Fraction 4 (8%) exhibited ir and nmr spectra that were the same as those of 2,4-dimethoxyaniline.

Fraction 5, compound IV (5%), exhibited ir (KBr) 3450, 3340, and 1640 cm^{-1}; nmr (CCl$_4$) δ 2.45 (s, 3), 3.75 (s, 3), 5.7 (s, 2), and 6.8 (m, 3).

Fraction 6, compound V (11%), exhibited ir (KBr) 3460, 3360, and 1660 cm^{-1}; nmr (CCl$_4$) δ 2.40 (s, 3), 3.85 (s, 3), 4.30 (s, 2), 6.55 (m, 1), and 7.30 (m, 2).

Anal. Calcd for C$_9$H$_{11}$NO$_2$: C, 65.44; H, 6.71. Found: C, 65.17; H, 6.79.

Fraction 7, compound III (63%), exhibited ir (KBr) 3460, 3340, 1640 cm^{-1}; nmr (CCl$_4$) δ 2.45 (s, 3), 3.70 (s, 3), 3.85 (s, 3), 6.10 (s, 2), and 6.50 (m, 2).

Anal. Calcd for C$_{10}$H$_{13}$NO$_3$: C, 61.53; H, 6.71. Found: C, 61.29; H, 6.59.

Fraction 8, compound II, exhibited ir and nmr spectra which were the same as those of the starting material.

Fractions 9 and 10 (9%) could not be isolated.

Irradiation of 2,4,6-Trimethylacetanilide.—The substrate (1 g) was dissolved in 240 ml of pure benzene and irradiated as described above. After the solvent was removed, only 2,4,6-trimethylaniline and starting anilide could be isolated from the reaction mixture. No material was observed in the vpc chromatogram with a retention time the same that of as 1,2,3,5-tetramethylbenzene.

Registry No.—II, 23042-75-3; III, 23042-76-4; IV, 23042-77-5; V, 22106-40-7; 2,4,6-triethylacetanilide, 5096-21-9.

A Photochemical Preparation of 4,11-Diphenylbisanthene

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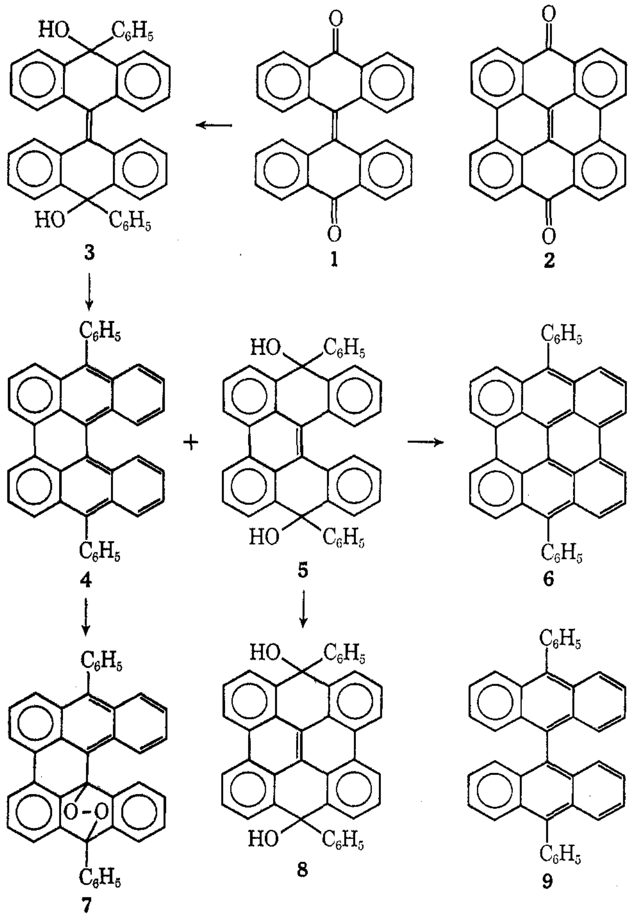
4,11-Diphenylbisanthene (**6**) is one of a few aromatic hydrocarbons from which fluorescence ($\Phi_F = 0.18$, λ_{max} 720 mμ in benzene) of moderate intensity has been detected in the infrared region.[1] A three-step synthesis of **6** with an overall yield of 20% had been described earlier by the sequence bianthrone (**1**) → 4,11-bisanthenequinone (**2**) → 4,11-dihydroxy-4,11-diphenyldihydrobisanthene (**8**) → **6**.[2] A more convenient approach appeared to be the photocyclization of the diphenylbianthracenediol **3**, which can be prepared from bianthrone in good yield.[3]

Ultraviolet irradiation of benzene solutions of **3** [λ_{max} 327 mμ (log ε 4.08)] and iodine exposed to the atmosphere did indeed produce hydrocarbon **6** in moderate yield. The only two products isolated were the deep blue diphenylbisanthene and the highly blue-fluorescing photooxide **7**. The easily identifiable intense bands at 683 and 625 mμ for product **6** facilitated the following of the reaction spectrophotometrically. A maximum buildup of diphenylbisanthene was quickly attained, but on prolonged irradiation the product was slowly decomposed. The concurrent appearance of a broad band centered near 400 mμ and the decrease in intensity of the peaks at 683 and 625 mμ imply the formation of a photooxide, since the absorption at shorter wavelengths is in the same region as that of the photooxide of bisanthene.[4] The photooxide of **6** could not be isolated; instead, only resinous material was obtained, as had been observed previously.[2]

Thus, the limiting factor in maximizing the yield of **6** is the photoinstability of the hydrocarbon. While yields were greatest when the reaction was carried out open to the atmosphere, the photooxidation of the product was also occurring. When following the reaction of 5.9×10^{-5} *M* **3** and 5.9×10^{-5} *M* iodine in a 1-cc cell, a yield of **6** as high as 59% was detected. On a larger scale, however, diphenylbisanthene was isolated in 20% yield.

Contrary to the observation that the yield of triphenylene in the photoaryl coupling of *o*-terphenyl is dependent on the iodine concentrations,[5] varying the amounts of iodine in the reaction of **3** to **6** had little affect on the yield, as demonstrated by the yields of **6** (50, 59, and 49%) when the ratios of diol **3**/I$_2$ were 10, 1.0, and 0.5. Iodine is essential to the reaction, however, since, without it, **6** was not formed as **3** was slowly consumed. Heating the product of the noncatalyzed reaction with hydriodic acid did not yield diphenylbisanthene. This result rules out dihydroxydiphenyldihydrobisanthene **8** as a product in the photochemical reaction in which iodine is not used.

Since the decomposition of **6** was much slower when irradiated under nitrogen, rather than when exposed to the air, solutions of **3** and iodine were irradiated in a nitrogen atmosphere. Under these conditions the yield of diphenylbisanthene was decreased to 5% and



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[1] M. M. Rauhut, D. R. Maulding, W. Bergmark, B. G. Roberts, R. A. Clarke and R. Coleman, unpublished work.

[2] G. Sauvage, *Ann. Chim.*, **2**,844 (1947).

[3] A. Schonberg and A. Ismail, *J. Chem. Soc.*, 201 (1945).

[4] H. Kuroda, *J. Chem. Phys.*, **33**, 1586 (1960).

[5] T. Sato, Y. Goto and K. Hata, *Bull. Chem. Soc. Jap.*, **40**, 1994 (1967).

diphenyldibenzoperylene **4** [$\lambda_{\max}$ 582 mμ (log ϵ 4.45) and $\lambda_{\max}$ 542 mμ (log ϵ 4.24)] became the major product. When exposed to oxygen hydrocarbon **4** was rapidly converted into a light yellow solid, mp 302–304°, having absorption peaks at 427, 403, and 382 mμ. The compound appears to be a photooxide of **4**, although the only known photooxide has a thermal decomposition point of 180°.[2] Other evidence which supports the photooxide structure is the elemental analysis, the bands in in infrared at 10.16, 10.53 (shoulder), and 10.62 μ (compare cluster of four bands centered at 11.0 μ for 9,10-diphenylanthracene photooxide), and the mass spectrum, with *m/e* 536, 431, and 353. The fragment at 431 (536 − $C_6H_5CO^+$) also indicates that one oxygen appears to be bonded to a carbon bearing a phenyl group, such as in structure **7**. This structure is also compatible with the absorption at 427, 403, and 382 mμ. Finally, the extreme photosensitivity of diphenyldibenzoperylene has already been observed.[2]

The possibility of **4** being an intermediate in the formation of **6** was considered, even though the related photocyclization of 1,1′-binaphthyl to perylene has not been observed.[6] The dehydrogenation of **4** to **6** might be expected to be a more favorable reaction because of the fixed geometry of **4** and its greater ability to stabilize the transition state. It is clear, however, from the isolation of only photooxide **7** from **4**, that diol **5** and not hydrocarbon **4** is responsible for the formation of diphenylbisanthene.

To confirm its intermediacy in the cyclization of **3** to **6**, diol **5** was prepared from helianthrone according to the method outlined by Sauvage.[2] Irradiation of benzene solutions of **5** in the presence of iodine gave **6** in 79% yield; however, without iodine the highly colored diphenylbisanthene was not formed. Hydriodic acid reduction of the crude product of the noncatalyzed reaction did form **6** in a moderate yield, thereby indicating the formation of **8**.[7]

10-10′-Diphenyl-9,9′-bianthranyl (**9**) was not detected in the reaction, and the possibility that it or its photooxide was an intermediate or product was excluded by recovering **9** unchanged after exposure to the same reaction conditions necessary for the conversion of **3** into **6**. This observation is in agreement with the report that **9** is resistant to photooxide formation.[8]

The photochemical transformation of **3** to **6** may be considered similar to the stilbene–phenanthrene and bianthrone–bisanthenequinone photocyclizations,[9] and the existence of dihydrophenanthrene-type intermediates is probable. It appears that the quantum yield of the reaction diol **5** to **6** is considerably less than that for reaction **3** to **5**, since the time required for the attainment of the maximum absorbance of diphenylbisanthene at 683 and 625 mμ in the reaction **5** to **6** was the same as that in the conversion of **3** into **6**.

Experimental Section

Equipment and Materials.—A General Electric BH6 lamp and a Pyrex filter were used in all of the photochemical experiments. The procedures described for making 10,10′-diphenyl-[$\Delta^{9,9'(10H,10'H)}$-bianthracene]-10,10′-diol (**3**)[3] and 3,10-dihydroxy-3,10-diphenyl-3,10-dihydro-1,2,11,12-dibenzoperylene (**5**)[2] from bianthrone (Aldrich) and helianthrone[2] were used without modification.

4,11-Diphenylbisanthene (6) from Diol 3.—A solution of 216 mg of **3**, 12 mg of iodine, and 500 ml of benzene was irradiated for 4 hr while exposed to the atmosphere. The visible absorption spectrum of an aliquot indicated that the yield of product was 33%. The benzene was removed and the dark solid was treated with boiling xylene. The cooled solution was passed through a column containing Woelm neutral alumina and xylene. Evaporation of xylene gave 54 mg of deep blue solid. Recrystallization from xylene gave 41 mg (20%): mp 300° (lit.[2] mp 430°); mass spectrum *m/e* 502; visible absorption in benzene, $\lambda_{\max}$ 683 mμ (log ϵ 4.69) and 625 (4.43) [lit.[2] $\lambda_{\max}$ 690 mμ (log ϵ 5.01) and 630 (4.75)].

Although the extinction coefficients are lower than those reported,[2] additional recrystallization from xylene or chromotography experiments did not increase the log ϵ values. Moreover, fluorescence measurements indicated that no visible fluorescing materials were present.

Anal. Calcd for $C_{40}H_{20}$: C, 95.62; H, 4.38. Found: C, 95.28; H, 4.16.

The filtrate contained 8 mg (4%) of a light yellow solid: mp 302–304° (toluene); visible absorption in benzene, $\lambda_{\max}$ 427 mμ (log ϵ 4.26), 403 (4.24), and 382 (3.97); infrared (Nujol) 10.16, 10.53 (shoulder), and 10.62 μ (compare cluster of four bands centered at 11.0 μ for the photooxide of 9,10-diphenylanthracene); mass spectrum *m/e* 536, 431, and 353. Benzene solutions gave strong blue fluorescence.

Anal. Calcd for $C_{40}H_{24}O_2$: C, 89.55; H, 4.48. Found: C, 89.21; H, 4.52.

Benzene solutions of **3** were irradiated in a 1-cc cell and the maximum yield of **6** was estimated by recording the visible absorption with a Cary 15 spectrophotometer. The yields of diphenylbisanthene with varied concentrations of iodine are given in Table I.

TABLE I

YIELDS OF 6 FROM 3 WITH VARIED IODINE CONCENTRATIONS

Concn of **3**, 10^4 *M*	Concn of I_2, 10^5 *M*	Yield of **6**,[a] %
8.22	0	0
1.35	1.35	50[b]
0.59	5.90	59
0.75	15.0	49

[a] Yields were based on log ϵ 4.69 for peak at 683 mμ. [b] Replacement of the Pyrex filter with a 250–370-mμ Corning glass filter lowered the yield of **6** to 36%.

4,11-Diphenylbisanthene from Diol 5.—The maximum yields of **6**, based on its absorption at 683 and 625 mμ, were obtained after irradiating benzene solutions of **5** and iodine at various concentrations (see Table II).

TABLE II

YIELDS OF 6 FROM 5 WITH VARIED IODINE CONCENTRATIONS

Concn of **5**, 10^5 *M*	Concn of I_2, 10^5 *M*	Yield of **6**, %
8.15[a]	0	0
8.15[a]	1.53	44
8.15[a]	8.15	56
8.15[a]	16.30	58
7.14[b]	15.30	79

[a] Reaction solution was exposed to atmosphere. [b] Reaction was carried out in nitrogen atmosphere.

Irradiation of 5 without Iodine.—A solution of 45 mg of **5** in 200 ml of benzene was irradiated for 2 hr. Evaporation of solvent gave a light yellow solid. A benzene solution of the product had no absorption in the 600–750-mμ region. The solid was heated in 20 ml of glacial acetic acid and 1 ml of 48% hydriodic acid on a steam bath for 10 min. Dilution with water gave 31 mg of blue-black material. The yield of diphenylbisanthene as determined by the visible absorption of the crude product was 65%.

10,10′-Diphenyl-9,9′-bianthranyl (9).—A solution of 175 mg of **3** in 40 ml of glacial acetic acid and 2 ml of 48% hydriodic acid

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(6) G. M. Badger and C. P. Whittle, *Aust. J. Chem.*, **16**, 440 (1963).

(7) Although experimental details were not given, Sauvage reported that diol **8** was formed when an ether solution of **5** was exposed to ultraviolet light. See G. Sauvage, *Compt. Rend.*, **225**, 247 (1947).

(8) C. Dufraisse and J. LeBras, *ibid.*, **216**, 60 (1943).

(9) F. R. Stermitz, in "Organic Photochemistry," *Vol. I, O. Chapman, Ed.*, Marcel Dekker, Inc., New York, N. Y., 1967, p 247.

was heated on a steam bath for 15 min. Dilution with water gave a solid which was recrystallized from toluene. The yield of light yellow solid,[8] mp >300°, mass spectrum *m/e* 506, was 73 mg or 45%. Benzene solutions gave strong blue fluorescence. The absorption spectrum of **9** in benzene had peaks at 403 mμ (log ϵ 4.47), 380 (4.36), and 360 (4.06).

Anal. Calcd for $C_{40}H_{26}$: C, 94.87; H, 5.13. Found: C, 94.63; H, 4.95.

Irradiation of 10,10′-Diphenyl-9,9′-bianthranyl (9).—The absorption spectrum of a solution of 43 mg of **9** and 2 mg of iodine in 400 ml of benzene, which has been irradiated for 6 hr, showed that only 1% of **9** had been destroyed.

3,10-Diphenyl-1,2,11,12-dibenzoperylene (4) from Diol 3.—Nitrogen was bubbled into a solution of 324 mg of **3** and 168 mg of iodine in 600 ml of benzene for 20 min. The bubbling of nitrogen was continued while the solution was irradiated for 6 hr. The solvent was evaporated and the solid was stirred in 30 ml of ethanol. Filtration gave 196 mg of red-purple solid: mp 366–369° (lit.[2] mp 371°); visible absorption at 582 mμ (log ϵ 4.45) and 452 (4.24) [lit.[2] 580 mμ (log ϵ 4.99) and 548 (4.80)]. The absorption spectrum indicated that 5% diphenylbisanthene was aso present.

Anal. Calcd for $C_{40}H_{24}$: C, 95.23; H, 4.77. Found: C, 94.62; H, 4.31.

Photooxidation of 4.—A blue-green solution with bright blue fluorescence developed when a red-purple solution of 50 mg of **4** in 100 ml of benzene was irradiated for 30 min. Evaporation of the solvent gave 48 mg of a green solid, mp 295–299°. Recrystallization from toluene gave light yellow crystals: mp 302–304°; visible absorption in benzene at 427, 430, and 382 mμ (log ϵ 4.28, 4.26, and 4.00).

Registry No.—**6**, 23102-61-1; **9**, 23102-67-2.

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Thermal Decomposition of Some *t*-Alkyl Peroxyoxalates

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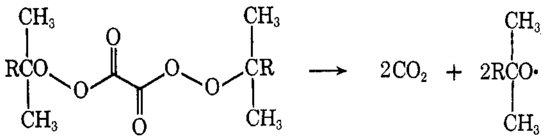
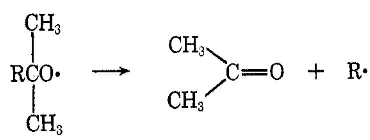
The thermal decomposition of di-*t*-butyl peroxyoxalate has previously been investigated by Bartlett,[1] Traylor,[2] and coworkers. It was shown that decomposition is quite facile at room temperature, and there is negligible cage recombination of the *t*-butoxy radicals formed.

A variety of *t*-alkoxy radicals is known to undergo β scission to afford a ketone and an alkyl radical.[3] The efficiency with which this fragmentation occurs is markedly dependent on both the structure of the *t*-alkoxy radical and on the solvent.

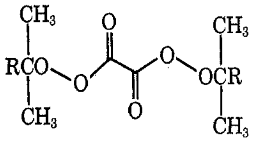
We sought *t*-alkyl peroxyoxalates as useful precursors for alkyl radicals at low temperatures in a process uncomplicated by cage reactions (eq 1, 2).[4] In this paper we wish to report the preparation of a series of *t*-alkyl peroxyoxalates I and the investigation of the rates and products of their thermal decomposition.



(1)



(2)



Ia, R = CH_3 c, R = $(CH_3)_2CH$
b, R = CH_3CH_2 d, R = $PhCH_2$

The peroxyoxalates were prepared by the method of Bartlett, *et al.*,[1] from the corresponding *t*-alkyl hydroperoxide and oxalyl chloride. *t*-Butyl peroxyoxalate is a white, crystalline solid which is stable at room temperature for short periods of time but explodes on pounding or scratching.[1] Compounds Ib[5] and Id were also obtained as white needles by crystallization from pentane at −30° or below. Compound Ic was an oil which we were unable to crystallize. All three of these compounds were unstable at room temperature. Compounds Ic and Id decomposed spontaneously with vigorous evolution of gas when allowed to warm to room temperature. All of these compounds were more stable in dilute pentane solutions and could be stored at −30° for days without appreciable decomposition.

The purities of the peroxyoxalates were determined by examination of their infrared spectra and by the yields of the carbon dioxide liberated in the thermal decomposition. Compounds Ia and Ib could also be analyzed by iodometric titration in acetic acid.[6] However, Ic and Id gave very low titres by this method owing to the rapid ionic decomposition in acetic acid solutions.

The rates of thermal decomposition of the four peroxyoxalates were measured in pentane solution at 25° by following the appearance of carbon dioxide. These results are shown in Table I. The reaction was first

TABLE I
RATES OF DECOMPOSITION OF *t*-ALKYL PEROXYOXALATES IN PENTANE AT 25°[a]

Compd	R	*k*, sec^{-1}	$t_{1/2}$, min
Ia	Methyl[b]	1.7×10^{-5}	700
Ib	Ethyl	2.6×10^{-5}	450
Ic	Isopropyl	6.0×10^{-5}	190
Id	Benzyl	6.7×10^{-5}	173

[a] Average of at least two determinations. [b] Literature[1] $k = 7.9 \times 10^{-6}$ sec^{-1} at 20° in benzene.

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(1) P. Bartlett, E. Benzing, and R. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

(2) (a) H. Kiefer and T. Traylor, *ibid.*, **89**, 6667 (1967); (b) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965).

(3) (a) F. D. Greene, M. L. Savitz, F. D. Osterholz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963); (c) C. Walling and P. Wagner, *ibid.*, **85**, 2333 (1963); (d) J. Bacha and J. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).

(4) A source of free alkyl radicals uncomplicated by cage reactions would be useful for measuring rates of bimolecular reactions of alkyl radicals in solution, *e.g.*, disproportionation–combination ratios which have been unambiguously measured heretofore only in the gas phase.

(5) C. Walling and J. A. McGuinness [*J. Amer. Chem. Soc.*, **91**, 2053 (1969)] have also recently prepared Ib.

(6) L. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).