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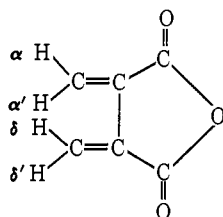
Photochromic Fulgides. Spectroscopy and Mechanism of Photoreactions

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Abstract: The photochromism of a number of fulgides has been studied, and the process has been shown to be a molecular phenomenon. The primary photochemical step is a photobridging process which accounts for the formation of a cyclic colored structure. Proof for the nature of the photocolored species is inferred from a subsequent reaction. Substitution has an effect on the relative concentration of the colored form at the photostationary state and is discussed. Fluorescence exists in some cases but no phosphorescence can be observed. Thermal and photoerasure of the colored form is possible.

The fulgides may be obtained by substitution of the lettered hydrogen positions in dimethylenesuccinic anhydride.



When one of the hydrogens is substituted by an aryl group, the crystals have initially a yellow to reddish shade. The effect of light is to deepen the color. Stobbe² first made a crystallographic and spectroscopic investigation and came to the conclusion that the photochromism of these substances was exclusively a crystalline phenomenon. Further, no identification of the nature of the colored species has ever been cited despite continued study by Hanel.³

All known photochromic fulgides contain a phenyl group. Also, 1-phenylnaphthalene-2,3-dicarboxylic acid anhydride was isolated on prolonged irradiation at room temperature of an iodine-containing solution of dibenzylidenesuccinic anhydride.^{4,5} Also, 1,4-diphenyl-1,3-butadiene undergoes photochemical reaction to 1-phenylnaphthalene.⁶

We anticipated that the photochromic behavior of the fulgides was a molecular phenomenon. Therefore, as a part of our continuing investigation to evaluate various spectroscopic parameters of molecules and their importance in photochemistry, we have investigated the spectroscopic and photochemical behavior of a number of fulgides. The purpose of the present study

is (1) to elucidate the nature and mechanism of production of the colored species, (2) to correlate the low-temperature absorption and emission characteristics with the photochemical behavior, and (3) to determine the effect of the nature of substitution on the photochemical and spectroscopic properties of the fulgides.

Experimental Section

In general, the syntheses followed those described in earlier work.¹ The itaconic esters (methylene succinic acid ethyl ester) were prepared by a modified Stobbe condensation of Johnson, *et al.*⁷ Further condensation of the itaconic ester with an appropriate aldehyde or ketone using sodium ethoxide yielded the corresponding substituted dimethylenesuccinic acid monoester. Hydrolysis in ethanolic potassium hydroxide solution gave the fulgenic acid (dimethylenesuccinic acid). This, in turn, was converted to the anhydride form by refluxing in an acetyl chloride solution. The anhydrides were purified by recrystallization in a variety of solvents depending on the solubility properties of the particular fulgide and also by chromatography on a neutral silica gel column. Purity was determined by thin layer chromatographic analysis as well as by melting point determination.

The low-temperature absorption measurements were obtained on a Cary Model 15 spectrophotometer using 2.0-mm rectangular quartz cells immersed in an optical dewar filled with liquid nitrogen. In every instance, 2-methyltetrahydrofuran (2MeTHF) was used as the solvent for both absorption and emission spectra. The 2MeTHF was purified by refluxing over lithium aluminum hydride and passage through an activated alumina column.

The emission set up consisted of a 1-kW xenon source, an exciting monochromator, and an analyzing monochromator with an EMI 9558 B photomultiplier. In all cases, the emission recorded was that from the front surface of the sample cell. A 150-W tungsten lamp with a built-in parabolic reflector was used to obtain the excitation spectra in the 400–500-m μ region. Some of the excitation spectra were corrected for the decrease in intensity of the source and for the change in efficiency of the exciting monochromator as a function of wavelength. For the same cases, the relative quantum efficiency of emission was also calculated. The emission spectra were not corrected for photomultiplier tube response as a function of wavelength.

The relative quantum yields of emission were calculated as follows

(7) W. Johnson, J. Peterson, and W. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).

(1) Taken from a thesis submitted in partial fulfillment for the M.S. degree.

(2) H. Stobbe, *Ann.*, **380**, 1 (1911).

(3) L. Hanel, *Naturwissenschaften*, **37**, 91 (1950).

(4) H. Stobbe, *Ber.*, **40**, 3372 (1907).

(5) A. El-Abbadly and L. El-Assal, *J. Chem. Soc.*, 1016 (1959).

(6) G. J. Fonken, *Chem. Ind. (London)*, 1327 (1962).

Table I. Spectroscopic and Photochemical Properties of Various Fulgides*

Compd	α	α'	δ	δ'	Absorption		
					Onset, ^b m μ	Longest λ_{\max} , ^b m μ	Longest λ_{\max} , ^c m μ (ϵ)
1	Ph	H	Ph	H	430	355	355 (9570)
2	Ph	Ph	H	Ph	490	408	390 (10,900)
3	Ph	Ph	H	<i>o</i> -MeOPh	505	415	405 (8950)
4	Ph	Ph	H	<i>p</i> -MeOPh	520	418	415 (12,800)
5	Ph	Ph	H	Piperonyl	515	420	420 (25,500)
6	Ph	Ph	H	Styryl	520	445	425 (26,200)
7	Me	Me	Ph	H	385	325	325 (6850)
8	Me	Me	Ph	Me	375	305	295 (9040)
9	Me	Me	H	Styryl	427	382, 368	369 (51,000)
10	Ph	Ph	Ph	Ph	540	443	418 (9950)

Compd	Absorption		Emission ^d		Fluorescence	Photochemistry Naphthalene derivative formed
	Color of photocolored form	Longest λ_{\max} photocolored form, m μ	Onset, ^b m μ	λ_{\max} , ^b m μ		
1	Red orange	485			Not detected	1-Ph-2-COOH-3-COOMe ^e
2	Red	535	490	610	Yes (w)	Yes
3	Red	540	505	600	Yes (s)	Yes
4	Red orange	515 (sh)	515	600	Yes (s)	Yes
5	None formed	None	505	588	Yes (s)	Yes
6	None formed	None	490	570	Yes (vs)	Yes
7	None formed	None			Not detected	No
8	None formed	None			Not detected	No
9	None formed	None	405	452	Yes (vs)	No
10	None formed	None			Not detected	No

* Blank indicates that no observation was made. ^b At -196° . ^c At 25° . ^d Abbreviations used are vs = very strong; s = strong; w = weak; sh = shoulder. ^e In methanol.

$$Q_{\text{rel}} = \frac{I(\lambda_e)}{I_0(\lambda_i)[1 - T(\lambda_i)]}$$

where $I(\lambda_e)$ = relative intensity of the emitted light at a wavelength λ_e , $I_0(\lambda_i)$ = relative intensity of the incident monochromatic light at a wavelength λ_i , and $T(\lambda_i)$ = transmittance of the solution at a wavelength λ_i . As indicated in the foregoing equation, only relative values for $I_0(\lambda_i)$ at various wavelengths were needed. These were measured by Bowen's "fluorescent screen" method as adapted for a somewhat similar purpose by Melhuish.⁸ This method is based on the observation that the fluorescence yield of Rhodamine B is virtually independent of the wavelength of the exciting light. There appears to be some systematic error since the calculated values are always less than the normalized value of 1 chosen for some wavelength. We expect the values to have a precision of ± 0.08 .

In the photoconversion of fulgides, quartz cells were immersed in a Dry Ice-isohexane bath contained in a quartz dewar flask. Irradiation was carried out with a 1-kW ac Hg-Xe arc using appropriate Corning glass filters. In cases where it was necessary to irradiate in a particular absorption band, narrow band-pass filters with half-widths of approximately 15 m μ were used. After photocoloration at -77° , appropriate hydrogen atom abstractors, such as oxygen, were introduced. The solvent was then removed *in vacuo* and the products were analyzed. IR spectra were taken on a Beckman IR-10 spectrophotometer. The nuclear magnetic resonance (nmr) spectra were obtained on a Varian high-resolution HA 100 spectrometer.

Photocoloration in the crystalline form was also attempted for some fulgides. The pulverized substance was mounted between two Suprasil windows and irradiated at room temperature. In some cases, fading was observed after the removal of the irradiation source.

Sensitization experiments were carried out with α,δ -diphenylfulgide at approximately $8 \times 10^{-3} M$ and thioxanthone as well as benzil at approximately $3 \times 10^{-2} M$. These were done in 2MeTHF at -196° . No sensitization of photocoloration appears to occur for either case.

Results and Discussion

Table I presents a summary of the spectroscopic and photochemical properties of the compounds considered in this investigation.

A. α,δ -Diphenylfulgide. Diphenylfulgide was studied the most thoroughly and will be discussed here in greater detail. The absorption spectrum at -196° showed no characteristic difference from that at room temperature, with onset near 435 m μ , maximizing in broad bands near 355 and 287 m μ , Figure 1. Irradia-

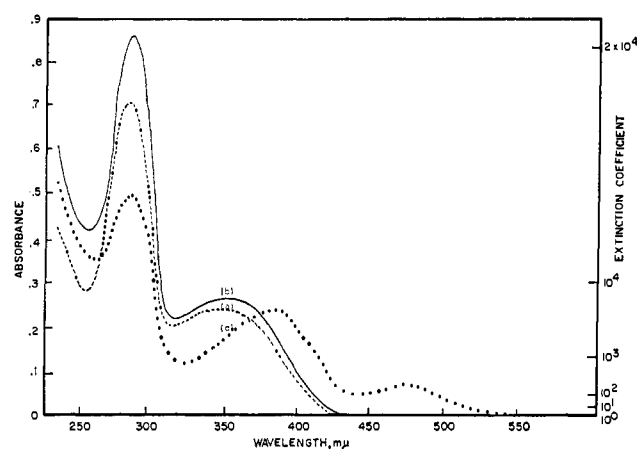


Figure 1. Absorption spectra of α,δ -diphenylfulgide in 2-methyltetrahydrofuran: (a) absorption spectrum, room temperature, right-hand ordinate; (b) absorption spectrum, -196° , before irradiation; (c) absorption spectrum, -196° , after 5-min irradiation.

tion at -196° in a rigid glass of 2-methyltetrahydrofuran in the absorption band at 355 m μ deepened the color to red orange. The same observation was also

(8) W. Melhuish. *J. Opt. Soc. Am.*, **52**, 1256 (1962).

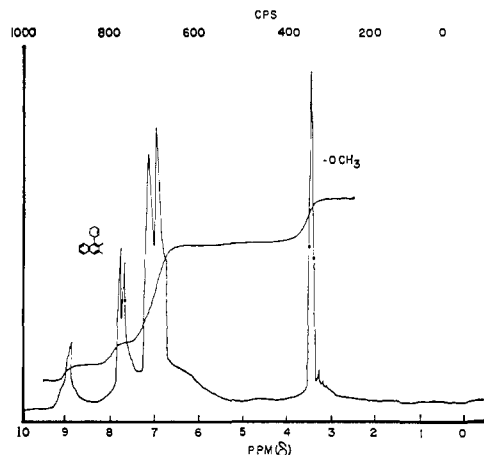
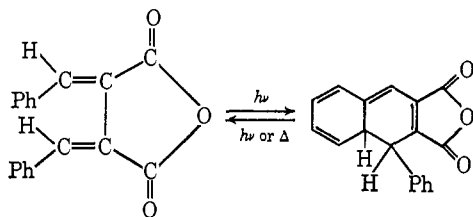


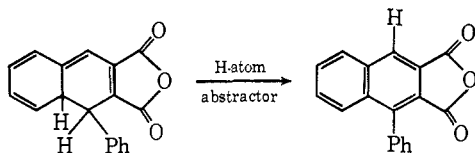
Figure 2. Nmr spectrum of 1-phenylnaphthalene-2,3-dicarboxylic acid monomethyl ester.

noted for the crystal. The photocolored species showed an absorption onset near $550\text{ m}\mu$ and a maximum near $485\text{ m}\mu$, Figure 1. This change was accompanied by a consequent decrease in intensity of the absorption bands at 287 and $355\text{ m}\mu$. There was approximately 87% reversion to the fulgide upon warming the solution to room temperature and approximately 95% reversion by irradiating into the $485\text{-m}\mu$ absorption band of the photocolored form. Moreover, the erasure of the colored form is extremely rapid. No emission from the colored form could be found. This probably occurs because of the rapid reverse reaction to the fulgide.

In order to investigate and identify the species responsible for the red-orange color, an additional reaction was carried out. It was suspected that the primary process producing the photocolored product was



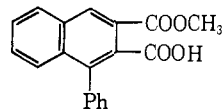
If this were so, the addition of a suitable hydrogen atom abstractor should produce the noncolored, appropriately substituted naphthalene-2,3-dicarboxylic anhydride as



Irradiation of a degassed solution at -77° produced the typical red-orange color which could be bleached by the addition of oxygen, O_2 . In particular, irradiation of a methanolic solution at -77° and bleaching with oxygen yielded a colorless product. The ultraviolet, infrared, and nmr spectra were all consistent with the presence of a naphthalene moiety.

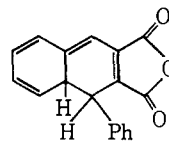
The ultraviolet spectrum was similar to that of 1-phenylnaphthalenes. The nmr spectrum, Figure 2, has a singlet of three protons at $\delta 3.48$ ($-\text{OCH}_3$), a singlet of one carboxylic proton at $\delta 11.8$ ($-\text{COOH}$, not shown),

and a set of ten aromatic protons at $\delta 7.00$ – 8.96 . The infrared spectrum of the pure compound has bands typical of dimeric and monomeric carboxylic groups in the regions 2700 – 3450 and 940 cm^{-1} . The above spectroscopic observations therefore verified the formation of a monoacid ester



or one in which the hydroxy and methoxy groups are interchanged. In any event, this possibility has no bearing on the main nature of the photocolored species.

The alcoholysis reaction of the anhydride to the acid ester at -77° may or may not involve a photochemical process. de Mayo⁹ reported a similar observation in the photolysis of methanolic solutions of α -pyrones at room temperature. Nonetheless, this result does not bear on the principal feature of importance, that is, the production of a naphthalene derivative. These observations thus provide strong evidence that the photocolored molecular species formed upon irradiation is



The emission characteristics of this compound requires some explanation. Early emission spectra from this compound later proved to be those arising from a photoproduct since the intensity of emission increased with time. It is interesting that we have found 1,1,4-triphenylbutadiene to have similar emission and excitation spectra although better resolved and with both shifted to shorter wavelengths. The absorption of the triphenylbutadiene is highly structured parallel to its excitation spectrum and similar to that observed for the photoproduct of the fulgide. Thus, we conclude that there is a competition between *cis-trans* isomerization about one or the other of the double bonds terminating at the α and δ carbons and photocyclization. The resulting isomerized photoproduct would then show emission and excitation spectra typical of a polyphenyl-substituted butadiene. The broader and longer wavelength spectra would be consistent with the structure of the resulting geometrically modified fulgide. Therefore, it appears as if the original fulgide emits only very weakly or not at all and the excitation energy is utilized for photochemical processes.

B. α,α',δ' -Triphenyl-, α,α' -Diphenyl-, δ -*o*-methoxyphenyl-, and α,α' -Diphenyl- δ' -*p*-methoxyphenylfulgides. Photocoloration was observed for these compounds when the crystals were irradiated at room temperature. The reddish brown color that developed at the surface of the exposed film gradually faded as soon as the irradiation source was removed.

The photochemical observations at -196° almost duplicated those of α,δ -diphenylfulgide. The principal differences noted were (1) the longest wavelength band of the colored forms was red shifted, Figure 3; and (2) less photocoloration was produced, and the rate of thermal fading of the colored form back to the fulgide

(9) P. de Mayo, *Advan. Org. Chem.*, **2**, 393 (1960).

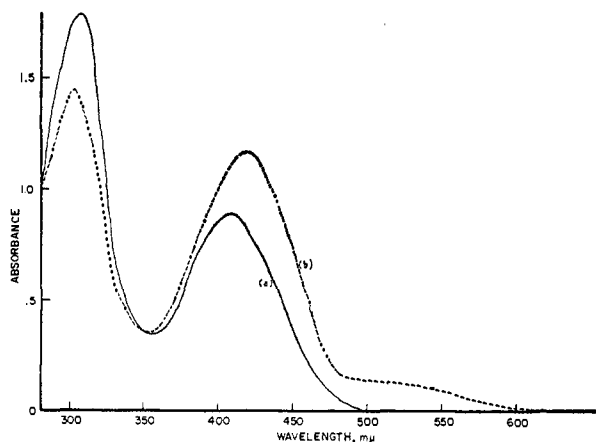


Figure 3. Absorption spectra of α, α', δ' -triphenylfulgide before and after irradiation, 2-methyltetrahydrofuran solution, -196° : (a) absorption spectrum before irradiation; (b) absorption spectrum after 10-min irradiation.

was more rapid. The decrease in photocoloration and the increase in fading rate indicate the consequences of steric and/or electronic effects from the additional substitution. Also, overlap of the bands of the colored form with those of the fulgide would increase the probability for photoerasure.

The absorption spectra of these fulgides are red shifted compared to the α, δ -diphenyl case. The fluorescence spectra are unresolved and maximize near $600 \mu\mu$, Table I and Figure 4.

The fluorescence emission of the triphenyl derivatives was monitored as a function of irradiation wavelength and time. No changes in shape were noted as a function of either parameter. Furthermore, the intensity did not change with irradiation time. The relative quantum yield of emission appears to decrease in the second electronic transition. This indicates another process is competing with emission. From other experience^{10,11} it is likely that this process is photochemistry. Also, it is possible that ultraviolet bands of the colored photoproduct could cause some internal filtering effects. No phosphorescence was observed up to $750 \mu\mu$.

In each case, the corresponding naphthalene derivatives were produced by allowing nondegassed solutions to sit at room temperature in room fluorescent light. These derivatives were characterized by comparison with the ultraviolet spectrum of the 1-phenylnaphthalene photoproduct obtained from the diphenylfulgide.

C. α, α' -Diphenyl- δ -piperonyl- and α, α' -Diphenyl- δ -styrylfulgides. The absorption and fluorescence emission characteristics were very similar to the other triphenyl derivatives but no photocoloration was observed, Figure 5. The excitation spectrum is also shown in Figure 5. No phosphorescence is observed to $750 \mu\mu$. Naphthalene derivatives were formed and characterized in a manner similar to that described above.

The inability to see the colored form at -196° , and yet produce the naphthalene derivatives at room temperature, indicates several features. The photostationary state has been shifted dramatically toward the fulgide. The rate of the back reactions (photochemical and

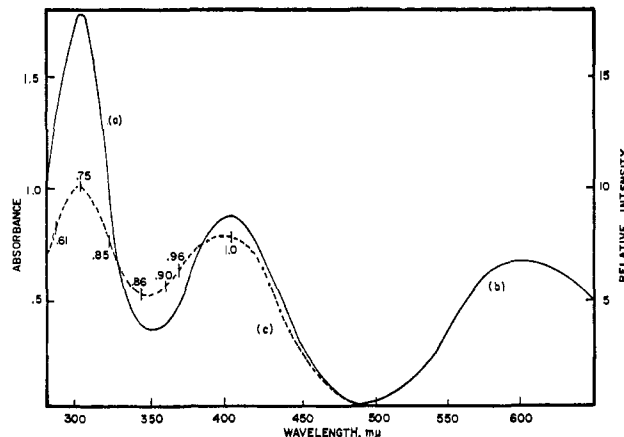


Figure 4. Absorption emission and excitation spectra of α, α', δ' -triphenylfulgide, -196° : (a) absorption spectrum; (b) emission spectrum; (c) excitation spectrum with relative quantum yield of emission.

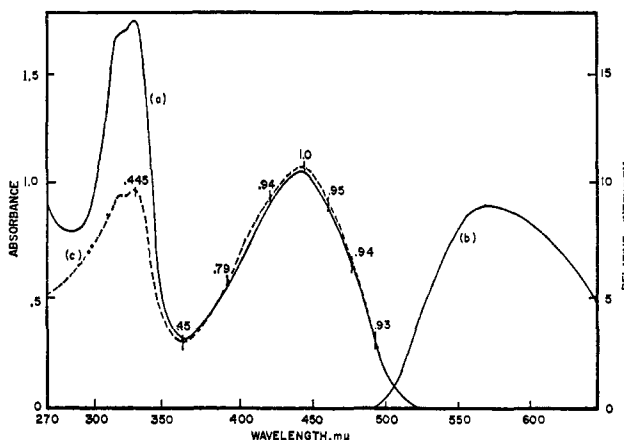


Figure 5. Absorption, emission, and excitation spectra of α, α' -diphenyl- δ -styrylfulgide, -196° : (a) absorption spectrum; (b) emission spectrum; (c) excitation spectrum with relative quantum yield of emission.

thermal) of the colored form to the fulgide must be sufficiently greater than the forward rate such that the equilibrium concentration of the colored form is below detectable limits. The longest wavelength absorption band of the colored form would be expected to overlap that of the fulgide in a manner similar to that found for the triphenyl derivatives considered above, Figure 3. Since the colored form was produced by exciting into the long wavelength absorption band of the fulgide, significant photoerasure could occur. All of these factors apparently are the principal ones accounting for the inability to observe the colored form.

At room temperature, the bimolecular rate for production of the naphthalene derivative must be of the same order of magnitude as the rate for the back reactions of the colored form to the fulgide. The bimolecular reaction most likely is that involving the colored form and oxygen. The rate constant for excited state quenching by oxygen¹² is approximately 10^{10} sec^{-1} .

The presence of strong fluorescence emission, particularly for the δ' -styryl case, indicates that the photochemical rate is less competitive with the fluorescence rate.

(10) J. Michl and R. S. Becker, *J. Am. Chem. Soc.*, **88**, 5931 (1966).

(11) R. S. Becker, E. Dolan, and N. Tyer, unpublished, University of Houston.

(12) G. Porter and M. Wright, *Discussions Faraday Soc.*, **27**, 18 (1959).

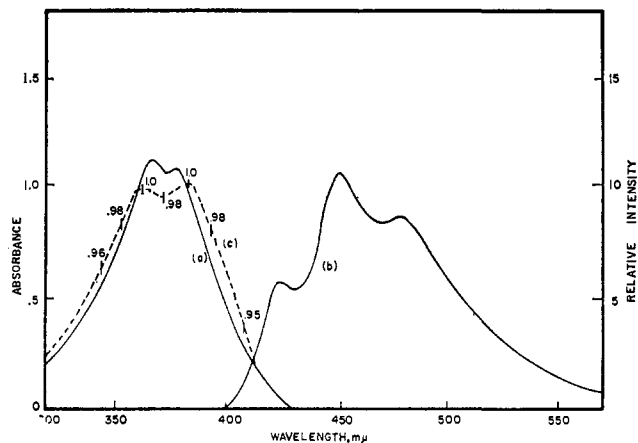


Figure 6. Absorption, emission, and excitation spectra of α,α' -dimethyl- δ -styrylfulgide, -196° : (a) absorption spectrum; (b) emission spectrum; (c) excitation spectrum with relative quantum yields of emission.

The relative quantum yield of emission shows a decrease at short wavelengths, particularly at the onset and within the second electronic transition (assuming the first band is only one transition). The reason for this is expected to be the same as that given in section B.

D. α,α' -Dimethyl-, δ -Phenyl-, α,α',δ' -Trimethyl-, δ -Phenyl-, and $\alpha,\alpha',\delta,\delta'$ -Tetraphenylfulgides. No photocoloration was observed in these compounds after prolonged irradiation in a rigid glass solution of 2-methyl-tetrahydrofuran at -196° . The same observation was noted when the crystals were irradiated at room temperature. Furthermore, no emission could be detected from these fulgides to $750\text{ m}\mu$.

It might be expected that, because of the nature of substitution, steric barriers to bridging could exist. The absence of fluorescence clearly indicates that the electronic energy is utilized totally for photochemistry and/or lost internally. Thus, the presence of photochemistry and internal conversion preclude the observation of fluorescence. Since no colored form was detectable, any photobridged product has back reaction rates to the fulgide faster than the forward one from the fulgide.

No naphthalene derivative could be isolated after prolonged irradiation of these fulgides. This is consistent with the fact that no hydrogen is situated at the α or α' and the δ or δ' positions, and, with bridging to a phenyl group, no oxidation to the naphthalene derivative is possible.

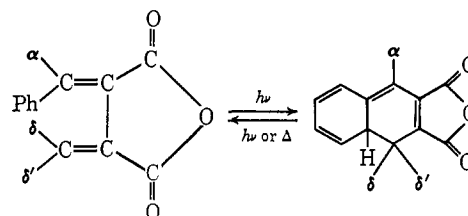
E. α,α' -Dimethyl- δ -styrylfulgide. No photocoloration was observed for this compound; however, the

intensity of fluorescence was extremely high, considerably greater than in all other cases, Figure 6. The fluorescence does not change as a function of exciting wavelength or time. Also, no phosphorescence was observed to $750\text{ m}\mu$. With reference to the proposed mechanism, this compound does not have the proper structural features for the photochemical bridging process to occur. Thus, the strong fluorescence is in agreement with expectation; that is, the electronic energy produced by excitation is not utilized photochemically and therefore is emitted as fluorescence.

The fact that the relative quantum yield of emission does not vary from 1, and the shape of the excitation is essentially that of absorption, is consistent with the foregoing conclusion. The reason for the slight variation in shape of the excitation and absorption curves is not known.

Summary and Conclusions

The photochromism of fulgides has been shown to be a molecular phenomenon resulting from the formation of a bridged ring structure. This occurs by the following primary process.



Substitution has a marked effect on the ability to observe the colored photoproduct. Furthermore, other photoreactions occur.

Fluorescence can be seen in some instances but no phosphorescence is observable. Excitation spectra indicate there is competition with internal conversion particularly from the second excited state. The competing process is probably photochemistry.

It is not possible to identify the multiplicity nature of the excited state from which the photochemical reaction occurs, although there are indications it is a singlet.

It is possible to cause the colored photoproduct to revert to the original fulgide either with heat or visible light.

Acknowledgment. We wish to thank Dr. M. R. Willcott of the University of Houston for assistance as well as for helpful discussion concerning the nmr spectra.