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Formation of an Unusual Fused-Ring Cyclic Carbonate and Its Photolytic Rearrangement into the Novel Heterocycle 2,5-Diphenylphenanthro[9,10-*b*]oxepin[1a,b]

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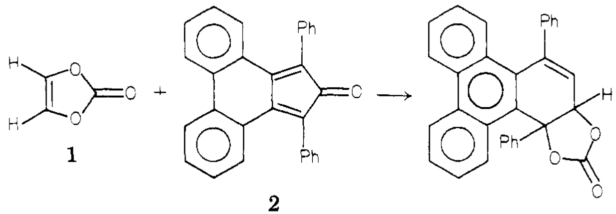
Vinylene carbonate (**1**) and phencyclone (**2**) react in refluxing bromobenzene to yield the cyclic carbonate ester of 1,4-diphenyl-1,2-dihydrotriphenylene-1,2-diol (90%, **3**), presumably by decarbonylation of the intermediate Diels–Alder adduct **6** followed by a [1,5] shift of the carbonate moiety. On photolysis (254 nm) **3** undergoes conversion to 1,4-diphenyltriphenylen-2-ol (15%, **9**) and 2,5-diphenylphenanthro[9,10-*b*]oxepin (43%, **8**), the first example of the hitherto unknown phenanthro[9,10-*b*]oxepin ring system. The structural assignments for **3** and **9** are based on spectroscopic and chemical evidence, while that of **8** follows unequivocally from single-crystal X-ray analysis. A possible rationalization for the formation of **8** and **9** from **3** is discussed, and evidence is presented which indicates that oxepin **8**, rather than arene oxide **14**, is the major component of any equilibrium which may exist between these two valence tautomers.

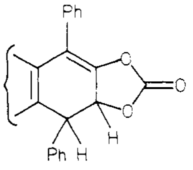
Several years ago one of us described a convenient synthesis of phenols[2] which involved thermolysis of the Diels–Alder adducts formed in situ from vinylene carbonate (**1**) and substituted cyclopentadienones. At that time it was noted that phencyclone (**2**) failed to undergo conversion to phenolic product under these conditions but produced, instead, a single "carbonyl-containing compound" in high yield. In this paper we present the physical and chemical evidence which has led to the assignment of rearranged carbonate structure **3** to the "carbonyl-containing compound". We also report on the photolytic transformation of **3** into the novel phenanthro[9,10-*b*]oxepin **8** and briefly describe some selected aspects of the chemistry of **8** which bear on the equilibrium between **8** and its valence tautomer **14**.

Heating a solution of **1** and **2** in bromobenzene for 48 h led to the evolution of a gas identified as carbon monoxide and afforded the single, crystalline product **3**, mp 244 °C, in 86% yield, whose structure was assigned as the cyclic carbonate ester of 1,4-diphenyl-1,2-dihydrotriphenylene-1,2-diol on the basis of the physical and chemical data outlined below. Structure **3** showed a parent peak at *m/e* 440 as well as peaks at *m/e* 396 ($M^+ - CO_2$) and 380 ($M^+ - CO_2 - O$) in the mass spectrum, infrared absorption[3] at 1805 cm^{-1}, NMR doublets at δ 5.12 (1 H, J = 6.8 Hz) and 6.10 (1 H, J = 6.8 Hz) in addition to the aromatic protons at 7.25–7.95 (18 H), and a molecular weight (by high-resolution mass spectrometry) consistent with the empirical formula $C_{31}H_{20}O_3$.

Although the above NMR spectral results pointed fairly strongly to **3** as the correct structure for the carbonyl-containing compound, it was felt that the results obtained from a simple hydrolysis experiment would provide additional reinforcement for this assignment and aid in ruling out the feasible alternative structure, **4**. Basic hydrolysis of **3** should produce diene diol **5** which would be readily distinguishable from the hydroxy ketone (or its enol form) expected from hydrolysis of **4**. The reaction of the carbonyl-containing compound with 3% aqueous sodium hydroxide at reflux for 24 h did in fact yield a single product whose spectral properties were in agreement with the proposed diene diol structure. For instance, the infrared spectrum of the hydrolysis product exhibited only hydroxyl absorption, while the position of the hydroxy signal (centered at δ 5.15, 2 H) in the NMR spectrum of the product indicated no enol form was present.[4] Furthermore, treatment of the hydrolysis product with acetic anhydride–pyridine gave a crude diacetate [NMR singlets at δ 2.05 (3 H) and 1.93 (3 H)] which exhibited infrared bands at 1710 and 1740 cm^{-1} (no band at 1760 cm^{-1}). Unfortunately, attempted purification of this diacetate led to extensive decomposition. Given the spectral information, the results of the hydrolysis experiment, and the fact that the carbonyl-containing compound yields oxepin **8** on photolysis, we feel that structure **3** is a reasonable assignment; however, structure **4** cannot be completely ruled out at this time.



1 **2** **3**



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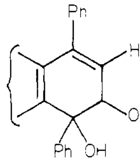

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[1] (a) A preliminary report on some of this work has been given: E. A. Harrison, Jr., Abstracts of Papers, 7th Central Regional Meeting of the American Chemical Society, Morgantown, WV, May 1975, No. 165. The structure of compound 8 was incorrectly given in the printed abstracts of the meeting. (b) Dr. K. L. Loening, Director of Nomenclature, Chemical Abstracts Service, provided us with the correct name and numbering for compound 8. We wish to thank Dr. Loening for his helpful interest.

[2] E. A. Harrison, Jr., *Org. Prep. Proced. Int.*, 7, 71 (1975).

[3] Compounds containing the five-membered cyclic carbonate group show an enhanced C=O stretching frequency in the IR when compared with the mixed ester type of carbonate, average values being 1820 and 1760 cm^{-1}, respectively. See L. Hough, J. E. Priddle, R. S. Theobald, G. R. Barker, T. Douglas, and J. W. Spoors, *Chem. Ind.* (*London*), 148 (1960).

[4] The hydroxylic absorption of enols normally occurs at very low fields (i.e., δ 15–16). See, for example, J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, NJ, 1965, p 91.

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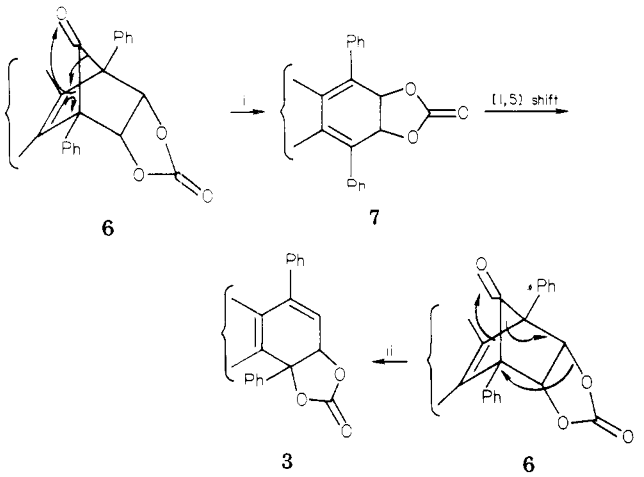
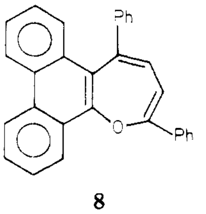
The formation of rearranged carbonate **3** can be postulated to proceed through the endo configuration of Diels–Alder adduct **6**, utilizing either one of two possible routes. Route i requires the loss of carbon monoxide through involvement of the C=C bond to afford the symmetrical diene carbonate **7**. The latter can then rearrange via a [1,5] carbonate shift to give **3**. Route ii utilizes a concerted carbonate migration with loss of carbon monoxide from **6** directly. The conversion of **6** into **7** parallels observations in the thermal behavior of other carbonyl bridge compounds,[5] while the rearrangement of **7** to **3** may be viewed as a concerted [1,5] sigmatropic shift which demonstrates the greater migratory aptitude of the cycloalkoxycarbonyl group in comparison with hydrogen. Subsequent to our preliminary paper[1] a number of [1,5] shifts involving similar groups in cyclic systems have been reported by other workers.[6] On the other hand, ii seems intuitively attractive inasmuch as participation of the C=C bond of **6** is not required. This avoids destruction of the aromatic resonance (i.e., central ring of phenanthrene nucleus) and the thermodynamic stability associated with it. Although the available information did not provide sufficient evidence to favor one route over the other, it was possible to show that Diels–Alder adduct **6** was involved in the overall conversion. This adduct, prepared in xylene solvent from **1** and **2** in 77% yield, was decomposed in refluxing bromobenzene to give 90% of rearranged carbonate **3**, carbon monoxide being evolved in the process.



The rearranged carbonate **3** was also found to exhibit interesting photochemistry. Irradiation of a degassed tetrahydrofuran solution of **3** with 254 nm wavelength light led to the evolution of carbon dioxide and yielded a mixture of 2,5-diphenylphenanthro[9,10-*b*]oxepin (**8**, 43%) and a second product (15%) which has been tentatively identified as 1,4-diphenyltriphenylen-2-ol (**9**). The structure of the triphenylenol was based on a parent peak at *m/e* 396 and a strong peak at 368 (M^+ − CO) in the mass spectrum, infrared absorption at 3515 cm^{-1}, an NMR singlet at δ 6.26 (1 H, D_2O exchangeable) plus an aromatic multiplet at 6.77–9.67 (19 H), and a high-resolution mass spectral molecular weight consistent with the empirical formula $C_{30}H_{20}O$. While these data supported a phenol structure for the product, they did not permit us to distinguish between **9** and other isomeric phenols which would be derived from migration of phenyl to various positions on the triphenylene backbone (e.g., **10**, **11**). Our choice of **9** was based on mechanistic considerations, taking into account the known photochemical behavior of other cyclic carbonate esters[7] and related systems.[5,8] In these cases the carbon backbone of the starting material remained intact, and no phenyl migration was observed during the photolysis. It should be pointed out that other workers[9] have observed some phenyl migration during the photolysis of compounds similar to **3**; however, these photolyses were carried out under irradiation conditions quite different from ours (i.e., high-pressure mercury lamp, Pyrex filter, and benzene solution).



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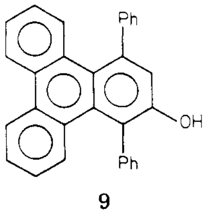

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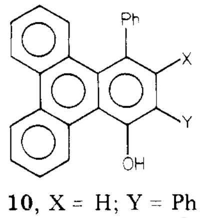
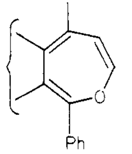


10, X = H; Y = Ph
11, X = Ph; Y = H

The structure of the major product (**8**) proved more difficult to assign. The infrared and mass spectral data (see Experimental Section) revealed that **8** contained oxygen and was isomeric with **9**, but it possessed neither hydroxy nor carbonyl functionalities. The NMR spectrum showed a pair of doublets at δ 6.97 (1 H, J = 5.6 Hz) and 6.21 (1 H, J = 5.6 Hz) as well as a multiplet at 7.10–8.37 (18 H). Interpreting these spectroscopic data in the light of Braun's observations concerning the thermolytic behavior of divinyl ethylene carbonate[10] led to the conclusion that a reasonable structure for the photolysis product could be chosen from among several isomeric oxepins (e.g., **8**, **12**) or arene oxides (e.g., **13**, **14**). Although the color of the product (yellow)[11] and the position of the downfield doublet[12] tended to favor the oxepin structures, a definitive



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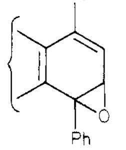

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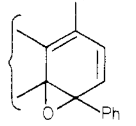

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(5) The formation of dienes derived from decarbonylation of carbonyl-bridge compounds similar to **6** is a well-known reaction. E.g., see: (a) C. F. H. Allen and J. A. Van Allan, *J. Am. Chem. Soc.*, **64**, 1260 (1942); (b) K. MacKenzie, *J. Chem. Soc.*, 473 (1960); (c) B. Fuchs, *J. Chem. Soc. C*, 68 (1968); (d) G. Kretschmer, I. W. McCay, M. N. Paddon-Row, and R. N. Warrener, *Tetrahedron Lett.*, 1339 (1975).

(6) E.g., see: (a) D. W. Jones and G. Kneen, *J. Chem. Soc., Perkin Trans. 1*, 171 (1975); (b) R. A. Abromovitch and I. Shinkai, *Acc. Chem. Res.*, **9**, 192 (1975), and references cited therein.

(7) E. A. Harrison, Jr., *J. Org. Chem.*, **44**, 1807 (1979).

(8) H. Prinzbach, R. Kitzing, E. Druckrey, and H. Achenbach, *Tetrahedron Lett.*, 4265 (1966); R. N. Warrener and J. B. Bremner, *Angew. Chem., Int. Ed. Engl.*, **5**, 311 (1966).

(9) R. N. Warrener and J. B. Bremner, *Tetrahedron Lett.*, 5691 (1966).

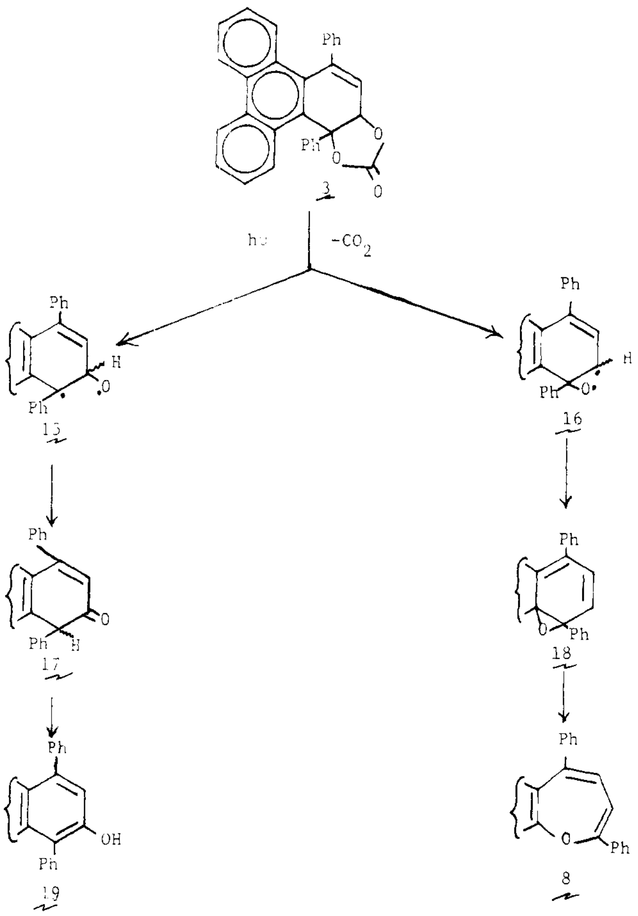
(10) R. A. Braun, *J. Org. Chem.*, **28**, 1383 (1963).

(11) Oxepins range in color from red-brown (e.g., 2-acetyloxepin) to intense yellow (e.g., 1-benzoxepin). E.g., see E. Vogel and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(12) The β protons of certain oxepins have been observed as far downfield as δ 6.6 [e.g., see H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem., Int. Ed. Engl.*, **5**, 1039 (1966)]; however, neither the oxirane proton of **13** (ref 13, and references cited therein) nor the olefinic protons of **13** and **14** would be expected to resonate as far downfield as δ 6.97.

assignment was not possible; therefore the structure was unequivocally established by a single-crystal X-ray structure analysis. To our knowledge, 8 represents the first example of the hitherto unknown phenanthro[9,10-*b*]oxepin system.

A possible rationalization of the photochemistry of rearranged carbonate **3** involves initial photoinduced decarboxylation[13] to yield isomeric diradicals **15** and **16**.



Hydrogen migration to yield **17** followed by tautomerization accompanies the conversion of **15** into triphenylenol **9**, while cyclization of **16** to arene oxide **18** and then valence isomerization produces oxepin **8**. The latter process (**16** → **8**) is analogous to that proposed by Brightwell and Griffin to explain the photochemical rearrangement of 9,10-epoxy-9,10-dihydrophenanthrene to 1,2:3,4-dibenzoxepin.[14]

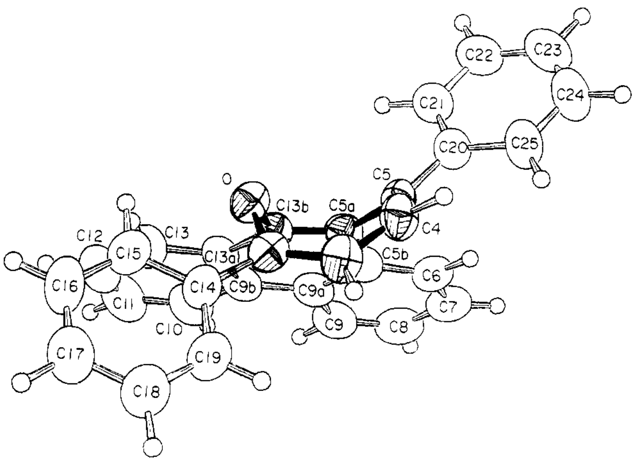
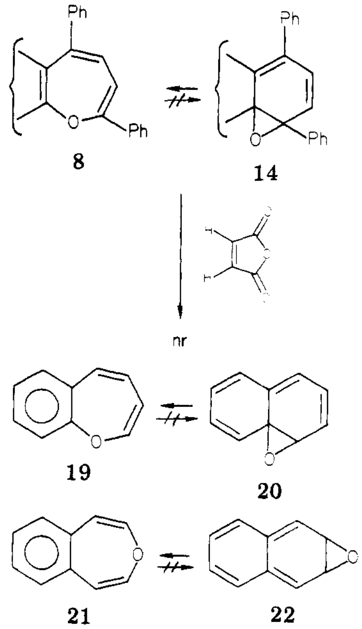


Figure 1. ORTEP drawing of 8 to illustrate the boat shape of the oxepin ring. 50% ellipsoids were used for C and O, and the H's are shown as 0.1 Å radius spheres. Atom labels for C2 and C3 in the oxepin ring were omitted for clarity.

The NMR spectrum attests to the homogeneity of **8** at room temperature, and the lack of reactivity toward the reagents/conditions described below reinforces this finding. Thus **8** was unreactive toward maleic anhydride in refluxing benzene (NMR analysis) and was recovered unchanged after treatment with 3 M sulfuric acid (18 h at room temperature). Similarly, the NMR spectrum of **8** underwent no change in the position or shape of the peaks on the addition of trifluoroacetic acid[15] or on cooling the sample tube to -60 °C.[11] This evidence strongly suggests that the equilibrium between valence tautomers **8** and **14** lies predominantly to the left, a result very much in keeping with findings for similar fused-ring systems (e.g., **19** $\rightleftharpoons$ **20**[11] and **21** $\rightleftharpoons$ **22**[16]).



The boat shape of the oxepin ring in **8** is illustrated in Figure 1, an ORTEP drawing from our X-ray crystallographic structure determination. On the basis of dihedral angles for the C2–C14 and C5–C20 bonds, the two aromatic rings are twisted by 17.9 and 34.5°, respectively, from the oxepin ring C2=C3 and C4=C5 bonds. The left-most benzene ring partially overlaps the phenanthrene nucleus: the C21···C5b and C22···C6 distances of 3.4 Å are equal to the face-to-face van der Waals separation of two aromatic nuclei. The average deviation of the phenanthrene carbon atoms from their least-squares plane is 0.03 Å, and the individual distances show that the two outer six-membered rings are twisted in opposite directions from the plane of the central one.

The bond lengths (Table I) are normal in most instances. The C6–C7–C8–C9 and C10–C11–C12–C13 regions of the phenanthrene ring show a marked short-long-short pattern, which is not observed in phenanthrene itself.[17] The

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[13] D. A. Jaeger, *J. Am. Chem. Soc.*, **96**, 6216 (1974), and references cited therein.

[14] N. E. Brightwell and G. W. Griffin, *Chem. Commun.*, 37, (1973).

[15] Acid-catalyzed isomerization of arene oxides to phenols is a well-documented occurrence. E.g., see: (a) D. M. Jerina, H. Yagi, and J. W. Daly, *Heterocycles*, 1, 267 (1973); (b) ref 13, and references cited therein.

[16] (a) K. Dimroth and G. Pohl, *Angew. Chem.*, **73**, 436 (1961); (b) K. Dimroth, G. Pohl, and H. Follmann, *Chem. Ber.*, **99**, 634 (1966).

[17] M. I. Kay, Y. Okaya, and D. E. Cox, *Acta Crystallogr., Sect. B*, 27, 26 (1971).

Table I. Bond Lengths (Å), Estimated Standard Deviations (in Parentheses), and HMO π-Bond Orders[a]

bond	length	π-bond order
O-C2	1.408 (4)	
O-C13b	1.398 (4)	
C2-C3	1.336 (4)	0.809
C2-C14	1.470 (5)	0.407
C3-C4	1.439 (5)	0.412
C4-C5	1.342 (5)	0.813
C5-C5a	1.491 (4)	0.274
C5-C20	1.489 (5)	0.355
C5a-C5b	1.459 (5)	0.494
C5a-C13b	1.356 (4)	0.721
C5b-C6	1.408 (5)	0.577
C5b-C9a	1.411 (4)	0.504
C6-C7	1.370 (6)	0.706
C7-C8	1.392 (5)	0.622
C8-C9	1.364 (6)	0.701
C9-C9a	1.417 (5)	0.590
C9a-C9b	1.451 (5)	0.461
C9b-C10	1.418 (4)	0.591
C9b-C13a	1.406 (5)	0.537
C10-C11	1.365 (6)	0.701
C11-C12	1.383 (6)	0.621
C12-C13	1.370 (5)	0.708
C13-C13a	1.403 (5)	0.572
C13a-C13b	1.443 (4)	0.506
C14-C15	1.400 (5)	
C14-C19	1.396 (5)	
C15-C16	1.374 (5)	
C16-C17	1.379 (7)	
C17-C18	1.383 (6)	
C18-C19	1.371 (5)	
C20-C21	1.391 (5)	
C20-C25	1.400 (5)	
C21-C22	1.378 (5)	
C22-C23	1.379 (6)	
C23-C24	1.366 (7)	
C24-C25	1.383 (6)	

[a] For the C-C bonds in the phenanthro[9,10-*b*]oxepin nucleus. Computed with the ω-HMO technique with the following coulomb and resonance integrals: $\alpha_0 = 2\beta_{C\text{-}C}$, $\beta_{C\text{-}O} = 0.8\beta_{C\text{-}C}$, $\beta_{C2\text{-}C14} = (\cos 17.9)\beta_{C\text{-}C}$, $\beta_{C3\text{-}C4} = (\cos 35.5)\beta_{C\text{-}C}$, $\beta_{C5\text{-}C20} = (\cos 34.5)\beta_{C\text{-}C}$, and $\beta_{C5\text{-}C6} = (\cos 46.5)\beta_{C\text{-}C}$.

oxepin ring carbon–carbon distances have the typical short–long–short sequence of 1,3,5-hexatrienes, but C5–C5a at 1.491 Å is unusually long. C(sp^2)–C(sp^2) single bonds in hexatrienes are normally 1.45–1.46 Å (e.g., *trans*-1,3,5-hexatriene = 1.457 Å,[18] *cis*-1,3,5-hexatriene = 1.462 Å,[19] and 1,3,5-cycloheptatriene = 1.446 Å[20]). Several ω-iteration HMO calculations[21] were performed to probe this possible bond length discrepancy. In one case a completely flat molecule was assumed whereas in another the resonance parameters for C2–C14, C3–C4, C5–C20, and C5–C6 were modified by the cosines of the appropriate twist angles. Both calculations provided remarkably good pictures of the carbon–carbon distances; π bond orders from the second calculation are included in Table I. C5–C5a was predicted to be the largest bond, the short–long–short patterns in C6–C7–C8–C9 and C10–C11–C12–C13 were found, and many of the more subtle bond length differences were paralleled by the π bond orders.

It is interesting to note that the nonplanar triene portion of the oxepin ring which emerges from analysis of the X-ray data could also have been qualitatively predicted from the coupling parameters of the olefinic protons of 8. The coupling constant $J_{3,4}$ should show a similar dependence on the dihedral angle to that observed for the analogous coupling in cycloheptatriene.[22] That the coupling constant $J_{3,4}$ for 8 (5.6 Hz) is practically equal to the corresponding constant for cycloheptatriene (5.5 Hz) suggested that the C_4–C_5 dihedral angle was about 35°.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlabs, Inc., and by Dr. Franz Kasler, Department of Chemistry, University of Maryland. IR spectra were obtained as paraffin oil mulls on Perkin-Elmer 599 and Beckman IR8 spectrophotometers. ^{1}H NMR spectra were measured on Varian A-60 and EM-360 spectrometers with Me_4Si as internal standard. The low- and high-resolution mass spectra were obtained on an AEI MS-902 instrument. Silica gel GF plates for analytical TLC were purchased from Analtech, Inc. Photolyses were carried out in a Rayonet Photochemical Reactor (Model RPR-100) equipped with 16 RPR 2537A lamps.

X-ray Diffraction Analysis of 8. Suitable diffraction crystals were grown from tetrahydrofuran. The Laue symmetry, systematic absences, and rough values of the lattice constants were obtained from oscillation and Weissenberg photographs taken with Cu radiation. The final cell parameter and all intensity measurements were made on a Picker FACS-1 diffractometer with graphite crystal monochromatized Mo radiation ($\lambda_{K\alpha}$ = 0.710 69 Å). A crystal with dimensions of 0.2 × 0.3 × 0.3 mm was mounted and aligned to place [2,0,–1] parallel to the ϕ axis of the instrument. The cell constants were calculated by the method of least squares from 12 Bragg angles determined from manual measurements of $\pm 2\theta$ for each reflection; the average value of $|2\theta_o - 2\theta_c|$ was 0.006°. The space group is the monoclinic $P2_1/c$, and the cell parameters are a = 12.128 (4) Å, b = 9.780 (5) Å, c = 17.659 (5) Å, and β = 101.08 (3)°. The intensity data were collected with the θ–2θ scan method at a 2θ scan speed of 2° min^{-1} and with 10-s background counts; the 2θ scan range was calculated from 1.8° + 0.69° tan θ. Three standard reflections were measured every 100 reflections to monitor intensity fluctuations (maximum of 2.2%). A total of 3081 data were collected to a 2θ maximum of 50°; 2680 of the data (excluding systematic absences) were unique; 1456 data were more than three standard deviations above background.

The data were reduced and scaled, E's were calculated, and the phases for 472 reflections (236 plus, 236 minus) were obtained in a straightforward way with the direct-methods program PHASE.[22] An E map computed with these 472 data revealed all of the C and O atoms, and an initial structure factor calculation gave an R index ($R = \sum|F_o - F_c|/\sum F_o$) of 0.26. The structure was refined with the full-matrix least-squares method, minimizing the function $\sum w(F_o - F_c)^{2}$[23]; unit weights (w = 1) were used initially, but Hughes-type[23] weights (w = 1 for $F_o \leq 50$, $w = (50/F_o)^2$ for $F_o > 50$) were applied in the later refinement cycles. A reflection was included in the structure refinement only in those cases in which $I_c > 3\sigma(I_o)$. The last cycles of refinement used anisotropic temperature factors for C and O and isotropic terms for H (H atoms were initially located in a difference map) and included a correction for isotropic secondary extinction[24] [r^* = 0.0099 (6)] (X-ray scattering factors: C, O;[25] H[26]). The final R index was 0.037; the weighted index ($[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$) was 0.047.

Preparation of the Cyclic Carbonate Ester of 1,4-Diphenyl-1,2-dihydrotriphenylene-1,2-diol (3) from 1 and 2. A

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[18] M. Traetteberg, *Acta Chem. Scand.*, **22**, 628 (1968).

[19] M. Traetteberg, *Acta Chem. Scand.*, **22**, 2294 (1968).

[20] M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

[21] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, Chapter 4.

[22] All calculations were carried out on a UNIVAC 1108 computer. The crystallographic codes were from J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Report TR-192, Computer Science Center, University of Maryland, 1972.

[23] E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

[24] A. C. Larsen, "Crystallographic Computing", F. R. Ahmed, S. R. Hall, and C. P. Huber, Eds., Munksgaard, Copenhagen, Denmark, 1970, p 291.

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solution of **1**[27] (1.00 g, 12.0 mmol) and **2** (1.90 g, 5.00 mmol) in bromobenzene (20 mL) was heated at reflux with stirring (48 h) in a flask fitted with tubing which ran into a test tube containing saturated $PdCl_2$ solution. Evolution of carbon monoxide during the reaction was evidenced by the formation of a palladium mirror on the walls of the test tube. Evaporation of solvent yielded a brownish semisolid which solidified on trituration with benzene. Filtration yielded 1.90 g (86.0%) of nearly pure **3**, which showed, after recrystallization from benzene, a melting point of 244 °C (gas evolution): IR (paraffin oil) 1805 cm^{-1}; NMR ($CDCl_3$) δ 7.95–7.25 (m, 18 H, aromatic), 6.10 (d, 1 H, J = 6.8 Hz, vinylic H), 5.12 (d, 1 H, J = 6.8 Hz, CHO); mass spectrum (70 eV), *m/e* 440 (molecular ion), 396 ($M^{+\cdot} - CO_2$), 380 (base, $M^{+\cdot} - CO_2 - O$). The analytical sample was homogeneous on TLC (1:5 Et_2O–hexane and $CHCl_3$).

Anal. Calcd for $C_{31}H_{20}O_3$: *m/e* 440.1412. Found: *m/e* 440.1399.

Preparation of 1,4-Diphenyl-1,2-dihydrotriphenylene-1,2-diol (5). A suspension of **3** (400 mg, 0.909 mmol) in 30 mL of 3% aqueous NaOH was stirred and heated at reflux for 24 h. The reaction mixture was cooled and filtered, and the resulting solid was taken up in acetone (100 mL). The solution was dried (molecular sieves) and concentrated to leave 250 mg (67%) of crude **5**. Recrystallization (acetone–H_2O) afforded pure **5**: mp 155 °C; IR (paraffin oil) 3480, 3360 cm^{-1}; NMR (Me_2SO) δ 8.83–7.00 (m, 18 H, aromatic), 6.30 (d, 1 H, J = 6.5 Hz, vinylic H), 5.15 (br s, 2 H, D_2O exchangeable, OH), 4.16 (d, 1 H, J = 6.5 Hz, carbinol H); mass spectrum (70 eV), *m/e* 414 (molecular ion). The analytical sample was homogeneous on TLC (1:1 Et_2O–hexane and $CHCl_3$).

Anal. Calcd for $C_{30}H_{22}O_2$: *m/e* 414.1618. Found: *m/e* 414.1627.

Reaction of 5 with Acetic Anhydride/Pyridine. Attempted Preparation of Diacetate Derivative. A solution of pyridine (3 mL) in acetic anhydride (30 mL) was heated at reflux for 15 min, cooled to room temperature, and added to a flask containing 430 mg (1.04 mmol) of crude **5**. The resulting solution was stirred for 5 h and poured over ice (~20 g), affording 415 mg (80%, assuming diacetate) of product: mp 123 °C (gas evolution); IR (paraffin oil) 1740, 1710 cm^{-1}; NMR ($CDCl_3$) δ 8.70–7.00 (m, 18 H, aromatic), 6.35 (d, 1 H, $J \approx$ 6.5 Hz, vinylic H), 5.39 (d, 1 H, $J \approx$ 6.5 Hz, CHOAc), 2.05 (s, 3 H, $OCOCH_3$), 1.93 (s, 3 H, $OCOCH_3$); mass spectrum (70 eV), *m/e* 396 ($M^{+\cdot}$ – HOAc – CH_2CO). Attempted recrystallization of the crude diacetate (benzene–petroleum ether or acetone) led to decomposition as indicated by TLC analysis ($CHCl_3$ or Et_2O–hexane, 1:1) of the "recrystallized" material.

Preparation of the Cyclic Carbonate Ester of 1,2,3,4-Tetrahydro-2,3-dihydroxy-1,4-diphenyl-1,4-methanotriphenylen-13-one (6). A solution of **1** (1.00 g, 12.0 mmol) and **2** (1.90 g, 5.00 mmol) in 20 mL of xylene was stirred and heated at reflux for 15 h. The reaction mixture was cooled to room temperature and then placed in a freezer overnight, during which time solid material deposited. Filtration yielded 1.8 g (77%) of nearly pure **6**, which showed, after recrystallization from benzene, a melting point of 264–266 °C (gas evolution): IR (paraffin oil) 1815, 1790 cm^{-1}; NMR ($CDCl_3$) δ 7.83–7.05 (m, 18 H, aromatic), 6.05 (s, 2 H, methine H); mass spectrum (70 eV), *m/e* 468 (molecular ion), 440 ($M^{+\cdot}$ – CO), 396 ($M^{+\cdot}$ – CO – CO_2).

Anal. Calcd for $C_{32}H_{20}O_4$: C, 82.04; H, 4.30. Found: C, 82.33; H, 4.39.

Thermolysis of 6 in Refluxing Bromobenzene. A solution of **6** (800 mg, 1.71 mmol) in bromobenzene (10 mL) was heated at reflux with stirring (24 h) in a flask fitted with tubing which ran into a test tube containing saturated $PdCl_2$ solution. Evolution of carbon monoxide during the reaction was evidenced by the formation of a palladium mirror on the walls of the test tube. Evaporation of solvent yielded crude **3** (680 mg, 90%) which, on recrystallization from benzene, was shown to be identical (IR, NMR, mixture melting point) with **3** obtained from **1** and **2**.

Preparation of 2,5-Diphenylphenanthro[9,10-*b*]oxepin (8) and 1,4-Diphenyltriphenylen-2-ol (9) by Photolysis of 3. In the best of several runs, a solution of **3** (445 mg, 1.00 mmol) in dry THF was purged with dry N_2 gas for 15 min and then photolyzed in an apparatus fitted with tubing which ran into a test tube containing saturated $Ba(OH)_2$ solution. The photolysis was allowed to proceed until TLC analysis (Et_2O–hexane, 1:5) indicated all of **3** had been consumed (3 h). During this time carbon dioxide was evolved as indicated by the formation of a white precipitate in the test tube. Evaporation of solvent yielded a pale yellow oil which crystallized on dissolution in ethanol followed by dropwise addition of water. Recrystallization from $CHCl_3$–EtOH (1:6) yielded nearly pure **8** (170 mg, 43%), mp 188–192 °C (shrinkage at 180 °C). A second recrystallization from $CHCl_3$–EtOH provided the analytical sample: mp 195–197 °C; IR (paraffin oil) 1100, 1020, 770, 760, 700 cm^{-1}; NMR ($CDCl_3$) δ 8.70–7.00 (m, 18 H, aromatic), 6.97 (d, 1 H, J = 5.6 Hz, vinylic H), 6.21 (d, 1 H, J = 5.6 Hz, vinylic H); mass spectrum (70 eV), *m/e* 396 (molecular ion, base peak). The analytical sample was homogeneous on TLC (1:5 Et_2O–hexane and $CHCl_3$).

Anal. Calcd for $C_{30}H_{20}O$: *m/e* 396.1513. Found: *m/e* 396.1533.

Slow evaporation of the above $CHCl_3$–EtOH filtrate yielded crude **9** (60 mg, 15%), mp 150–158 °C. Recrystallization from EtOH–H_2O provided the analytical sample: mp 161–163 °C; IR (paraffin oil) 3525 cm^{-1}; NMR ($CDCl_3$) δ 9.67–6.77 (m, 19 H, aromatic), 6.26 (s, 1 H, D_2O exchangeable, OH); mass spectrum (70 eV), 396 (molecular ion), 368 ($M^{+\cdot}$ – CO).

Anal. Calcd for $C_{30}H_{20}O \cdot 0.1H_2O$: C, 90.47; H, 5.11. Found: C, 90.30; H, 5.17. Calcd for $C_{30}H_{20}O$: *m/e* 396.1513. Found: *m/e* 396.1509.

Behavior of 8 toward Various Reagents/Conditions. A. Maleic Anhydride. A solution of **8** (100 mg, 0.25 mmol) and maleic anhydride (31.1 mg, 0.30 mmol) in benzene (10 mL) was heated at reflux with stirring for 26 h, after which the solvent was evaporated to yield a yellow oil. NMR analysis of the oil ($CDCl_3$) indicated the presence of only oxepin (δ ~6.9 and 6.2) and maleic anhydride (δ 7.13).

B. CF_3COOH. The NMR spectrum of **8** (~50 mg in 1 mL of $CDCl_3$) underwent no change in the position or shape of the peaks on addition of CF_3COOH; however, the acidified solution took on a reddish color.

C. H_2SO_4. A solution of **8** (20 mg, 0.05 mmol) in THF (5 mL) was treated with 3 M H_2SO_4 (5 mL) and then stirred at room temperature for 18.5 h. TLC analysis (Et_2O–hexane, 1:5) showed **8** to be the only component present. The solvent was evaporated to yield a yellow oil which was taken up in benzene, washed with $NaHCO_3$ solution (2 × 10 mL), H_2O (1 × 10 mL), and brine (1 × 10 mL), and dried over molecular sieves (4A). Removal of the solvent on a rotary evaporator gave 14 mg (70%) of recovered **8**.

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Registry No. **1**, 872-36-6; **2**, 5660-91-3; **3**, 72659-35-9; **5**, 72659-36-0; **5** diacetate, 72659-37-1; **6**, 56406-98-5; **8**, 72672-39-0; **9**, 56406-93-0.

Supplementary Material Available: Tables of the atomic fractional coordinates and temperature factors and bond lengths and bond angles involving the hydrogen atoms for **8** (3 pages). Ordering information is given on any current masthead page.

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[27] Aldrich Chemical Co., No. V-260-7.