References and Notes

(1) (a) Taken in part from the Ph.D. dissertation of W.L.M., Fordham University, 1974. (b) Some of the photochemical results were the subject of a preliminary communication: W. L. Mandella and R. W. Franck, *J. Amer. Chem. Soc.*, **95**, 971 (1973).

(2) (a) For a review, see E. E. van Tamelen, *Accounts Chem. Res.*, **5**, 186 (1972); (b) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962).

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Infrared Liquid-Phase Chemiluminescence from Reactions of Bis(2,4,6-trichlorophenyl) Oxalate, Hydrogen Peroxide, and Infrared Fluorescent Compounds

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Several polycyclic aromatic hydrocarbon derivatives provide infrared fluorescence quantum yields on the order of 0.30 in solution. The infrared fluorescers were combined with a peroxyoxalate chemiluminescent system based on bis(2,4,6-trichlorophenyl) oxalate to provide solution-phase infrared chemiluminescence with quantum yields as high as 0.06 einstein mol^{-1}. The effect of fluorescer concentration on chemiluminescence quantum yield indicated the theoretical maximum yield of excited emitter to be 49% with the fluorescer 16,17-dihexyloxyviolanthrone. Theoretical considerations relating to infrared fluorescence and chemiluminescence are discussed.

Infrared chemiluminescence, unlike visible chemiluminescence, is unlikely to be discovered by accidental observation, and few examples are known. The examples are confined to gas-phase reactions which produce vibrationally excited states,[1] to emission from singlet oxygen,[2] and to reaction of violanthrone with singlet oxygen.[3]

It is well recognized that efficient liquid-phase chemiluminescence requires the efficient formation of an electronically excited singlet product in a chemical reaction and that the excited product must be an efficient fluorescer.[4,5] The modification of a chemiluminescent reaction to produce emission in a specified spectral region is generally difficult, however. Most chemiluminescent reactions produce their excited products directly from the energy releasing reactants, and it is difficult to modify the structure of the fluorescent product while at the same time retaining the efficient excitation capability of the reactant.[6]

Peroxyoxalate chemiluminescence, however, differs from most chemiluminescent reactions in that the emission spectrum depends on the fluorescence spectrum of a compound which is added independently of the reactants.[7,8] Through the use of a variety of fluorescers, emission almost spanning the visible spectrum has been obtained.[7-9] This property, along with its inherent efficiency, encouraged us to select the peroxyoxalate reaction as the basis for infrared chemiluminescence research.

The peroxyoxalate reaction of bis(2,4,6-trichlorophenyl) oxalate with hydrogen peroxide and sodium salicylate was chosen because this reaction has been shown to provide quantum yields as high as 0.20 einstein mol^{-1} with the fluorescer rubrene.[10] A search of the literature for organic infrared fluorescers failed to reveal an acceptable prospect, although several dyes have been reported to luminesce in the infrared on fibers,[11] and several red fluorescers have spectral distributions extending into the infrared in solution.[12] Two useful criteria are available for fluorescer design. First, the intrinsic probability of radiative transition from an excited electronic level increases with the extinction coefficient of the electronic absorption of that level.[13] Thus, compounds having extinction coefficients above about 10^4 have a relatively high fluorescence probability. Secondly, according to Stokes' law the emission spectral distribution of an organic fluorescer in general approximates the mirror image of the absorption spectrum and usually is displaced 50–200 nm toward longer wavelengths.[14] Thus, organic compounds having first absorption bands at wavelengths longer than 650 nm, and with extinction coefficients greater than 10^4, are potential infrared fluorescers. In general, compounds having these properties will have a rigid structure with a high degree of conjugated unsaturation, and polycyclic aromatic hydrocarbon derivatives appeared particularly attractive. Advantage was also taken of bathochromic spectral shifts produced by substituents such as alkoxy[13] and phenylethynyl[15,16] to extend the emission wavelengths of red fluorescers into the infrared.

Results

Infrared Fluorescers. The compounds investigated as fluorescers are illustrated in Chart I, and their absorption and fluorescence properties are summarized in Table I. Fluorescence spectra and quantum yields were usually measured in ethyl benzoate (EB) or *o*-dichlorobenzene (DCB) solutions to facilitate subsequent chemiluminescence studies, but several fluorescers were measured in benzene or (because of solubility difficulties) in 1,2,4-trichlorobenzene (TCB). Five of the 11 compounds in the table (Ib–d, IV, and VI) are predominately infrared fluorescers with emission maxima above 700 nm while the others provided appreciable red as well as infrared emission.

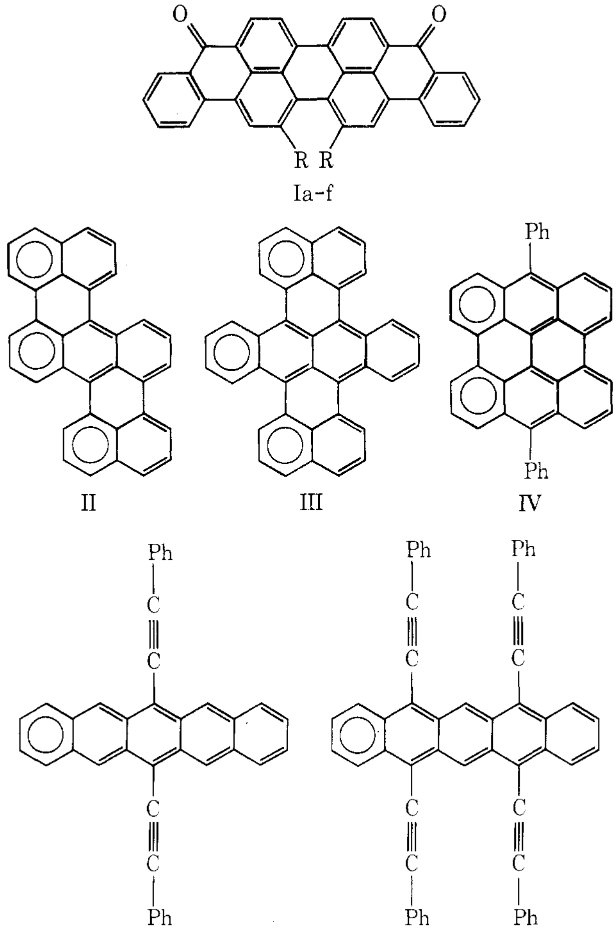
In the violanthrone series alkoxy substituents in the 16,17 positions (compounds Ib–d) provided bathochromic shifts of approximately 85 nm into the infrared, but had relatively little effect on the fluorescence quantum yield.[17] In the pentacene series substitution by two or four phenylethynyl substituents also produced substantial bathochromic shifts as has been discussed separately.[15]

For most of the compounds fluorescence quantum yields in the range of 18–51% were obtained. Solvent effects on quantum yield were noted in two cases. With IV a higher quantum yield was obtained in benzene than in ethyl benzoate or *o*-dichlorobenzene, and with Id the addition of 13% *tert*-butyl alcohol to dichlorobenzene decreased the quantum yield substantially. It is likely that the quantum yield of VI might be considerably higher in another solvent than in the 1,2,4-trichlorobenzene actually used, but the low solubility of VI prevented such measurements.

Infrared Chemiluminescence. Chemiluminescent reactions under several conditions with bis(2,4,6-trichlorophenyl) oxalate (TCPO), hydrogen peroxide, a basic catalyst, and six red or infrared fluorescers are summarized in Table II. Highest quantum yields of infrared radiation were obtained from diphenylbisanthene (IV) and from violanthrone derivatives Ib and Id. Substantially, lower quantum yields were obtained unexpectedly from the other violanthrone derivatives. There does not appear to be a straightforward correlation between either the fluorescence quantum yield or fluorescer structure and chemiluminescence quantum yield, and the variations obtained may result from decomposition of some fluorescers during the course of reaction. Two fluorescers, III and V, decomposed rapidly during chemiluminescent reactions, and reliable chemiluminescence emission data could not be obtained. The more detailed experiments with fluorescer Id indicate that higher quantum yields are obtained in ethyl benzoate than in dichlorobenzene and that quantum yields tend to decrease with increasing concentrations of TCPO.

Spectral distributions in chemiluminescence tend to be shifted toward longer wavelengths from the normal fluorescence spectra because of reabsorption of short-wavelength chemiluminescent emission by the fluorescer in the bulk solution. Self-absorption in chemiluminescence is minimized at low fluorescer concentrations, and it is evident from the comparison of chemiluminescence and fluorescence spectra in Figure 1 that singlet emission from the fluorescer is the source of chemiluminescence radiation.

Chart I
Red and Infrared Fluorescers[a]



[a] Ia (R = H), violanthrone; Ib (R = OCH_3), 16,17-dimethoxyviolanthrone; Ic (R = $OCH(CH_3)_2$), 16,17-diisopropoxyviolanthrone; Id (R = OC_6H_{13}), 16,17-dihexyloxyviolanthrone; Ie (R = OCH_2CH_2O–), 16,17-(1,2-ethylenedioxy)violanthrone; If (R = $OCOCH_3$), 16,17-diacetoxyviolanthrone; II, tetrabenzo[*de,hi,op,st*]pentacene; III, 7,8,15,16-dibenzoterrylene; IV, 4,11-diphenylbisanthene; V, 6,13-bis(phenylethynyl)pentacene; VI, 5,7,12,14-tetrakis(phenylethynyl)pentacene.

The effect of fluorescer concentration on chemiluminescence quantum yield under otherwise constant conditions is indicated by the experiments with 16,17-dihexyloxyviolanthrone (Id) in Table III. A low concentration (0.0010 *M*) of bis(2,4,6-trichlorophenyl) oxalate (TCPO) was used in the experiments to minimize possible quenching effects of TCPO and the reaction by-products on the quantum yield, and to minimize consumption of the fluorescer during the reaction. It is evident that the quantum yield increases with increasing fluorescer concentration to a limiting value. The rate of intensity decay also increases with increasing fluorescer concentration at the low concentration levels.

Discussion

Infrared fluorescence requires excited molecules having energies below 40.8 kcal mol^{-1} (>700 mμ). Since the Einstein probability for spontaneous emission of dipole radiation is proportional to the third power of the excitation en-

Table I
Absorption and Fluorescence Data

Fluorescer	Solvent[b]	Fluorescence data[a] Excitation λ_{max},[d] nm	Concn, 10^4 *M*	Quantum yield	Emission λ_{max},[c] nm	Absorbance data[e] λ_{max}, nm	ε
Ia	EB	550	5	0.35	630	607	
	DCB	550	5	0.36	637		
Ib	EB	600	7.5	0.32	713		
	DCB	600	7.5	0.29	720	658	40,340
	DCB	600	0.5	0.29	720		
Ic	EB	600	7.5	0.25	715		
	EB	600	15.0	0.27	720	648	36,630
	DCB	600	7.5	0.24	725		
	DCB	600	15.0	0.26	725		
Id	EB	600	7.5	0.29	720		
	EB	600	15.0	0.27	725		
	DCB	600	7.5	0.26	725	660	43,520
	DCB	600	15.0	0.26	725		
	DCB 87% TBA 13%	600	10	0.14	736		
Ie	EB	600	10	0.34	680	616	
	DCB	600	7.5	0.32	680		
	DCB	600	15.0	0.34	680		
If	EB	550	5	0.67	625	582	40,800
	DCB	550	5	0.61	628		
II	Benzene	600	10	0.51	690	628	43,700[f]
	DCB	678	10	0.51	678		
III	Benzene	600	5	0.21	630, 810	750	42,200
IV	EB	600	10	0.10	730	694	30,900
	DCB	600	10	0.10	736		
	Benzene	600	5	0.18	720		
V	Benzene	600	5	0.26	680, 730	668	25,300
VI	TCB	600	5	0.08	740, 790	705	26,900

[a] Fluorescence was excited at the front surface of the sample using an excitation wavelength as indicated. [b] EB, ethylbenzoate; DCB, dichlorobenzene; TBA, *tert*-butyl alcohol; TCB, trichlorobenzene. [c] Spectral emission maxima. [d] Wavelength used for fluorescence excitation. [e] First absorption band. Absorption data obtained in *o*-dichlorobenzene, except note *f*. [f] Absorption data obtained in benzene.

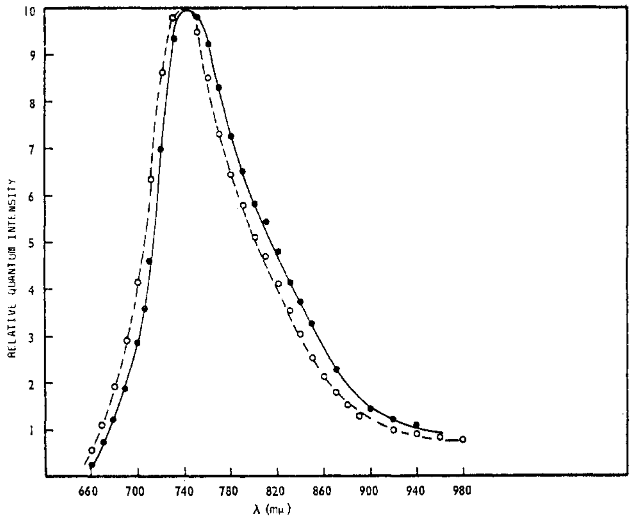


Figure 1. Id fluorescence and chemiluminescence emission. Fluorescence and chemiluminescence spectra of 16,17-dihexyloxyviolanthrone (Id) systems in 90% *o*-dichlorobenzene–10% *tert*-butyl alcohol at 25°: (○) fluorescence of 6.7×10^{-5} *M* Id; (●) chemiluminescence from reaction of 0.0010 *M* bis(2,4,6-trichlorophenyl) oxalate (TCPO), 0.010 *M* H_2O_2, 1.67×10^{-4} *M* sodium salicylate, and 6.7×10^{-5} *M* Id.

ergy, infrared fluorescers in general would be expected to have longer excited state lifetimes and lower emission efficiencies than visible fluorescers.[18] Thus, other factors being equal, fluorescent emission at 1000 nm in the infrared is 8 times less probable than green emission at 500 nm. Moreover, quenching of electronic excitation energy in internal and external vibrational modes becomes increasingly probable as the energy of the electronic transition approaches the energy of available vibrational modes.[19] Radiative efficiency losses from such internal conversion are thus more probable for infrared fluorescers than for visible fluorescers. Fluorescence theory thus indicates that the combination of low emission probability and high internal conversion probability should act to make infrared fluorescence relatively uncommon.

Available experimental data bear out these theoretical expectations; blue and green fluorescers tend to have higher quantum yields than red fluorescers even in related structural series, and red fluorescers are relatively uncommon. In spite of such considerations, however, the data in Table I show that moderately efficient fluorescence can be obtained in the 690–740 nm (41.4–38.6 kcal mol^{-1}) spectral range, although the fluorescence quantum yields are well below the values near unity available from many higher energy fluorescers.[20]

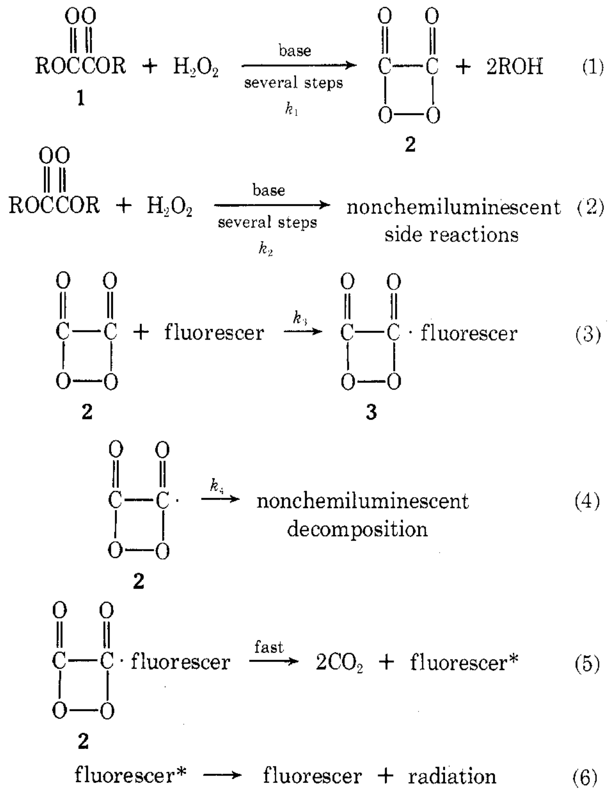
The chemiluminescence experiments (Tables II and III) combine moderately efficient infrared fluorescers with the highly efficient peroxyoxalate chemiluminescent system to produce infrared chemiluminescence quantum yields as high as 6%. Such quantum yields are high for chemiluminescent reactions in general where quantum yields well below 1% are typical,[4] but are well below quantum yields obtained with blue and yellow fluorescers in peroxyoxalate chemiluminescence.[7,8]

Table II
Infrared Chemiluminescence[a]

Fluorescer	Concn, 10^4 M	[TCPO],[b] 10^2 M	$[H_2O_2]$, 10^2 M	[Catalyst],[c] 10^3 M	Solvent[d]	Spectral emission max, nm FL	CL	Quantum[e] yield, 10^2 einsteins mol^{-1}	T,[f] min	Max int,[g] nm ml^{-1}
IV	7.0	1.0	2.5	NaSal 1.33	DCB	736	760	2.1	5.9	168
IV	7.0	2.0	5.0	NaSal 1.33	DCB	736	760	1.2	4.2	179
If	5.0	1.0	2.5	NaSal 1.33	DCB	628	643	0.18	57	2.0
If	5.0	2.0	5.0	NaSal 1.33	DCB	628	643	0.07	20	2.7
Ie	5.0	1.0	2.5	NaSal 1.33	DCB	680	680	0.37	85	4.0
Ie	5.0	2.0	5.0	NaSal 1.33	DCB	680	680	0.10	19	4.5
Ic	7.0	1.0	2.5	NaSal 1.33	DCB	725	735	0.33	33	78
Ib	4.5	1.0	2.0	NaSal 1.33	DCB	730	740	3.1	52	
Ib	1.5	1.0	2.5	NaSal 1.33	DCB	720	740	2.8	85	37
Ib	1.5	2.0	5.0	NaSal 1.33	DCB	720	740	1.1	20	62
Id	2.2	0.5	2.5	NaSal 0.50	DCB		740	2.4	30	31
Id	4.4	1.0	2.5	NaSal 0.50	DCB	725	760	2.3	71	54
Id	10.0	1.0	2.5	NaSal 1.33	DCB	730	776	2.9	30	120
Id	10.0	2.0	5.0	NaSal 1.33	EB	725	755	3.6	16	259

[a] Reactions at 25 ± 1°. [b] TCPO, bis(2,4,6-trichlorophenyl) oxalate. [c] NaSal, sodium salicylate. [d] DCB, 90% *o*-dichlorobenzene-10% *tert*-butyl alcohol; EB, 90% ethyl benzoate-10% *tert*-butyl alcohol. [e] Based on TCPO. [f] Time required for emission of three-quarters of the total radiation. [g] Maximum intensity in microwatts per milliliter of reaction mixture.

Mechanistic Significance and the Yield of the Key Intermediate. The mechanism proposed for oxalic ester chemiluminescence[8] involves the following essential steps (eq 1–6). According to this mechanism the chemiluminescence quantum yield (Q) will be the product of (a) the yield of key intermediate 2 from oxalate ester 1 (Y_{ki}) in competing steps 1 and 2, (b) the yield of complex 3 from 2 (Y_{cT}) in competing steps 3 and 4, (c) the yield of excited fluorescer from decomposition of 3 in step 5 (Y_{ex}), and (d) the fluorescence yield of the fluorescer in step 6 (Y_{fl}):



$$Q = Y_{ki} Y_{cT} Y_{ex} Y_{fl}$$

The yield of complex (Y_{cT}) from competive steps 3 and 4, provided the fluorescer concentration is constant during an experiment, will be

$$Y_{cT} = \frac{k_3[FLR]}{k_3[FLR] + k_4}$$

Thus the quantum yield, Q, in experiments carried out at constant fluorescer concentration will be

$$Q = Y_{ki} Y_{ex} Y_{fl} \frac{k_3[FLR]}{k_3[FLR] + k_4}$$

Inverting this equation one obtains

$$1/Q = \frac{1}{Y_{ki} Y_{ex} Y_{fl}} + \frac{1}{Y_{ki} Y_{ex} Y_{fl}} \frac{k_4}{k_3} \frac{1}{[FLR]}$$

The mechanism thus predicts that under constant reaction conditions where Y_{ki}, Y_{ex}, and Y_{fl} are constant, a plot of the reciprocal of the quantum yield *vs.* the reciprocal of the fluorescer concentration will give a straight line with an intercept of $1/Y_{ki}Y_{ex}Y_{fl}$, and a slope of $(1/Y_{ki}Y_{ex}Y_{fl})(k_4/k_3)$. The ratio k_3/k_4 is then available as the quotient of intercept/slope.

A plot of $1/Q$ *vs.* $1/[FLR]$ for the data of Table III is shown in Figure 2. A satisfactory straight line is obtained having an intercept of 14.5 and a slope of 2.2×10^{-3}. The quantum yield for the reaction at infinite fluorescer con-

Table III
Effect of 16,17-Dihexyloxyviolantrone (Id) Concentration on Chemiluminescence Quantum Yield and Reaction Rate[a]

[Id], 10^4 M	Quantum yield, 10^2 einsteins mol^{-1}	Emission[b] lifetime, min
0.67	2.16	40
1.67	3.50	21
3.33	4.58	21
6.67	6.02	16
10.00	5.94	17

[a] Reactions of 0.001 M bis(2,4,6-trichlorophenyl) oxalate, 0.01 M H_2O_2, and 1.67×10^{-4} M sodium salicylate in 87% *o*-dichlorobenzene–13% *tert*-butyl alcohol at 25 ± 1°. [b] Time required for emission of 75% of the total radiation output.

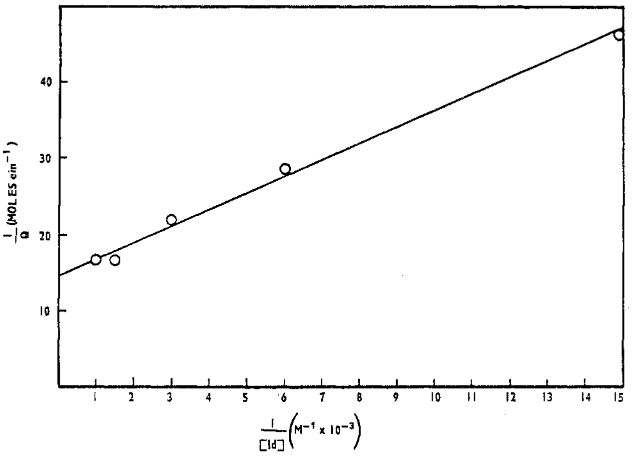


Figure 2. Relationship of chemiluminescence quantum yield, *Q*, to fluorescer (Id) concentration. Data from Table III.

centration is the reciprocal of the intercept or 0.069 einstein mol^{-1}. Since the fluorescence quantum yield under the reaction conditions is 0.14, the yield of excited fluorescer based on the concentration of TCPO is 0.069/0.14 or 49%. Since the yield of excited fluorescer in step 5 cannot be greater than unity, the yield of **2** must also be at least 49% under the reaction conditions employed in the experiments.

The rate ratio k_3/k_4 obtained from the quotient of intercept/slope is 6.6 × 10^3. This high value confirms earlier experiments which indicated that the fluorescer acts as a catalyst for the decomposition of key intermediate **2**.[8]

Although the time required for the emission of three-quarters of the total radiation is not an accurate measure of the reaction rate, the increase in rate of intensity decay with increasing fluorescer concentration between 0.67×10^{-4} and 1.67×10^{-4} *M* suggests that step 3 may in part be rate determining at very low fluorescer concentrations. The similar decay rates obtained at fluorescer concentrations of 1.67×10^{-4} *M* and higher, however, indicates that step 3 is fast relative to step 1 when sufficient fluorescer is present.

Experimental Section

Materials. *o*-Dichlorobenzene (Eastman) and *tert*-butyl alcohol (Eastman) were fractionally distilled; reagent 98% hydrogen peroxide was obtained from BeccoChemical Division, FMC Co. The 16,17-disubstituted violanthrones, dihydroxy- and dimethoxy-Ib, diisoproxy-Ic, ethylenedioxy-Ie, and diacetoxy-If were obtained from the Organic Chemical Division, American Cyanamid Compound, Bound Brook, N.J. The high melting compounds Ib and Ie were purified by extraction in a Soxhlet thimble with pyridine; the diisopoxy derivative Ic, mp 342°, was purified by chromatography on alumina with pyridine–ethyl acetate; recrystallization of If from pyridine gave crystals, mp 300°. Hydrocarbons II,[21] V,[15] and VI[15] were prepared by methods previously described. Iodine-catalyzed photocyclization of 10,10′-diphenyl[$\Delta^{9,9'(10H,10'H)}$-bianthracene]-10,10′-diol afforded 4,11-diphenylbisanthene (IV).[22] Bis(2,4,6-trichlorophenyl) oxalate, mp 190.5–192.5°, was prepared as previously described.[8]

16,17-Dihexyloxyviolanthrone (Id). To a mixture of 76.7 g (0.16 mol) of 16,17-dihydroxyviolanthrone and 153.5 g of potassium carbonate in 400 ml of 1,2,4-trichlorobenzene heated to 120° was added during 3 hr 133 g (0.81 mol) of *n*-hexyl bromide. The mixture was heated at 120–130° for another 8 hr, cooled, and poured into 1.5 l. of water. The solid was separated and washed with 1200 ml of refluxing methanol. An absorption spectrum indicated that the 46.2 g of product was 80% pure. Recrystallization from benzene gave dark maroon crystals, mp 242–243°.

Anal. Calcd for $C_{46}H_{40}O_4$: C, 84.12; H, 6.14. Found: C, 84.06; H, 6.22.

5,12-Dihydroxy-5,12-dinaphthyl-5,12-dihydronaphthacene. A modification of an earlier method[23] gave a diol which had a substantially higher melting point than reported. To 1-naphthyllithium, prepared from 8.69 g (0.042 mol) of 1-bromonaphthalene and 0.56 g (0.08 g-atom) of lithium in 30 ml of anhydrous ethyl ether, was added 2.58 g (0.01 mol) of 5,12-naphthacenequinone[24] and 70 ml of anhydrous benzene. The mixture was refluxd for 2 hr, then decomposed by the addition of 25 ml of ethanol. Dilution with water gave a solid which was recrystallized from xylene. The yield of the colorless product, mp 297–299° (lit.[23] mp 242°), was 3.75 g (73%); mass spectrum had *m/e* 514, 512, 496, 480, and 370. The single peak at 3572 cm^{-1} ($CHCl_3$) established the trans reationship of the two hydroxy groups.

Anal. Calcd for $C_{38}H_{26}O_2$: C, 88.72; H, 5.05. Found: C, 88.56; H, 5.36.

7,8,15,16-Dibenzoterrylene (III). A previously described[23] cyclization of 5,12-dihydroxy-5,12-dinaphthyl-5,12-dihydronaphthacene was followed to obtain III. The crude material was chromatographed on silica gel with 1,2,4-trichlorobenzene to obtain 12% of III as a green solid, mp 360°; mass spectrum *m/e* 476.

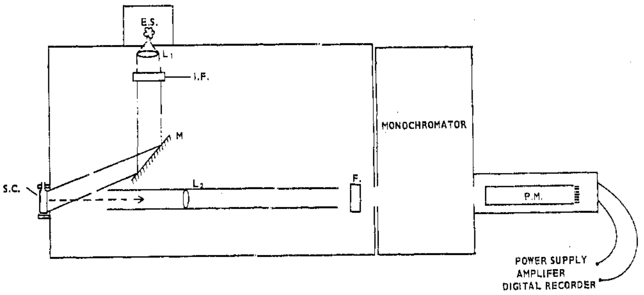


Figure 3. Diagram of spectroradiometer: S.C., sample cell; E.S., excitation source; $L_1 + L_2$, focusing lens; I.F., interference filter; F., blocking filter; P.M., photomultiplier.

Instrumentation. Description. A diagram outlining the essential features of the spectroradiometer is shown in Figure 3. The excitation source was a Quartz-Iodine, 40-W tungsten lamp mounted vertically inside a housing equipped with a collimating glass lens. Provision was made to insert 2-in.-square interference filters into the excitation beam to isolate appropriate wavelength regions. The sample cuvette (1 cm thick, 22 mm diameter) and collimetor lens (1.5 in. diameter, 10 cm focal length) were positioned 40 and 20 cm, respectively, from the monochromotor entrance slit. A blackened aluminum tube served as a lens holder and light baffle, to reduce stray light. The monochromotor was a Jarrell-Ash 0.25-m Ebert type with fixed 1-mm interchangeable slits and incorporated two gratings blazed at 0.6 and 1.2 *μ*. The S-1 response detector was a Fairchild-Dumont No. 6911 photomultiplier mounted inside a cooled Electro Optics Associates housing assembly No. P.M. 101. A Fluke Model 412B and a Keithley Model 414 were used as photomultiplier power supply and amplifier, respectively. The photomultiplier was operated at −78° through Dry Ice cooling. Operating the photomultiplier at 1000 V and the amplifier at 10^{-8} A produced excellent linearity and reproducibility.

Data (amplifier output) were recorded digitally on a United Systems DIGITEC Assembly consisting of a Model 201-N digital voltmeter, Model 661 digital clock, and a Model 611/620 printer system. Printed, paper tape data were then processed by an S.D.S. 930 computer programmed with the calibration data.

Calibration. Relative calibration was obtained using a National Bureau of Standards lamp; absolute calibration was made by reference to an absolute Roberts-Hirt spectroradiometer.[25]

Light Measurements. Fluorescence and chemiluminescence experiments were carried out as previously described.[8]

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Registry No.—Ia, 116-71-2; Ib, 128-58-5; Ic, 53418-57-8; Id, 53418-58-9; Ie, 6424-76-6; If, 53418-59-0; I (R = OH), 128-59-6; II, 191-79-7; III, 187-96-2; IV, 23102-66-1; V, 18826-31-8; VI, 18826-38-5; 10,10′-diphenyl[$\Delta^{9,9'(10H,10H)}$-bianthracene]-10,10′-diol, 53418-60-3; *n*-hexyl bromide, 111-25-1; 5,12-dihydroxy-5,2-dinaphthyl-5,12-dihydronaphthacene, 53418-61-4; 1-bromonaphthalene, 90-11-9; 5,12-naphthacenequinone, 1090-13-7; bis(2,4,6-trichlorophenyl) oxalate, 1165-91-9.

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Stereochemistry of the Exchange Reaction between Lithium Tetrachloropalladate and Alkylmercury Compounds

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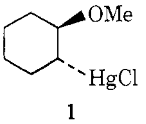
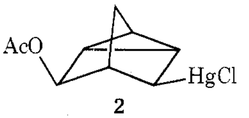
The carbomethoxylation of several σ-bonded organomercurials (derived from the oxymercuration of cyclohexene and norbornadiene) in the presence of stoichiometric amounts of lithium tetrachloropalladate and carbon monoxide was found to proceed with predominant retention of configuration at carbon. Since the carbomethoxylation of alkylpalladium compounds occurs with complete retention of configuration at carbon, therefore the exchange of palladium for mercury occurs with predominant retention of configuration.

The organometallic exchange reaction is a generally employed method for the generation of transition metal–carbon σ bonds[1] and the formation of σ-bonded organopalladium complexes *via* palladium exchange with organomercurials has been used extensively in the arylation, methylation, and carbomethoxylation of olefins.[2-5] Alkylmercury compounds of known configuration can be readily obtained *via* the solvomercuration of olefins and the stereochemistry of addition to simple olefins is trans.[6] The exchange of palladium for mercury is, therefore, a possible method of stereospecifically synthesizing palladium–carbon σ-bonded complexes. The stereochemistry of the exchange process can be determined by trapping the unstable alkylpalladium intermediate with carbon monoxide in methanol[5] since the conversion of alkylpalladium complexes to esters has been shown to proceed with complete retention of configuration at the carbon bearing the metal.[7] Structural analysis of the methyl ester formed would establish the stereochemistry of the exchange reaction. (See Scheme I.)

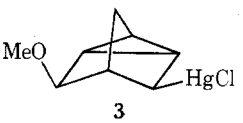
Thus, the carbonylation of alkylmercury compounds **1**,[8] **2**,[9] and **3**,[10] in the presence of lithium tetrachloropalladate in methanol was investigated to determine the stereochemistry of the exchange process.



1

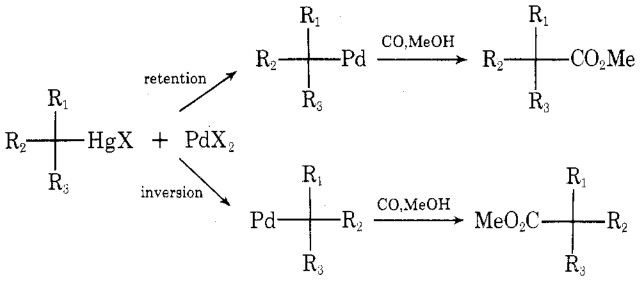


2



3

Scheme I



Results and Discussion

The carbonylation of *trans*-2-methoxycyclohexylmercuric chloride (**1**) in methanol in the presence of sodium acetate was effected by treatment of **1** with lithium tetrachloropalladate and carbon monoxide (1 atm) at room temperature. The reaction afforded methyl *trans*-2-methoxycyclohexylcarboxylate (**4**)[5] in a 7% yield. No attempts were made to isolate low-boiling organic products which were removed during the work-up. The low yield of **4** suggests the carbonylation did not compete favorably with the decom-