T. *Kem. Ind.* **2001**, *50*, 129.
2. Dilthey, W.; Henkels, S.; Leonhard, H. *J. Prakt. Chem*. **1938**, *151*, 97.
3. Foote, C. S.; Wexler, S. *J. Am. Chem. Soc*. **1964**, *86*, 3879.
4. Foote, C. S.; Clennan, E. L. in: *Active Oxygen in Chemistry*, Foote, C. S.; Valentine, J. S.; Greenberg, A.; Liebman, J. F., Eds., Blackie Academic & Professional: New York, 1995, Chapter 4, pp 105-140.
5. Seip, M.; Brauer, H. D. *J. Am. Chem. Soc*. **1992**, *114*, 4486.
6. Acene endoperoxides frequently undergo thermal decomposition to afford $^1O_2$; see: Saito, I.; Matsuura, T. in: *Singlet Oxygen*, Wasserman, H. H.; Murray, R. W., Eds. Academic Press: New York, 1979, pp 524-526.
7. (a) Dilthey, W.; ter Horst, I.; Schommer, W. *J. Prakt. Chem*. **1935**, *143*, 189. (b) Pascal Jr., R. A.; Engen, D. V.; Khar, B.;McMillan, W. D. *J. Org. Chem*. **1988**, *53*, 1687.
8. Baidossi, W.; Schumann, H.; Blum, J. *Tetrahedron* **1996**, *52*, 8349.
9. *SAINT*, Version 6.02, *Bruker Analytical X-ray Systems, Inc.* Copyright 1997-1999.
10. *SHELXTL* , Version 5.1, *Bruker Analytical X-ray Systems, Inc.* Copyright 1998.
11. (a) Spek, A.L. *Acta Cryst.* **1990**, *A46*, C34. (b) Spek, A. L. *PLATON - A Multipurpose Crystallographic Tool*, University of Utrecht, Utrecht, The Netherlands (2001).