Experimental Section[15]

Phenylthioureas.—All of the phenylthioureas were prepared by the following procedure. To a solution of 10 mmoles of phenyl isothiocyanate in 10 ml of 95% ethanol were added 11 mmoles of the appropriate amine or amine hydrochloride. In cases where the hydrochloride was used, a slight excess of triethylamine was added. The mixture was allowed to stir at ambient temperature for 1–2 hr. In some cases the product crystallized from the reaction mixture and in others it was necessary to dilute the solution with a small amount of water and/or scratch the sides of the reaction vessel with a glass rod. Each phenylthiourea so produced was recrystallized from 60 to 90% ethanol and all melted within 2° of the reported value.

1-Cyclohexyl-3-phenyl-2-thiourea-1,3-d_2 (II, R = D; R′ = H).—A solution of cyclohexylamine (99 mg, 1 mmole) in methanol-d (2 ml) and deuterium oxide (1 ml) was heated at reflux for 2 hr. After cooling the mixture to room temperature phenyl isothiocyanate (135 mg, 1 mmole) was added and the mixture was heated to boiling. Cooling to 0° resulted in the deposition of fine crystals which were collected by filtration and twice recrystallized from methanol-d–D_2O: yield 150 mg (65%), mp 147–148°. The isotopic purity was 90% d_2 and 10% d_1 as determined from the mass spectrum.

1-(2,2,6,6-d_4-Cyclohexyl)-3-phenyl-2-thiourea (II, R = H; R′ = D).—A solution of cyclohexanone (300 mg, 3 mmoles) and sodium methoxide (300 mg) in methanol-d (3 ml) and deuterium oxide (10 ml) was heated at reflux for 2 hr. After cooling, the mixture was extracted with ether, the ether layer was dried, and the solvent was evaporated. The resulting product was subjected to the exchange procedure a second time under the same conditions. After the reflux period, hydroxylamine hydrochloride (200 mg, 3.3 mmoles) was added and the mixture was allowed to stand for several hours. The oxime was isolated with ether in the usual way and reduced, without purification, with excess $LiAlH_4$ (200 mg) in ether. The resulting amine was treated with phenyl isothiocyanate (135 mg, 1 mmole) in methanol and the deuterated product IV, collected by filtration, showed mp 146–148°. The mass spectrum showed that the isotopic purity was 95% d_4 and 5% d_3.

Thermal Fragmentation of 1-Cyclohexyl-3-phenyl-2-thiourea in Gas Chromatograph.—A saturated solution (0.3 ml) of 1-cyclohexyl-3-phenyl-2-thiourea in methanol was injected into a Varian Aerograph Hi-Fi III gas chromatograph. The injection port was maintained at 250° and the column (5 ft × $^1/_8$ in. 20% Dowfax 9N9, 2% KOH on Chromsorb W) at 180°. The methanol peak was recorded within a few seconds. The retention times for the cyclohexylamine and aniline were 0.75 and 2.05 min relative to methanol. The cyclohexyl isothiocyanate and phenyl isothiocyanate were not separated under these conditions and appeared as a broad composite peak with a retention of 4.05 min relative to methanol.

Registry No.—II (R = D; R′ = H), 15093-56-8; II (R = H; R′ = D), 15093-57-9.

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(15) Mass spectra were determined using an Atlas CH-4 mass spectrometer equipped with the TD-4 ion source. High-resolution mass measurements were kindly performed by Dr. J. K. MacLeod of Stanford University on an AEI MS-9 mass spectrometer operating at a resolution of 20,000. The thermal measurements were determined with a CEC 21-103C mass spectrometer equipped with an all-glass heated (150°) inlet system. 1,3-Dicyclohexyl-2-thiourea was kindly donated by Abbott Laboratories, North Chicago, Ill.

Chemiluminescence from Reactions of Electrophilic Oxamides with Hydrogen Peroxide and Fluorescent Compounds

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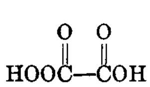
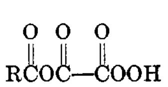
Received July 21, 1967

Chemiluminescence has been observed from the reactions of electrophilic oxamides with hydrogen peroxide in the presence of fluorescers. A general relationship was found between the efficiency of the light emission and the reactivity of the oxamide toward hydrogen peroxide. The intensity of chemiluminescence varied substantially with the solvent, catalyst, fluorescer, and peroxide. The emitting species in the chemiluminescent reactions was shown to be the first excited singlet state of the fluorescer.

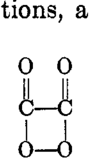
Oxalyl chloride[1,2] and certain oxalic anhydrides[3] and esters[4] react with hydrogen peroxide in the presence of fluorescent compounds to generate light with unusual efficiency. Chemiluminescence quantum yields for such reactions have been reported to be as high as 5, 13, and 23%, respectively,[2-4] in contrast to yields on the order of 1% reported for earlier chemiluminescent reactions such as the 3-aminophthalhydrazide (luminol[4]) reaction with hydrogen peroxide.[5,6] Mechanism studies of oxalate chemiluminescent systems have tentatively indicated that peroxyoxalate derivatives such as I–III can be formed, depending on the reactants and reaction conditions, and that concerted multiple bond cleavage decomposition of such intermediates is the source of the large and synchronous energy release required for electronic excitation of the emitting fluorescer.[2-4]


$\mathrm{HOO}\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}\mathrm{OH}$

I


$\mathrm{R}\overset{O}{\overset{\|}{C}}\mathrm{O}\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}\mathrm{OOH}$

II



III

These earlier studies indicated that the oxalic starting material must have a high order of reactivity toward hydrogen peroxide to exhibit appreciable chemiluminescent activity. Although oxamides in general are less active toward nucleophiles than oxalic esters, a series of oxamide–hydrogen peroxide–fluorescer reactions has been examined to define the limits of the peroxyoxalate chemiluminescent system.

Results

A variety of oxamides was treated with hydrogen peroxide and the fluorescer 9,10-diphenylanthracene under several reaction conditions and the reactions were examined visually for chemiluminescence. Typical results are summarized in Table I. Simple oxa-

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(1) E. A. Chandross, *Tetrahedron Letters*, No. 12, 761 (1963).

(2) M. M. Rauhut, B. R. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966).

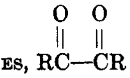
(3) L. J. Bollyky, R. H. Whitman, B. G. Roberts, and M. M. Rauhut, *ibid.*, **89**, 6523 (1967).

(4) M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, and A. M. Semsel, *ibid.*, **89**, 6515 (1967).

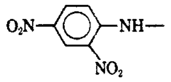
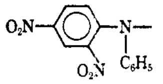
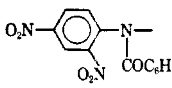
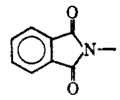
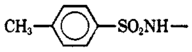
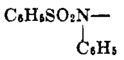
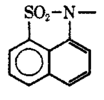
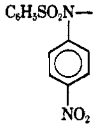
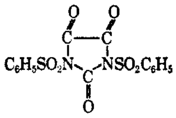
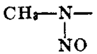
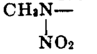
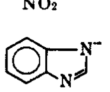
(5) J. Lee and H. H. Seliger, *Photochem. Photobiol.*, **4**, 1015 (1965); M. M. Rauhut, A. M. Semsel, and B. G. Roberts, *J. Org. Chem.*, **31**, 2431 (1966).

(6) For recent reviews on chemiluminescence, see: F. McCapra, *Quart. Rev.* (London), **20**, 485 (1966); K. D. Gunderman, *Angew. Chem. Intern. Ed. Engl.*, **4**, 566 (1965); E. J. Bowen, *Pure Appl. Chem.*, **9**, 423 (1964).

TABLE I
CHEMILUMINESCENCE FROM ELECTRONEGATIVELY
SUBSTITUTED OXAMIDES,



$R\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}R$

Compd	R	Solvents[b]	Chemiluminescent test results[a] A (H₂O₂)	B (H₂O₂ + base)	C (H₂O₂ + F₃CCO₂H)
IV		DME	N[c]	VW[d]	N
V		DME, DMF	N	N	N
VI		DME, DMF	N	VW	N
VII	$(C_6H_5CO)_2N$—	DME, DMF, DMP	N	N	N
VIII		DMF DME	N N	N VW[d]	N VW
IX		DME, DMF	N	N	N
X	 $C_6H_5SO_2\underset{\displaystyle C_6H_5}{\underset{\vert}{N}}$—	DME, DMF	W	M	N
XI		DMF	W	M	N
XII		DMF	W	M	N
XIII		DME	M	M	M
XIV	 $CH_3\underset{\displaystyle NO}{\underset{\vert}{N}}$—	DME, DMF	N	N	N
XV	 $CH_3\underset{\displaystyle NO_2}{\underset{\vert}{N}}$—	DME, DMF	M	MS	N
XVI		DME, DMP DMF	MS S	S S	S S

[a] Test A: approximately 0.2 ml of 90% H_2O_2 was added to 5 mg of oxamide and 1 mg of 9,10-diphenylanthracene in 5 ml of solvent. Test B: approximately 0.2 ml of 10% K_2CO_3 was added under the conditions of test A. Test C: approximately 0.2 ml of trifluoroacetic acid was added under the conditions of test A. [b] Solvents used were 1,2-dimethoxyethane (DME), dimethylformamide (DMF), and dimethylphthalate (DMP). [c] No light (N), very weak (VW), medium (M), and strong (S). [d] The base was 50% aqueous KOH.

mides such as oxanilide were not chemiluminescent under the neutral, alkaline, or acidic conditions investigated (See Experimental Section) and even the more electrophilic 2,2′,4,4′-tetranitrooxanilide (IV) gave only a very weak emission. Oxamides having electronegative groups such as nitro and phenyl sulfonyl substituted directly on oxamide nitrogen, however, gave appreciable emission, as indicated in Table I. In general, the strongest intensities were obtained under alkaline conditions.

The emission intensities and lifetimes of the reactions were markedly dependent on the reaction conditions.

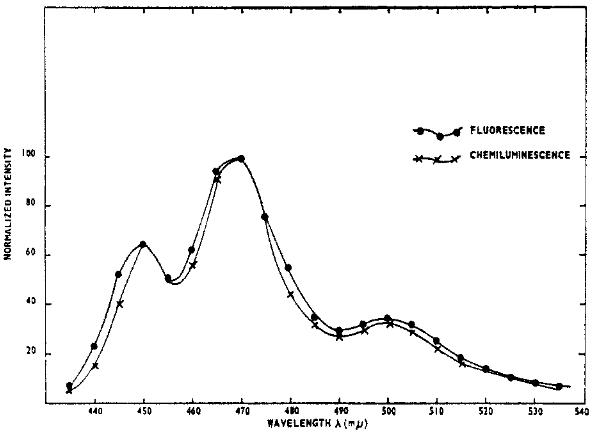


Figure 1.—Emission spectra from perylene (5.0×10^{-4} M) fluorescence in 1,2-dimethoxyethane and from the chemiluminescent reaction of 2.5×10^{-3} M with 5.0×10^{-2} M H_2O_2, 5.0×10^{-2} M aqueous potassium carbonate, and 5.0×10^{-4} M perylene in 1,2-dimethoxyethane at 25°.

Thus N,N′-bis(phenylsulfonyl)oxanilide (X), hydrogen peroxide, potassium carbonate, and fluorescein gave appreciable chemiluminescence in dimethyl formamide or 1,2-dimethoxyethane, but no light was obtained in triethyl phosphate, water, or 30% aqueous hydrogen peroxide. When potassium carbonate was replaced with a catalytic amount of 50% aqueous potassium hydroxide or triethylamine, little emission was obtained. Chemiluminescence was also not observed when hydrogen peroxide was replaced with cyclohexanone hydroperoxide, peroxy-4-nitrobenzoic acid, or cumene hydroperoxide. The fluorescers 9,10-diphenylanthracene and perylene appeared to provide substantially more light than the fluorescers rubrene and fluorescein.

Chemiluminescence quantum yields were measured quantitatively for three of the more efficient compounds. The results summarized in Table II show that quantum yields near 1% were obtained under the best conditions studied.

To identify the emitting species, the spectral distribution of emission from a reaction of X with hydrogen peroxide, potassium carbonate, and perylene in 1,2-dimethoxyethane was compared with the fluorescence spectral distribution of perylene. As indicated in Figure 1 the spectra were essentially identical showing that the first excited singlet state of perylene is the emitter.

The absence of chemiluminescence from N,N′-bis(2,4-dinitrophenyl)oxanilide (V) could, in principle, be caused by an excessively slow initial reaction between V and hydrogen peroxide. This possibility was examined by comparing the rate of disappearance of V in reaction with hydrogen peroxide with the rate of disappearance of the chemiluminescent N,N′-bis(phenylsulfonyl) oxanilide (X) under identical conditions. The reactions were carried out under pseudo-first-order conditions with excess hydrogen peroxide and were followed by measuring amide carbonyl absorbance as a function of time. Linear plots of log absorbance *vs.* time were obtained for both reactions. The results summarized in Table III show that under the conditions studied V reacts one-fifth as rapidly as X.

TABLE II

QUANTUM YIELDS FOR SEVERAL OXAMIDE CHEMILUMINESCENT REACTIONS[a]

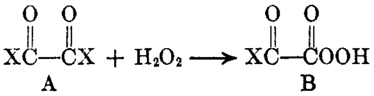
Oxamide	Oxamide concn, *M*	H_2O_2 concn, *M*	Aqueous K_2CO_3 concn, *M*	Max intensity, foot-lamberts/cm	Lifetime,[b] $T_{1/4T}$	$T_{3/4R}$,[c] min	Quantum yield,[d] Einsteins mole^{-1} × 10^2
N,N′-Dimethyl-N,N′-dinitrooxamide (XV)	1×10^{-3}	0.1	4.83×10^{-2}	1.9	<1.0	2.1	0.92
	1×10^{-2}	0.1	4.83×10^{-2}	0.25	<1.0	10.0	0.24
N,N′-Bis(phenylsulfonyl)oxanilide (X)	2.5×10^{-3}	0.05	4.83×10^{-2}	0.001	67.4	287.4	0.25
N,N′-Oxalyl bis(benzimidazole) (XVI)	2.5×10^{-3}	0.01	None	0.06	8.0	5.9	0.98
	2.5×10^{-3}	0.1	None	0.13	1.7	1.3	0.45

[a] Reactions with 6.0×10^{-4} *M* 9,10-diphenylanthracene in 1,2-dimethoxyethane at 25°. [b] Time required for the decay of intensity to one-fourth of the maximum. [c] Time required for three-fourths of total light emission. [d] Based on oxamide.

Discussion

The maximum efficiency of the oxamide–peroxide–fluorescer system under the conditions studied was found to be of the same order as the efficiencies of classical chemiluminescent reactions (1%),[5,6] but substantially less than the efficiencies of related oxalyl chloride,[2] oxalic anhydride,[3] and oxalate ester reactions.[4] The results indicate a general correlation between the efficiency of light emission and the reactivity of the oxalic derivative toward nucleophiles. Thus oxamides were less efficient than the more reactive oxalic esters and within the oxamide series efficiency increased with increasing electronegative substitution. Moreover, the reaction of nonchemiluminescent N,N′-bis(2,4-dinitrophenyl)oxanilide (V) with hydrogen peroxide was found to be about five times slower than the corresponding reaction of chemiluminescent N,N′-bis(phenylsulfonyl)oxanilide (X). On this basis chemiluminescence would be expected from 1,1′-oxalyl bis(benzimidazole) (XVI), since acetylbenzimidazole is known to hydrolyze relatively rapidly;[7] the benzimidazole derivative XVI indeed provided the strongest intensities observed in the study. Although substantial susceptibility toward nucleophilic attack seems required for appreciable emission in peroxyoxalate chemiluminescent systems, it is clear that other factors are also important in determining relative efficiencies, since oxalyl chloride, the most reactive member of the class, is among the less efficient.

In spite of the relationship between nucleophilic reactivity and chemiluminescence efficiency, it is unlikely that chemiluminescence efficiency is determined by the rate of an initial nucleophilic reaction between the oxalic derivative and hydrogen peroxide (eq 1).



$$\underset{A}{X\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}X} + H_2O_2 \longrightarrow \underset{B}{X\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OOH} \qquad (1)$$

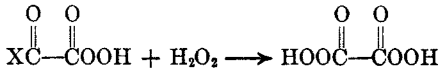
Even if reaction of A with hydrogen peroxide were slow, A should eventually be converted completely into peroxy intermediate B. Thus the rate of reaction 1, if slow, would control the intensity but not the efficiency of chemiluminescence. The results reported here and those obtained from electrophilic oxalates[4] imply that the relationship between structure and efficiency appears therefore to reflect the rate of nucleophilic displacement of X in intermediate B (eq 2a or 2b). It would appear that a nonnucleophilic, nonchemiluminescent reaction of B (eq 3) competes with a nucleophilic reaction leading to the key chemiluminescent intermediate and that the nonnucleophilic, nonchemiluminescent reaction becomes dominant when X in B is not highly reactive to nucleophilic displacement.

TABLE III

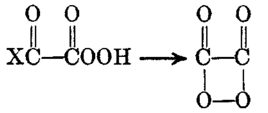
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTIONS OF OXAMIDES V AND X WITH HYDROGEN PEROXIDE[a]

Time, min	Absorbance		Pseudo-first-order rate constants, *k*, sec^{-1} × 10^{-4}	
	V	X	V	X
0	0.47	0.23		
4	0.45	0.19	1.81	7.94
8	0.44	0.17	1.37	6.29
12	0.43	0.15	1.23	5.93
16	0.42	0.13	1.17	5.94
20	0.40		1.34	
			1.38	6.52

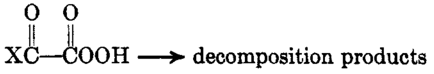
[a] Concentrations in 1,2-dimethoxyethane were, for the oxamides, 2.0×10^{-2} *M*; hydrogen peroxide, 7.5×10^{-2} *M*; potassium carbonate, 3.0×10^{-2} *M*.



$$X\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OOH + H_2O_2 \longrightarrow HOO\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OOH \qquad (2a)$$



(2b)



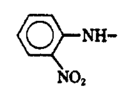
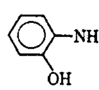
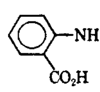
$$X\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OOH \longrightarrow \text{decomposition products} \qquad (3)$$

Experimental Section

Materials.—9,10-Diphenylanthracene (Aldrich) was recrystallized from a mixture of absolute ethanol and chloroform to obtain material, mp 250–251° (lit.[8] mp 250–251°). Fluorescein and rubrene (Eastman) were not repurified. Hydrogen peroxide solutions were prepared from the 98% reagent grade (Becco Chemical Divisions, F.M.C. Co.).

Oxamides.—In addition to those listed in Table I the oxamides (RCOCOR) given in Table IV were nonchemiluminescent under the conditions described in Table I.

TABLE IV

No.	R	No.	R
XVII	CH_3NH-	XX	
XVIII		XXI	$(C_6H_5)_2N-$
XIX		XXII	 $C_6H_5CON(C_6H_5)-$

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(7) H. A. Staab, *Angew. Chem. Intern. Ed. Engl.*, **1**, 351 (1962).

(8) G. Wittig and R. W. Hoffmann, *Ber.*, **95**, 2718 (1962).

N,N′-Bis(phenylsulfonyl)oxanilide (X),[9] N,N′-oxalyl bis-(1,8-naphthosultam) (XI), N,N′-bis(phenylsulfonyl)parabanate (XIII),[10] N,N′-dimethyl-N,N′-dinitrosooxamide (XIV),[11] N,N′ dimethyl-N,N′-dinitrooxamide (XV),[12] N,N′-dimethyloxamide (XVII),[13] N,N′-bis(*o*-hydroxyphenyl)oxamide (XVIII),[14] N,N′-bis(*o*-carboxyphenyl)oxamide (XIX),[14] N,N′-bis(*o*-nitrophenyl)-oxamide (XX),[14] and tetraphenyloxamide (XXI)[15] were prepared according to previously described procedures.

2,2′,4,4′-Tetranitrooxanilide (IV).—Oxalyl chloride (20 ml, 0.23 mole) was added dropwise to 100 ml of dimethyl formamide (DMF) at 25° to form a tan slurry. A solution of 18.3 g (0.1 mole) of 2,4-dinitroaniline in 50 ml of DMF was added during 30 min to the slurry at room temperature. After stirring for 3 hr the reaction mixture was poured into 400 ml of ice water and 18.7 g of solid precipitated. Recrystallization from ethyl ether gave yellow crystals: mp 171–174°, with some decomposition at 135 and 168°; infrared, 2.90 (W), 3.0 (S), and 5.83 (VS).

Anal. Calcd for $C_{14}H_8N_6O_{10}$: C, 40.00; H, 1.92; N, 20.00. Found: C, 39.70; H, 2.40; N, 19.94.

N,N′-Bis(2,4-dinitrophenyl)oxanilide (V).—To a solution of 2.59 g (10 mmoles) of 2,4-dinitrodiphenylamine and 25 ml of anhydrous tetrahydrofuran was added portionwise 0.48 g of a 50% suspension of sodium hydride in mineral oil (0.24 g, 10 mmoles of sodium hydride). The deep red slurry was stirred at room temperature for 10–15 min. Oxalyl chloride (0.63 g, 5 mmoles) was added dropwise and the deep red color became red-brown. The mixture was stirred at room temperature for 30 min, then poured into 200 ml of water. Recrystallization of the precipitated solid from benzene gave 2.75 g (76%) of light brown needles: mp 110–112°; infrared, 5.90 and 5.95 μ. The elemental analysis indicated that the product contained two molecules of benzene per molecule of oxamide.

Anal. Calcd for $C_{38}H_{26}N_6O_{10}$: C, 62.65; H, 3.91; N, 11.64. Found: C, 62.40; H, 3.86; N, 11.76.

N,N′-Dibenzoyl-2,2′,4,4′-tetranitroxanilide (VI).—Oxalyl chloride (0.65 g, 5 mmoles) was added dropwise to an ice-cooled mixture of 2.87 g (10 mmoles) of 2,4-dinitrobenzanilide in 125 ml of anhydrous tetrahydrofuran containing 1.1 g of triethylamine. The turbid mixture was stirred under nitrogen at room temperature for 24 hr. The triethylamine hydrochloride was removed by filtration. Evaporation of the solvent from the filtrate at room temperature gave a sticky solid, which became a powder when triturated with petroleum ether (bp 30–60°). The weight of the product, which decomposed above 85°, was 3.41 g. Attempted recrystallization in refluxing benzene gave only 2,4-dinitrobenzanilide. The analysis of the solid formed by trituration with petroleum ether indicated that two molecules of tetrahydrofuran per molecule of the oxanilide were present. The infrared spectrum of the product contained peaks at 5.77 (shoulder), 5.81, and 5.89 μ.

Anal. Calcd for $C_{36}H_{32}N_6O_{14}$: C, 55.90; H, 4.14. Found: C, 55.71; H, 3.72.

Tetrabenzoyloxamide (VII).—To an ice-cooled solution of 2.25 g (10 mmoles) of dibenzamide and 1.0 g (10 mmoles) of triethylamine in 25 ml of anhydrous tetrahydrofuran was added dropwise 0.64 g (5 mmoles) of oxalyl chloride. The slurry was stirred at room temperature for 2 hr. The triethylamine hydrochloride which precipitated was collected and washed with tetrahydrofuran. Evaporation of the filtrate gave a solid that was recrystallized from benzene. The yield of the colorless solid (mp 175–178°; infrared peaks at 5.72 (shoulder), 5.80, 5.89, and 5.93 μ (shoulder)) was 1.62 g (3.2 mmoles) or 64%.

Anal. Calcd for $C_{30}H_{20}N_2O_6$: C, 71.43; H, 3.97; N, 5.57. Found: C, 71.48; H, 4.06; N, 5.67.

N,N′-Oxalyldiphthalimide (VIII).—Oxalyl chloride (1.27 g, 10 mmoles) was added dropwise to an ice-cooled mixture of 2.94 g (20 mmoles) of phthalimide, 2.2 g (22 mmoles) of triethylamine, and 80 ml of anhydrous benzene in an atmosphere of nitrogen. After the addition of the oxalyl chloride was completed the mixture was stirred at room temperature for 24 hr. The solid material was dissolved in chloroform and the solution was washed with water and dried with anhydrous magnesium sulfate. Evaporation of the solvent at room temperature gave 2.48 g (7.1 mmoles) or 71% of the oxamide: mp 255–260° dec (benzene–hexane); infrared, 5.51 and 5.73 μ.

Anal. Calcd for $C_{18}H_8N_2O_6$: C, 62.07; H, 2.32; N, 8.04. Found: C, 62.32; H, 2.33; N, 8.22.

N,N′-Bis(*p*-toluenesulfonyl)oxamide (IX).—A mixture of 3.4 g (20 mmoles) of *p*-toluenesulfonamide and 1.27 g (10 mmoles) of oxalyl chloride was heated in 50 ml of refluxing ethylene dichloride for 6.5 hr. All the solid dissolved when the solvent reached reflux temperature and after 2.5 hr a white solid precipitated. Recrystallization from acetonitrile gave 1.37 g of white needles: mp 276–278°;[16] infrared, 3.1, 4.47 (VW), and 5.75 μ. The analysis indicated that one molecule of acetonitrile was present for every two molecules of oxamide.

Anal. Calcd for $C_{34}H_{35}N_5O_{12}S_4$: C, 49.00; H, 4.20; N, 8.50; S, 15.35. Found: C, 49.18; H, 4.26; N, 8.82; S, 15.36.

N,N′-Bis(phenylsulfonyl)-4,4′-dinitrooxanilide (XII).—Oxalyl chloride (0.41 g, 3.25 mmoles) was added dropwise to 1.8 g (6.5 mmoles) of N-phenylsulfonyl-*p*-nitroanilide in 25 ml of anhydrous pyridine. The solution was heated at 85–90° for 1 hr and became dark. The cooled solution was poured into water and an oil formed which became crystalline when triturated with benzene. The yield of buff-colored oxamide recrystallized from acetonitrile was 285 mg (14%). Its infrared spectrum had carbonyl peaks at 5.86 and 5.91 μ.

Anal. Calcd for $C_{26}H_{18}N_4O_{10}S_2$: C, 51.20; H, 2.95; N, 9.15; S, 10.45. Found: C, 50.86; H, 2.83; N, 9.42; S, 10.44.

1,1′-Oxalylbis(benzimidazole) (XVI).—A solution of 5.9 g (50 mmoles) of benzimidazole and 5.05 g (50 mmoles) of triethylamine in 150 ml of tetrahydrofuran was treated at 0° with 3.17 g (25 mmoles) of oxalyl chloride during 15 min. The mixture was stirred at room temperature for 2 hr. The solids collected after filtration were washed with chloroform and water. The remaining white solid, 640 mg, mp 200° dec, was analyzed without further purification. The infrared spectrum had bands at 5.81 and 5.88 μ. Attempted recrystallization from organic solvents caused decomposition to benzimidazole.

Anal. Calcd for $C_{16}H_{10}N_4O_2$: C, 66.20; H, 3.47; N, 19.31. Found: C, 66.35; H, 3.69; N, 19.83.

N,N′-Dibenzoyloxanilide (XXII).—A slurry of 7.88 g (40 mmoles) of benzanilide and 4.04 g (40 mmoles) of triethylamine in 50 ml of benzene was treated with 2.55 g (20 mmoles) of oxalyl chloride during 15 min. The mixture was stirred at room temperature for 1 hr, then poured over 200 g of ice. After filtration to remove unreacted starting material the filtrate was concentrated to obtain 0.345 g of desired product. The oxamide was recrystallized from acetic acid to obtain material, mp 209–210° (lit.[17] mp 209–210°).

Kinetics of the Hydrogen Peroxide. Oxamide Reactions.—Appropriate aliquots of stock solutions of oxamides V and X, hydrogen peroxide, and potassium carbonate in 1,2-dimethoxyethane were combined to give solutions of final concentrations: amide = 2.0×10^{-2} *M*; $K_2CO_3 = 3.0 \times 10^{-2}$ *M*; and $H_2O_2 = 7.5 \times 10^{-2}$ *M*. The hydrogen peroxide was always added last and the timer was started with peroxide addition. A Perkin-Elmer 221 grating infrared spectrophotometer was used to follow the loss of the carbonyl frequencies (1692 cm^{-1} for X and 1681 cm^{-1} for V) of each sample in an 0.5-mm thick NaCl cell compensated with an identical cell containing 1,2-dimethoxyethane in the reference beam of the instrument. Reactions were followed for 20 min and the log of the absorbance *vs.* time was plotted to yield straight lines. The calculated pseudo-first order rate constants are given in Table III.

Quantum yield determinations were carried out as previously described.[2,18]

Registry No.—IV, 14805-54-0; V, 14760-92-0; VI, 14760-93-1; VII, 14760-94-2; VIII, 14760-95-3; IX, 4083-66-3; X, 14805-55-1; XI, 14783-51-8; XII, 14805-

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56-2; XIII, 14760-97-5; XIV, 7601-87-8; XV, 14760-99-7; XVI, 14805-57-3; XXII, 14805-58-4; hydrogen peroxide, 7722-84-1.

Acknowledgments.—Research reported in this publication was supported by the Advanced Research Projects Agency under contract to the Office of Naval Research. We gratefully acknowledge our great debt to the late Dr. Robert C. Hirt who designed the spectroradiometer used in this study. The authors thank Mr. A. M. Semsel for his assistance with the kinetic measurements.

Photocyclizations of Compounds Containing Two Anthracene Rings

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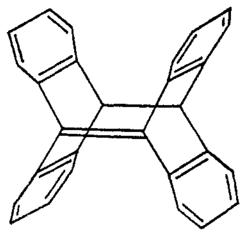
Received August 10, 1967

It has been found that di-9-anthryl carbonate, 9-anthryl-9-anthramide, and 9,9′-azoanthracene undergo photocyclizations readily to give the cyclic carbonate, β-lactam, and cyclic azo compound, respectively. The last substance proved unexpectedly stable, no nitrogen being evolved under pyrolytic or photolytic conditions. Attemps to photocyclize 1,2-bis-10′-bromo-9′-anthrylethane, bis-10-bromo-9-anthrylmethane, 10-chloro-9-anthroic anhydride, and 10-bromo-di-9-anthrylmethane all failed.

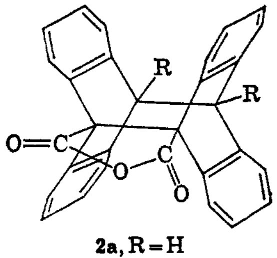
Previous work in this laboratory on the anthracene photodimers[1] has been directed toward a synthesis of the bridgehead olefin, 9,9′-dehydrodianthracene (**1**).



1

Though neither **1** nor any derivative of it has been isolated, evidence for the intermediacy of such a structure in the reaction of the photodimer of 9-chloroanthracene with phenyllithium has been offered.[1] A significant difficulty in the synthesis of olefins of type **1** is the unwillingness of most anthracene photodimerizations to give vicinal bridgehead functional groups, preferring to give the head-to-tail dimers from 9-substituted anthracenes[2] and usually no dimers from 9,10-disubstituted anthracenes.[3]

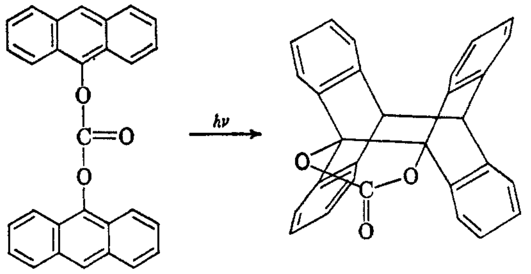
Exceptions are the photocyclization of 9-anthroic anhydride to give **2a**[4] and other similar reactions of molecules containing more than one anthracene ring.[5,6]



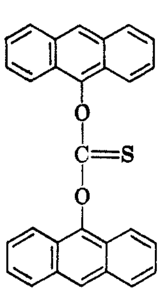
2a, R = H
b, R = Cl

The aim of the present work was to exploit the photocyclization reaction in systems where the resulting bridgehead functionality would offer rational syntheses of the bridgehead olefin.

Di-9-anthryl carbonate (**3**) was prepared by the reaction of the enolate of anthrone with phosgene in tetrahydrofuran (85% yield) and was photocyclized in benzene to **4** (52% yield) (eq 1). The carbonyl absorption frequencies of **3** and **4** are at the expected values of 1770 cm^{-1} and 1815 cm^{-1}, respectively.[7] It was hoped that **4** might be converted with P_2S_5 to the thionocarbonate, which would be an ideal starting material for the Corey olefin synthesis (with trialkyl phosphite).[8,9] Alternatively, if **3** could be converted to the corresponding thionocarbonate (**5**), photocyclization of this might give the same olefin precursor. Neither of these possibilities was realized under various conditions with P_2S_5. Direct synthesis of **5** from



3 **4** (1)



5

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