

The value of pK_4 is then $pK_1 + pK_3 - pK_2 = 6.5$. The electrostatic effect of the development of a positive charge upon the ionization of the hydroxyl group and of a negative charge on the ionization of the ammonium group is in each case $pK_3 - pK_2 = pK_4 - pK_1 = 4.8$ units, in agreement with a previous estimate of 4.7 units.⁵ The (uncorrected) electrostatic effect of the positive charge on the ionization of **8** ($R = H, CH_3$) at ionic strength 1.0 M is 4–5 pK units.⁵⁷

We estimate that the individual pK_a values are prob-

(57) A. Hilton and D. L. Leussing, *J. Amer. Chem. Soc.*, **93**, 6831 (1971). Professor Leussing has kindly informed us that the correct values of $\log K_{12}$ are 4.81 and 3.1 for **8**, $R = H$ and CH_3 , respectively.

ably accurate to within 1 pK unit. The estimates are based, as far as possible, on pK_a values at low or zero ionic strength and shifts on the order of 0.1–0.2 unit, upwards for ammonium and downwards for hydroxyl ionizations, may be expected at ionic strength 1.0 M.

Supplementary Material Available. Tables I and III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-1436.

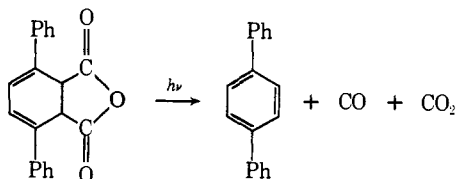
Photogeneration of Fluorescent Hydrocarbons from Cyclic 1,2- and 1,4-Dicarboxylic Anhydrides

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Abstract: Several cyclic 1,2- and 1,4-dicarboxylic anhydrides were prepared. Their photochemistry was examined and spectroscopic changes in fluorescence as well as absorption were monitored. Both types of anhydrides underwent efficient direct, but not sensitized, photofragmentation, generating carbon monoxide, carbon dioxide, and new unsaturation. These photoreactions proceeded without discernible differences in mechanism. Extended Hückel molecular orbital calculations were carried out in an attempt to trace how anhydride orbitals may evolve into product orbitals with or without crossing of filled and empty orbitals. Although these calculations suggested the possibility that product molecules from 1,4-cyclic anhydrides might emerge from the reaction coordinate in an excited singlet state, detailed dynamic photoluminescence measurements conducted during the course of photolysis of 9,10-diphenyl-1,4-dihydroanthracene-1,4-dicarboxylic anhydride provided no support. These measurements showed that not more than 1 in 10,000 of the 9,10-diphenylanthracene product molecules emerge from the reaction coordinate in an excited singlet state.

The fluorescence of a product can be a useful characteristic for probing the potential energy surface of photochemical reactions since prompt product fluorescence resulting from reactant absorption indicates an adiabatic excited singlet state transformation.¹ The photogeneration of fluorescent products also has imaging applications.² Since *p*-terphenyl is an efficient fluorescer³ its reported^{4–6} photogeneration together with carbon monoxide and carbon dioxide in high yield from 1,4-diphenyl-1,3-cyclohexadiene-5,6-dicarboxylic anhydride led us to further investigations of anhydride photolyses. We have previously described



(1) (a) T. Forster, *Pure Appl. Chem.*, **24**, 443 (1970); (b) J. Menter and T. Forster, *Photochem. Photobiol.*, **15**, 289 (1972).

(2) A. Zweig, Symposium III, Unconventional Photographic Systems, Oct 1971, SPSE Abstracts, p 79.

(3) R. C. Sangster and J. W. Irvine, Jr., *J. Chem. Phys.*, **24**, 607 (1956).

(4) P. Courtot and R. Rumin, *Tetrahedron Lett.*, 1091 (1968).

(5) R. Kitzing and H. Prinzbach, *Helv. Chim. Acta*, **53**, 158 (1970).

(6) H. Prinzbach, R. Kitzing, E. Druckrey, and H. Achenbach, *Tetrahedron Lett.*, 4265 (1966).

related photochemical studies with aza⁷ and diaza⁸ succinic anhydrides. Reported here are the results of studies on the photofragmentation of several dihydroanthracene anhydrides and 2,3-diphenylsuccinic anhydride.

Dihydroanthracene Dicarboxylic Anhydrides. Although several 9,10-dihydroanthracene-9,10-dicarboxylic anhydrides (**3**) are known,^{9,10} no photochemical studies have been reported for these or other anhydrides of 1,4-dicarboxylic acids. Their investigation attracted our attention because of the well-characterized excited-state properties, including generally high quantum yields of fluorescence of the anticipated anthracene photoproducts. In addition, comparisons with investigations on anhydrides of 1,2-dicarboxylic acids could provide mechanistic information on the nature of the fragmentation processes.

Anhydrides **3a** and **3b** were prepared from the corresponding anthracene by slight modification of literature procedures⁹ (Chart I). Difficulties were encountered, however, in the cyclization of the *cis* diacid

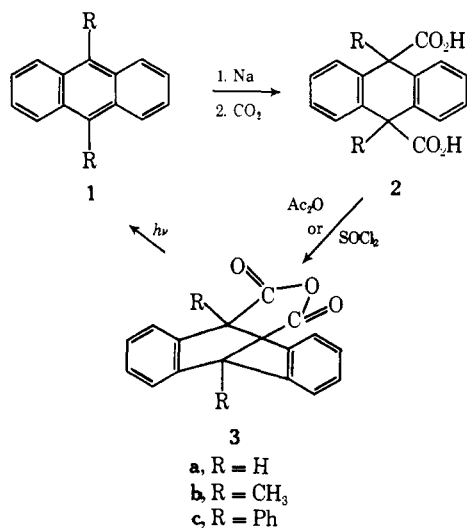
(7) W. A. Henderson, Jr., and A. Zweig, *Tetrahedron*, **27**, 5307 (1971).

(8) W. A. Henderson, Jr., and A. Zweig, *J. Chem. Soc. D*, 169 (1972).

(9) A. H. Beckett, R. G. Lingard, and B. A. Mulley, *J. Chem. Soc.*, 3328 (1953).

(10) M. M. Rauhut, D. Sheehan, R. A. Clarke, and A. M. Semsal, *Photochem. Photobiol.*, **4**, 1097 (1965).

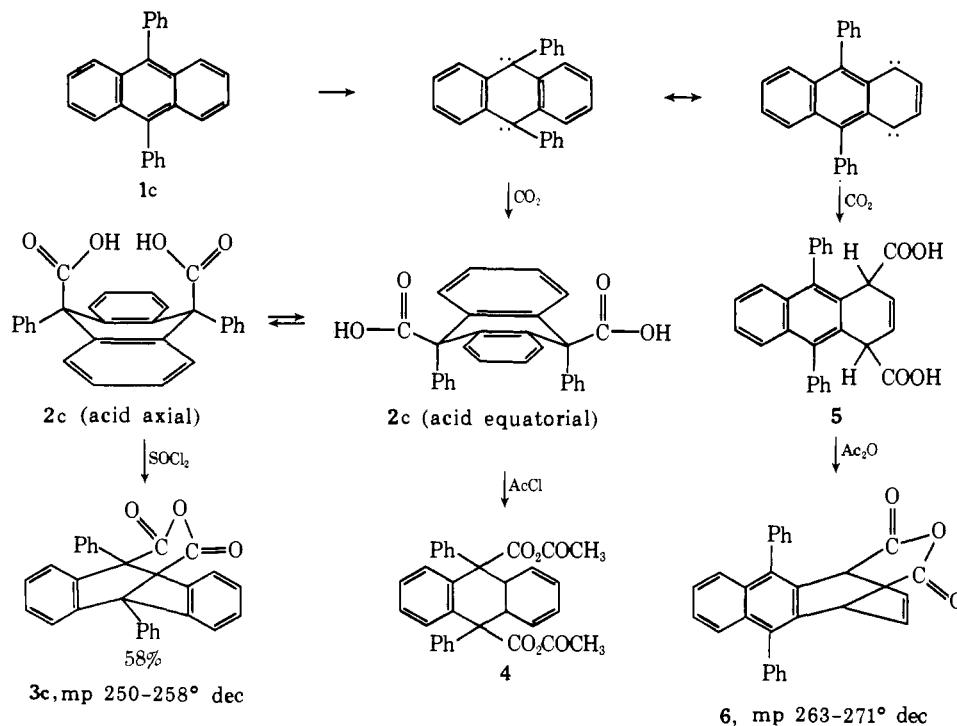
Chart I



2c.¹¹ Although some anhydride was formed in reactions carried out according to the published procedure,¹⁰ our attempts to isolate pure **3c** were unproductive; thus more efficient methods for conversion of **2c** to **3c** were sought.

Only mixtures of intermolecular anhydrides were obtained from reaction of **2c** with either acetic anhydride or dicyclohexylcarbodiimide, while acetyl chloride produced only the bisacetic anhydride **4**. The reluctance of **2c** to cyclize appears to derive from a preference for the conformation in which the bulky phenyl groups assume the less hindered pseudoaxial positions^{12,13} (Chart II), whereas ring closure requires the

Chart II



conformation with pseudoaxial carboxyl groups. The anhydride **3c** was eventually prepared in good yield by

(11) W. Schlenk, E. Bergmann, *et al.*, *Justus Liebigs Ann. Chem.*, **463**, 98 (1928).

(12) A. H. Beckett and B. A. Mulley, *J. Chem. Soc.*, 4159 (1955).

(13) P. Courtot, P. Derible, and L. H. Danh, *Bull. Soc. Chim. Fr.*, 2602 (1964).

simply refluxing **2c** in excess thionyl chloride. The reaction thus appears to proceed through an intermediate which undergoes conformational reequilibration with resultant cyclization in preference to bis-acid chloride formation.

Purification of **2c** by trituration with methylene chloride gave a noncrystalline acidic residue. Treatment of this crude mixture with acetic anhydride afforded an isomer of **3c**. This product was identified as 9,10-diphenyl-1,4-dihydroanthracene-1,4-dicarboxylic anhydride (**6**) by its uv spectrum (Table I), consistent with

Table I. Absorption Maxima and Photofragmentation Quantum Yields of Dihydroanthracene Dicarboxylic Anhydrides

Compd	$\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$, nm (ϵ)	Φ anthracene product 254 nm
3a	245 (3180), 250 (2820), 262 (1270), 268 (1000)	0.42
3b	245 (3200), 250 (2800), 267 (1000), 273 (500)	0.67
3c	242 (7800), 271 (2470), 279 (2000)	0.46
6	241 (68,000), 290 (19,200), 300 (13,600), 337 (3200)	0.65 ^a

^a Same value measured at 313 nm.

the presence of a 1,4-diphenylanthracene chromophore,¹⁴ and by its mass spectrum which showed a parent (M) peak as well as a strong M - C₂O₃ peak, but no M - CO or M - CO₂ peak. The mass spectrum indicated a lesser thermal stability for **3c** which decom-

posed rapidly in the spectrometer inlet (115-170°) so that M - C₂O₃ but no parent peak was obtained. The isolation of **6** requires the formation of some 1,4-dihydro-9,10-diphenylanthracene-1,4-dicarboxylic acid (**5**)

(14) A. Zweig and J. B. Gallivan, *J. Amer. Chem. Soc.*, **91**, 260 (1969).

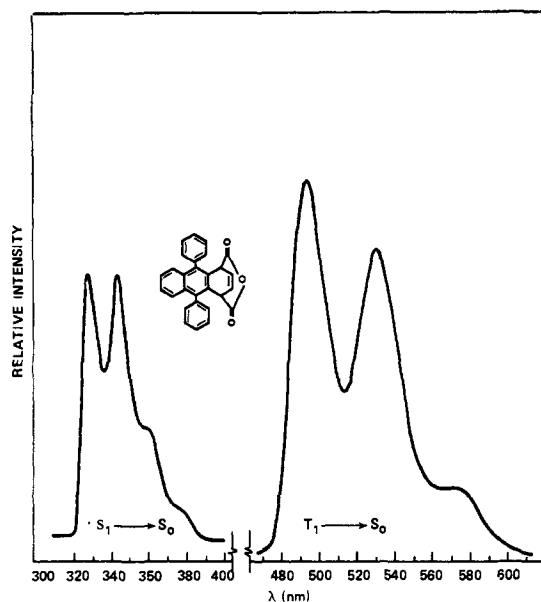


Figure 1. Emission spectra of 1,4-dihydro-9,10-diphenylanthracene-1,4-dicarboxylic anhydride 10^{-4} M in 3-methylpentane at 77°K.

in the carbonation step, which in turn implies reaction of the dianion at the 1,4 positions.

A small amount of product derived from reaction at the 1,4 positions had been reported in the alkylation of the dianion of 9,10-diphenylanthracene with benzyl chloride.¹⁵

As expected, the anhydrides 3a-c exhibited typical benzenoid absorption and no fluorescence, while 6 showed besides its characteristic naphthalenic absorption (Table I), a very weak naphthalenic fluorescence in methylene chloride solution. Both the fluorescence and phosphorescence of 6 observed at 77°K in 3-methylpentane solution are shown in Figure 1. The excitation spectra of both emissions compared favorably with the absorption spectrum of 6. The maxima of the 0-0 bands of absorption, fluorescence, and phosphorescence are respectively 337, 338, and 497 nm, as compared to 320, 324, and 480 nm, respectively, for naphthalene. The greatly reduced fluorescence lifetime (estimated at <20 nsec from L_0/L values) as compared to the 97 nsec lifetime of naphthalene is consistent with the reduced symmetry which would enhance the rate of the radiative process and the alternative pathways (notably the photofragmentation reaction) which serve to depopulate the excited state. The phosphorescence lifetime (τ_m) of 2.8 sec in 3-methylpentane at 77°K is actually slightly longer than the ~ 2.5 sec τ_m of naphthalene under the same conditions. One interpretation consistent with this observation is that the number of C-H bonds on the naphthalene moiety has been reduced from eight in naphthalene itself to four in 6, reducing the pathways for radiationless dissipation of the excitation energy.

Exposure of dilute (10^{-3} - 10^{-4} M in methylene chloride) solutions of all four of these anhydrides to broad band (240-400 nm) ultraviolet radiation resulted in rapid photochemical cleavage to give the corresponding anthracene products. The latter were initially char-

(15) A. L. J. Beckwith, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 171 (1958).

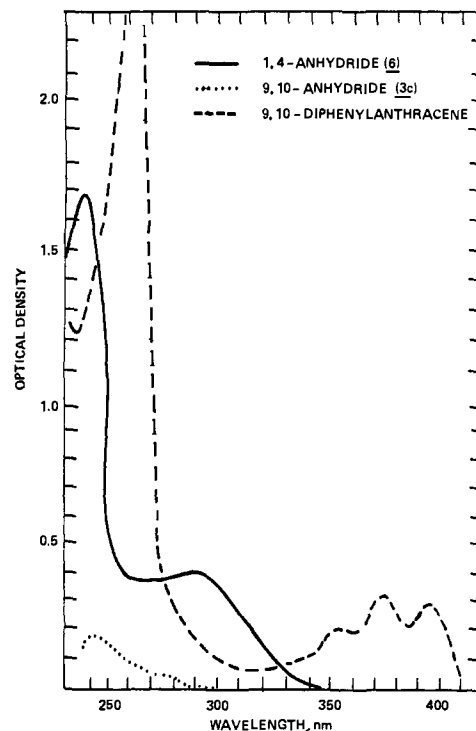


Figure 2. Absorption spectra in methylene chloride.

acterized by uv spectral changes and the appearance of strong blue fluorescence which could be monitored as the photolyses proceeded. In preparative scale photolyses, 1c was isolated in 83% yield from 6 and in 16% yield from 3c. The difference in isolated yields appeared to be primarily a result of differences in absorption spectra. As illustrated in Figure 2, the photo-generated 1c absorbs more strongly than 3c over the spectra range covered, but in the 300-340-nm range it does not absorb more strongly than 6. Thus an internal filtering effect acts to prevent preparative conversion of 3c to 1c in high yields. Spectroscopically determined quantum yields of formation of the respective anthracenes at low conversions were quite high (Table I) and in the case of 6 were essentially the same for 254- and 313-nm excitation.

The photolysis of 3c and 6 could not be effected by high energy triplet sensitizers such as acetone or acetophenone or singlet sensitizers such as benzene. The effect of oxygen on the efficiency of these phototransformations was slight and for 6 this was consistent with the very small oxygen effect on its fluorescence intensity. The ratio of fluorescence intensities for degassed and aerated solutions (L_0/L) of 6 was 1.18:1 in methylene chloride, which is consistent with a lifetime (τ_m) of $<20 \times 10^{-9}$ sec.¹⁶ A comparison of emission intensity with that of 1-phenylnaphthalene ($\phi_F = 0.3$) at matching absorptions indicated a ϕ_F of <0.04 for 6 at 10^{-4} M in methylene chloride. By spectrofluorometrically following the growth in fluorescence intensity due to 1c produced by irradiating 6 at different wavelengths, it could be established that the photodecomposition of the latter was not measurably wavelength dependent through its absorption spectrum nor temperature dependent in the 77-300°K range.

2,3-Diphenylsuccinic Anhydride. The report⁵ that

(16) I. B. Berman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York, N. Y., 1971, p 59.

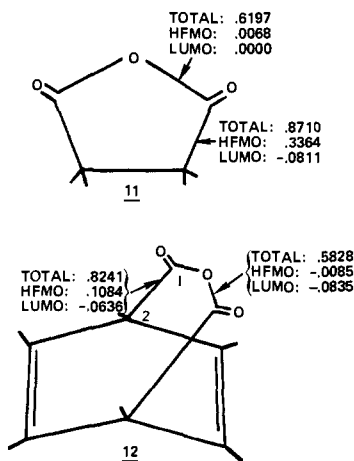
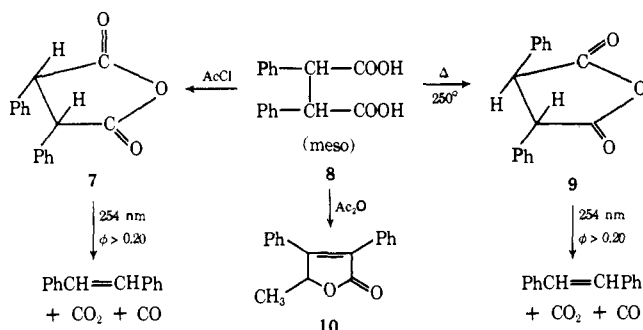


Figure 3. Overlap populations.

2,3-diphenylsuccinic anhydride (stereoisomer not specified) did not undergo the photoelimination course followed by other 1,2-dicarboxylic anhydrides appeared to us to be due to a mismatch of absorption spectrum (benzenoid) and light source (medium-pressure mercury arc). An authentic sample of *cis*-2,3-diphenylsuccinic anhydride (**7**) was prepared by treatment of *meso*-2,3-diphenylsuccinic acid (**8**) with acetyl chloride, while the thermodynamically more stable *trans* isomer (**9**) was prepared by pyrolysis (250°) of **8**. Reaction of **8** with acetic anhydride gave a mixture from which an 11% yield of 3,4-diphenyl-5-methyl-2(5*H*)-furanone (**10**), a new compound, was isolated.



Photolysis of 10⁻³ M degassed methylene chloride solutions of both isomeric 2,3-diphenylsuccinic anhydrides **7** and **9** with 254-nm radiation from a low-pressure Hg lamp gave mixed *cis* and *trans* stilbenes with quantum yields that were established as greater than 0.20. Because the stilbene photoproducts absorb more strongly than their anhydride precursor and because of their efficient photolytic interconversion and spectral indication of side products, a more accurate assessment was not made. The photodecomposition of these anhydrides could not be sensitized by benzene or acetophenone. In the presence of air, a major product of the photolysis was phenanthrene. Although the isomer distribution of the primary photolysis products was not established in these cases, the related diphenyldiazasuccinic anhydride had been shown to photoeliminate stereospecifically to give an azobenzene photoproduct which is initially 88% *cis*.⁸

Mechanistic Analysis and Discussion

Extended Hückel molecular orbital calculations¹⁷

(17) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

were made on succinic anhydride (**11**) and 1,4-cyclohexadiene-3,6-dicarboxylic anhydride (**12**) as representative 1,2- and 1,4-cyclic dicarboxylic anhydrides. The molecular orbital parameters for carbon and hydrogen atoms were those suggested by Hoffmann¹⁷ while for oxygen atoms, values of -33.8 eV (2s) and -17.6 eV (2p) were chosen for the Coulomb integrals from a consideration of valence state ionization potentials.^{18,19} The structures of the model molecules were uniquely defined for the purposes of the calculations by the standard bond lengths suggested by Pople and Gordon.²⁰

Although calculations such as these are quantitatively unreliable, they have yielded qualitative features of other molecular problems.²¹ For an indication of what the driving force for these anhydride photofragmentations may be, we examined the coefficients of their highest filled (HFMO) and lowest unfilled (LUMO) molecular orbitals. As shown in Figure 3 there is a large contribution to the overlap population of the critical carbon-carbon (the bonds that break in the fragmentation process) bond orders in the HFMO's of both types of anhydrides and much smaller contributions to the overlap population of the critical carbon-oxygen bond orders. The contributions to these carbon-carbon bond orders in both types of cyclic anhydrides are negative (antibonding) in their LUMO's. A difference is noted, however, in the LUMO overlap populations of the critical carbon-oxygen bonds of the two anhydrides. Those of the 1,4-anhydride are negative (antibonding) while those for the 1,2-anhydride are zero (nonbonding). While any quantitative interpretation of this difference is disclaimed, it suggests sources for potential differences in fragmentation pathways for 1,2- and 1,4-cyclic dicarboxylic anhydrides. In view of the observed reaction products and the results of these MO calculations which suggest a concerted cleavage of the carbon-carbon bonds under consideration, additional MO calculations were carried out on molecular structures simulating decomposition along a possible reaction coordinate. Since calculation of standard heats of reaction for fragmentation of both 1,2- and 1,4-cyclic dicarboxylic anhydrides into carbon monoxide, carbon dioxide, and unsaturated or aromatic residues indicates that these processes are thermodynamically favorable in both ground and excited states,²² the potential energy barriers along the respective reaction coordinates must govern the conditions of their occurrence.

To examine the orbital correlation along a reaction pathway suggested by the MO calculations, the indicated carbon-carbon bonds of the anhydrides shown in Figures 4 and 5 were stretched from their normal 1.52 Å lengths by three increments of 0.5 Å. The lowest 19 of the 32 molecular orbitals of succinic anhydride (**11**) are filled in the neutral ground-state molecule. The calculated energies of this molecule's four highest filled and five lowest vacant orbitals are shown at the left of Figure 4. Similarly, the lowest 28 of the 50

(18) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

(19) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

(20) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(21) R. Hoffmann, S. Swaminathan, B. B. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(22) Δ*H* = -7.3 and -1.2 kcal/mol at room temperature for fragmentation of **3c** and **9**, respectively.

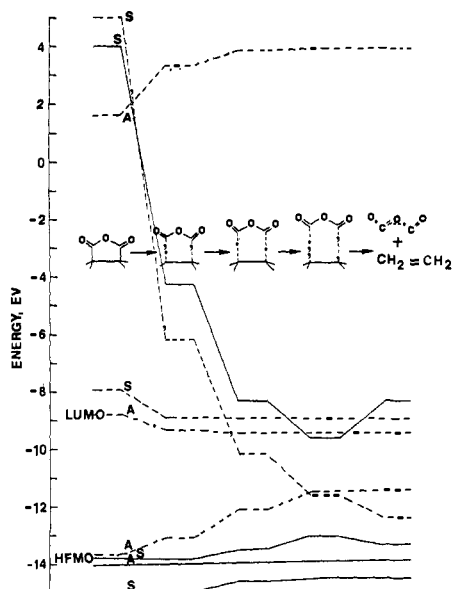


Figure 4. Correlation diagram of fragmentation of succinic anhydride.

molecular orbitals of the cyclohexadiene dicarboxylic anhydride (**12**) are filled in its neutral ground state and the energies of its six highest filled and six lowest empty orbitals are shown at the left of Figure 5.

By tracing the symmetry and distribution of the coefficients of the wave functions as the molecules were altered, the sources of the orbitals of the primary products (hydrocarbon diradical and C_2O_3 moiety) of this process were determined. The orbitals of the primary hydrocarbon diradicals were then traced as they correlated with ethylene and benzene, respectively (solid lines in Figures 4 and 5). In this particular pathway, the only orbital crossing occurred (Figure 4) as a result of the orbital tracing of the generation of the C_2O_3 moiety as it emerged from the reaction coordinate from the 1,2-anhydride and *not* as it emerged from the 1,4-anhydride. These results, though suggestive, must be regarded cautiously since different pathways can produce different orbital correlations between these starting materials and products, as further calculations show.

Another related, unanticipated aspect of the orbital correlations shown in Figures 4 and 5 is the nondegeneracy of the HFMO and LUMO of the developing W-shaped C_2O_3 moiety, which by valence bond conventions would be described as a diradical with unpaired electrons localized on the carbon atoms. The only conventional nonionic valence bond structure that can be used to describe this species is that of oxiranedione (**13**).²³ An examination of the wave function of the W-shaped C_2O_3 moiety showed a relatively large (0.08) C-C ground-state overlap population considering the considerably larger than bonding distance (2.22 Å) involved. A calculation on the oxiranedione structure with normal bond lengths and angles ($O-C=O \angle = 150^\circ$), as shown in Chart III, indicates that this structure is 2.97 eV more stable than the W-shaped C_2O_3 moiety and that the orbitals of the two species smoothly correlate with no crossing of filled and empty orbitals. Crossings which occur in orbital correlations between

(23) A search of Beilstein and *Chem. Abstr.* (through Vol. 75) revealed only two references to C_2O_3 , both erroneous. One reference was to a chromium oxide and the other to carbon suboxide.

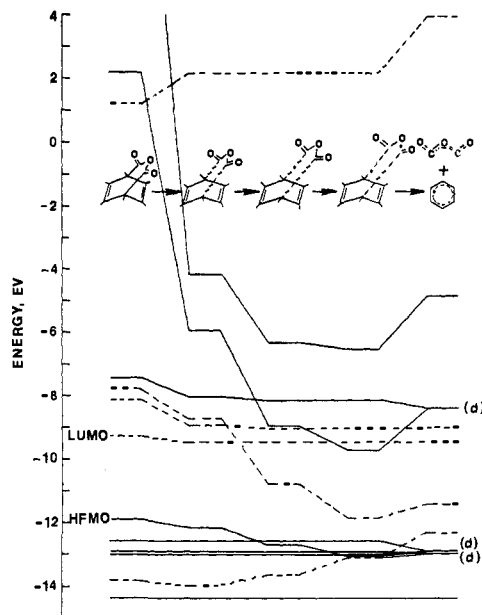


Figure 5. Correlation diagram of fragmentation of 1,4-cyclohexadiene-3,6-dicarboxylic anhydride.

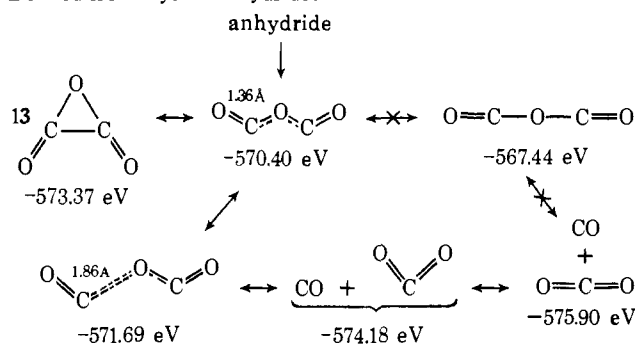
species described in Chart III are indicated by crosses along the connecting paths.

To further assess the likelihood of oxiranedione (**13**) forming from the W-shaped C_2O_3 moiety and being an intermediate in the generation of CO and CO_2 from cyclic anhydride, we compared the possibility of its formation to the two other transformations shown in Chart III. The first of these, indicated to the right of the W-shaped moiety, involves straightening out to a linear C_2O_3 . Calculations show this product to be less stable than the W structure and to be a conventional diradical with degenerate HFMO and LUMO. A tracing of the orbitals between the W shaped and linear C_2O_3 species shows that the HFMO of the former correlates with a symmetric σ orbital of an upper unfilled degenerate orbital pair of the latter. Stretching a C-O bond of the linear C_2O_3 species to generate CO and linear CO_2 , while calculated to be a thermodynamically favorable process, also produces a crossing, this time between a very high unfilled nondegenerate MO of the linear C_2O_3 and the HFMO of the CO product. The calculations thus are taken as an indication that this overall pathway is not one of the more likely ones for anhydride fragmentation to follow.

The alternate pathway indicated in Chart III for fragmentation of the W-shaped C_2O_3 moiety is through stretching of a C-O bond to yield CO and bent CO_2 . Tracing the orbitals along this path produces a smooth correlation with no crossing and the product bent CO_2 orbitals also correlated with those of a linear²⁴ CO_2 structure with no crossing. These changes occur with a monotonically decreasing (greater stability) total energy to the final products calculated to be 5.53 eV lower in energy than the W-shaped C_2O_3 moiety and 2.53 eV lower than the oxiranedione (**13**). This pathway to final products from cyclic anhydrides thus offers an alternative to formation of **13** but does not preclude the

(24) The ground state of CO_2 is linear. Cf. G. Herzberg, "Molecular Spectra and Molecular Structure III, Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967, p 598.

Chart III. Energies and Orbital Crossings of Carbon Oxides
Derived from Cyclic Anhydrides



existence of the latter. The overall fragmentation of **12** with breaking first of C–C and then a C–O bond is thus favored in its first excited state by the appropriate changes in overlap population (Figure 3) and exhibits continuously decreasing energy on orbital transformation from starting material to final products. If this were the operable mechanism,²⁵ the transformation could adiabatically produce excited-state products.²⁶

Requirements for Characterization of Adiabatic Excited Singlet State Phototransformations. Since the short wavelength ultraviolet photons absorbed by the 1,2- and 1,4-cyclic dicarboxylic anhydrides promote these species to excited singlet states and since their fragmentation cannot be induced by sensitization or retarded by quenching, it appears that the ensuing decompositions proceed from the singlet manifold and not through intervening triplet states. These considerations together with the preceding molecular orbital correlations prompted efforts to detect the excited singlet state of a fragmentation product of a 1,4-cyclic dicarboxylic anhydride by its fluorescent emission as it emerges from the reaction coordinate. There are numerous examples in the literature where products have been experimentally shown to be photolytically produced in fluorescent states. In most of these cases, however, the excited products are either protolysis products²⁷ or excimers²⁸ or exciplexes²⁹ which do not have a stable ground state under the emitting conditions. Indeed, the experimental evidence for these examples being produced in the fluorescent state is most convincing because the photoproduct has no stable ground state under the photolysis conditions and therefore the emission cannot be due to the trivial two quantum process of ground-state product formation and subsequent excitation. When a stable fluorescent product is formed, the experimental problem arises of how to differentiate between the direct single quantum conversion to an excited product and the two quantum conversion to the same excited product.

The recent description^{30,31} of a method of detection of adiabatically photogenerated triplet products through flash photolysis and characterization by triplet–triplet absorption is not presently applicable to detection of

(25) There are many other fragmentation pathways for such anhydrides which were not examined and which could be more favorable; for example, cf. J. Michl, *Mol. Photochem.*, **4**, 287 (1972).

(26) R. C. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971).

(27) A. Weller, *Progr. React. Kinet.*, **1**, 187 (1961).

(28) T. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).

(29) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(30) E. W. Forster and K. H. Gröllmann, *Chem. Phys. Lett.*, **14**, 536 (1972).

(31) E. W. Forster and E. Fisher, *J. Chem. Soc., Chem. Commun.*, 131 (1972).

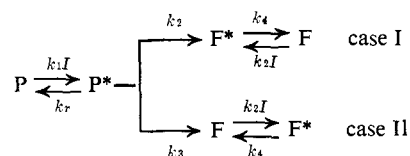
these short-lived singlets. To avoid buildup of stable fluorescent products when irradiating with conventional light sources, Forster and Menter utilized a flow system.¹ The spectroscopic changes that occur during the photofragmentation of anhydride **6**, shown in Figure 2, however, provide advantageous conditions for accurately detecting the occurrence of its adiabatic singlet state phototransformation without flow systems and with conventional light sources and fluorometric equipment. These conditions include a high ($\phi = 0.65$) photoconversion efficiency, high product (**1c**) solution fluorescence quantum efficiency ($\phi = 0.90$), well-separated from the weak precursor fluorescence, and a precursor (**6**) extinction coefficient 6–10 times as large as that of the product (**1c**) at wavelengths near 313 nm corresponding to readily isolated mercury arc emission lines (Table II).

Table II. Molar Absorptivities of Precursor **6** and Photoproduct **1c**

λ , nm	$\epsilon_6 \times 10^4$	$\epsilon_{3c} \times 10^4$	ϵ_6/ϵ_{3c}
296.7	1.14	0.15	7.6
302.1	1.06	0.10	10.6
312.5	0.54	0.08	6.8
313.1	0.51	0.08	6.4
334.1	0.02	0.26	0.1

The kinetic schemes to be considered in differentiating between single and two photon conversion of a precursor (P) such as anhydride **6** to an excited fluorescent product (F*) such as 9,10-diphenylanthracene are indicated in Chart IV. Single arrows in the chart denote irreversible steps.

Chart IV



In case I the fluorescer is generated along the reaction coordinate in an excited singlet state, F*, and emerges as an independent entity identical in all respects with F* generated by any other means. In case II the fluorescer is generated along the reaction coordinate in a nonluminescent electronic state of lower energy than the lowest excited singlet state by the time it emerges from the reaction path as an independent entity. Insofar as observable kinetics are concerned, we represent this state as the ground state F. Letting these symbols also represent concentrations and assuming that I , the intensity of exciting radiation, is restricted to a narrow range (corresponding to wavelengths around 300 nm) and that variation in the molar absorptivity (ϵ) for P in that range is small relative to its absolute value, we can write

$$\frac{dP}{dt} = -\phi_P \frac{2303\epsilon(\nu)}{N h \nu} P(x, y, z, t) I(x, y, z, t) \quad (1)$$

for the rate of disappearance of P in the small volume element $dx dy dz$, where ϕ_P is the probability that P* dissociates into product F, N is Avogadro's number, and h is Planck's constant.

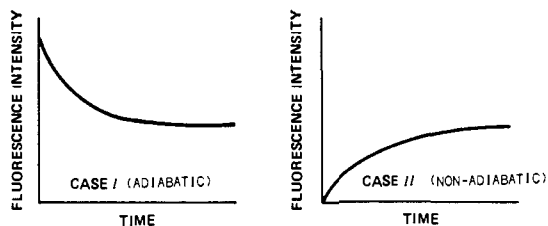


Figure 6. Changes in fluorescence emission intensity with time under adiabatic and nonadiabatic conditions.

If the variation of I in the liquid is small compared with its magnitude,³² the variation in both P and I with x , y , and z can be neglected. Thus

$$\frac{dP}{dt} = -\phi_P K_1 P(t) I(t) \quad (2)$$

where $K_1 = 2303\epsilon/Nh\nu$. Since the quantum yield of photofragmentation is high, k_3 and/or $k_2 > k_1 I(t)$, so P^* always is small. Using P_0 for initial concentration, $I(t < 0) = 0$, and $I = I(t)$ for $t \geq 0$, the solution for (2) takes the form

$$P(t) = P_0 \exp\left\{-\phi_P K_1 \int_0^t I(t) dt\right\} \quad (3)$$

For the experimental conditions under consideration, excited-state species concentrations will be small relative to ground-state concentrations, so, at any given time t , $P + F \cong P_0$. Also under such conditions P^* and F^* are in locally steady states, $dP^*/dt \cong 0 \cong dF^*/dt$.

Case I. For a system where adiabatic photogeneration of excited fluorescer occurs (case I in Chart IV), $dP^*/dt = -dP/dt - k_2 P^* \cong 0$ and $dF^*/dt = k_2 P^* + K_2 IF - k_4 F^* \cong 0$. Defining fluorescence intensity, I_t , as $\phi_t k_4 F^*$, where ϕ_t is the fluorescence quantum efficiency, one arrives at the expression

$$\frac{dI_t}{dt} = \phi_t I_0 \frac{dP}{dt} [\phi_P K_1 - K_2] \quad (4)$$

for constant excitation intensity $I(t) = I_0$, and where $K_2 = (\text{molar absorptivity of } F) \times 2303/Nh\nu$. Since $\phi_P K_1 \gg K_2$ and $dP/dt \leq 0$, dI_t/dt is negative in case I (decreasing) at $t = 0$ and approaches zero in the limit as I_t approaches a constant value, as illustrated in Figure 6.

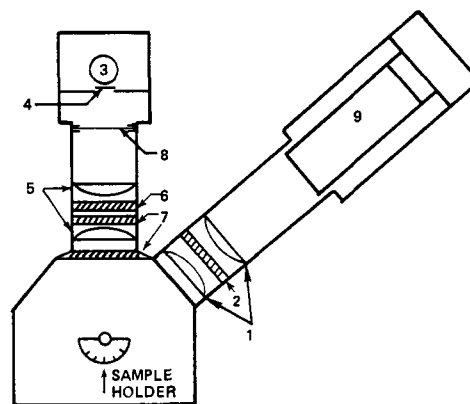
Case II. When the product is generated in a state which is nonemitting and which cannot convert to an emitting state without additional absorption of radiation, as in case II of Chart IV, $dP^*/dt = -dP/dt - k_3 P^* \cong 0 \cong dF/dt - k_3 P^* \cong -K_2 IF + k_4 F^*$. Utilizing a constant excitation intensity $I(t) = I_0$, one arrives at the expression

$$I_t(t) = \phi_t K_2 P_0 I_0 \{1 - \exp[-\phi_P K_1 I_0 t]\} \quad (5)$$

Taking the derivative of (5) with respect to time, one obtains

$$\frac{dI_t}{dt} = \phi_t \phi_P K_1 K_2 P_0 I_0^2 \exp[-\phi_P K_1 I_0 t] \quad (6)$$

(32) For example, when the maximum concentration of P is $10^{-4} M$ and with its molar absorptivity at 313 nm being 0.53×10^4 (Table II), the variation in I (313 nm) will be 12% of the mean value in a 2 mm thick sample.



1. ACHROMATIC LENSES, 36 mm DIA., 100 mm F.L.
2. BLUE TRANSMITTING FILTER
3. MEDIUM PRESSURE MERCURY ARC
4. GROUND QUARTZ DIFFUSER
5. QUARTZ LENSES, 50 mm DIA., 100 mm F. L.
6. QUARTZ FILTER CELL, LIQUID PATHLENGTH 10 mm
7. SCHOTT UG11 FILTERS, THICKNESS 3 mm EACH
8. MANUALLY OPERATED SHUTTER
9. RCA NO. 6217 PHOTOMULTIPLIER

Figure 7. Optical system of photometer.

As illustrated in Figure 6, as a consequence of (6) for such a case II situation, I_t is zero at zero time and will increase initially with the square of the incident excitation intensity, and dI_t/dt will again approach zero at long times.

For fitting data we can write (5) in the dimensionless form

$$\frac{I_m}{I_m - I_t} = \exp \gamma t \quad (7)$$

where $I_m = \phi_t K_2 P_0 I_0$ and $\gamma = \phi_P K_1 I_0$.

Dynamic Photoluminescence Measurements. Employing the equipment and optical configuration shown in Figure 7, the development of a photoluminescence signal in the 420–490-nm region on exposure of a $10^{-4} M$ solution of 6 in methylene chloride to 313-nm radiation was followed continuously. The solution was contained in a 1.5–2.0 mm i.d. capillary closed at one end and positioned³³ and filled to allow the entire volume to be irradiated simultaneously so that analysis of the results by eq 2 *et. seq.* would be possible. Utilizing an oscilloscope for the first 40 sec of irradiation and a strip chart recorder for the entire study, the luminescence signal was recorded during and subsequent to opening of the shutter at position 8 in Figure 7, continuing until an essentially unchanging value was obtained.³⁴ The chart record of the luminescence signal, after the background signal at zero time³⁵ was subtracted, as shown in Figure 8, was indistinguishable from that predicted from the case II (nonadiabatic) kinetics shown in Figure 6. That the results indeed closely

(33) At an angle such that the normal to its frontside bisected the acute angle between excitation and detection sections.

(34) Continued irradiation after the intensity maximum was reached produced a slight decrease in signal from the undegassed solution.

(35) This base line was identical with that of the pure methylene chloride solvent within the accuracy of repeated experiments in the same tube.

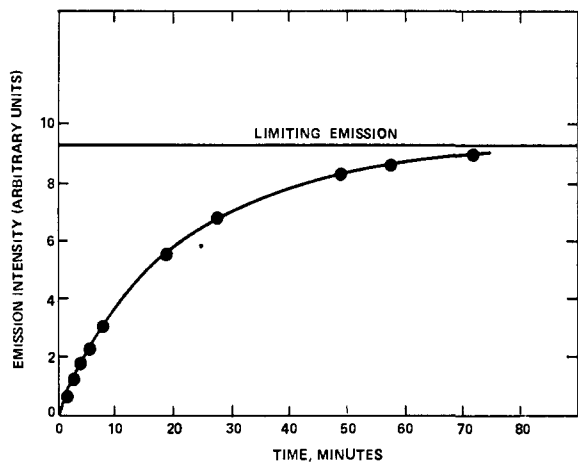


Figure 8. Emission (420–490 nm) development vs. exposure time (313 nm) of $10^{-4} M$ anhydride 6 in methylene chloride.

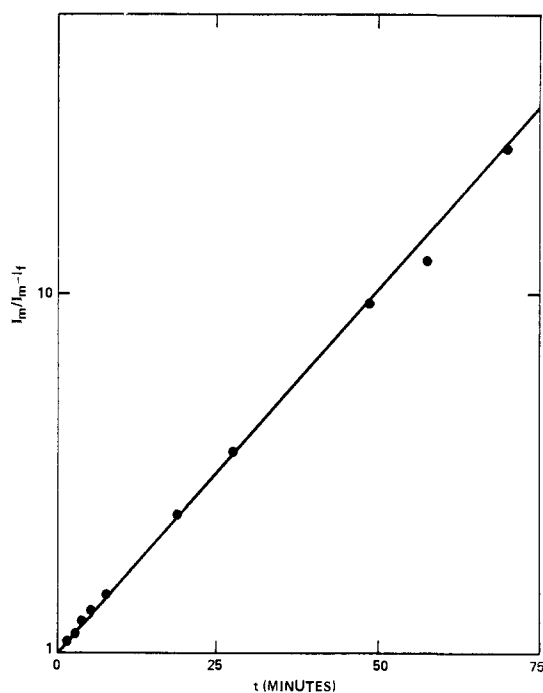


Figure 9. Plot of $I_m/I_m - I_t$ vs. time.

match those calculated for a nonadiabatic phototransformation can be seen from the close correspondence to a straight line obtained from plotting the data points as $\log(I_m/I_m - I_t)$ vs. time, the relationship predicted by eq 7,^{36–38} as shown in Figure 9. The initial slope of the chart-recorded data gave the same slope as the oscilloscope data points within a few per cent.

Quantification of the observation that in precursor solutions the emission base line in the product fluorescence region appeared indistinguishable from that of the solvent³⁵ produced a more sensitive test for an

(36) The maximum fluorescence signal generated during the run was used for I_m . The point at 70 min in Figure 9 corresponds to $0.96I_m$.

(37) When an interference filter (peak transmission at 318 nm) replacing K_2CrO_4 liquid filter produced a fivefold reduction in excitation intensity, the initial slope of the corrected fluorescence growth was reduced about 30-fold, roughly the square of the excitation ratio as predicted by eq 6.

(38) The results also indicate a lack of quenching by 6 of the emission from 1c at the concentrations employed. Since self-quenching of 1c is known to be negligible¹⁶ at these concentrations, no corrections for these factors are needed.

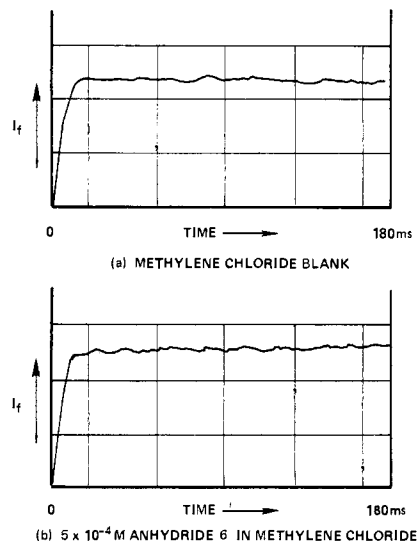


Figure 10. Sketches of oscilloscope traces of signal (1000 V on photomultiplier).

adiabatic excited singlet pathway in the subject phototransformation. A 1 cm \times 1 cm rectangular cuvette was placed so that the normal to its surface was parallel to the optical axis of the excitation source in the photometer shown in Figure 7. The luminescence signal produced during and subsequent to opening of the shutter at position 8 as a result of solutions contained within the cuvette was observed *via* the oscilloscope. The sweep was triggered by the signal and a record of the first 200 msec after opening of the shutter was thus obtained. By repeated filling and resetting the same cuvette positioned with the same surface presented to the exciting radiation in the photometer reproducibility of the initial luminescence signal from the methylene chloride solvent was found to be good. Stretches of oscilloscope traces for a solvent blank and for a $5 \times 10^{-4} M$ solution of anhydride 6, obtained under identical conditions, are shown in Figure 10. Estimates of initial signal were obtained by extending the linear portion of the rise time until it intersects with a linear back extrapolation of the horizontal portion.³⁹ A sequence of initial signal measurements made in this way for alternating fresh solvent blanks and portions of a stock $5 \times 10^{-4} M$ anhydride 6 solution is given in Table III.

Table III. Sequence^a of Initial Luminescence Signals^b

Methylene chloride (blank)	$5 \times 10^{-4} M$ anhydride 6c in methylene chloride
34.1	33.2
33.7	32.5
33.5	35.3
35.2	37.5

^a Indicated by arrows. ^b In arbitrary units.

The significant feature of this sequence, confirmed in other similar experimental sequences, is that in con-

(39) Analysis of temporal effects justifies this simple back extrapolation procedure.

secutive readings the difference is never greater than one unit. This is about the value of the instrumental jitter produced under use conditions. Thus within this limitation, the initial luminescence signal reaching the detector from the anhydride solution is indistinguishable from that of the solvent blank.

To provide a calibration for the emission from adiabatically produced singlet excited 9,10-diphenylanthracene (**1c**) which might be detected under these conditions, the luminescence signal from solutions of this fluorescent product was examined with the same optical configuration. Based on the molar absorptivities in Table II and the wavelength distribution of the radiation reaching the cuvette, $3.2 \times 10^{-3} M$ **1c** is equivalent in absorptivity to $5 \times 10^{-4} M$ anhydride **6**. In these circumstances the excitation events will have the same spatial geometry and frequency in the cuvette, and the emitted radiation will exhibit comparable detector response efficiency.⁴⁰ The emission intensity for this **1c** concentration in terms of units of oscilloscope deflection measured in Table III was determined to be 15,000 units.⁴¹ Since only 67% of the photons absorbed by anhydride **6** produce **1c** in any state, and taking one unit in Table III as representing the uncertainty in equivalence in signal from $10^{-4} M$ anhydride **6** solution and blank, it is concluded that not more than one 9,10-diphenylanthracene in 10,000 could be formed adiabatically in an excited singlet state under these conditions.⁴²

The electronic states of products as they emerge from photochemical reactions are generally not known. Recent results indicate that photochemical induction of reactions which are thermally chemiluminescent produce electronically excited products.⁴³ Anhydride decompositions indeed bear resemblance to chemiluminescence processes¹⁰ but neither this resemblance nor the indications provided by the extended Hückel calculations proved to be accurate guides. Caution is required in interpreting dissociative processes by extended Hückel theory.⁴⁴ The one-electron MO model is considerably suspect. Recent studies have shown that configuration indications can have far-reaching effects on $2 + 2$ cycloaddition when the addends have widely different polarities.⁴⁵

Experimental Section

Synthetic. 9,10-Dihydroanthracene-9,10-dicarboxylic Anhydride (3a). Anthracene in tetrahydrofuran was stirred with a dispersion of sodium in toluene, the resulting dianion was carbonated, and the acid fraction was treated with refluxing acetic anhydride in a slight modification of the literature procedure.⁹ The anhydride **3a** was

(40) At the concentrations involved neither **6** nor **1c** will produce an inner filter effect on primary detectable fluorescence. Since self-absorption of primary fluorescence from **1c** is negligible at these concentrations, secondary fluorescence cannot contribute to the measured signal.

(41) The signal for $3.2 \times 10^{-3} M$ **1c** was obtained from a curve of signal vs. concentration developed in the same experimental configuration, with a calibrated reduction in photomultiplier sensitivity at the higher concentrations to avoid nonlinearity. The curve was readily described over its 25-fold concentration range by a two-parameter equation derived from geometrical considerations.

(42) Since the fluorescence quantum yield of **1c** is nearly unity

(43) N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, **33**, 369 (1973).

(44) W. L. Bloemer and B. L. Bruner, *Chem. Phys. Lett.*, **17**, 452 (1972), reported the disconcerting extended Hückel prediction that benzene smoothly decomposes to three acetylenes. However, such MO errors are most pronounced in cases involving triple-bonded products: B. L. Bruner, private communication.

(45) N. E. Epiotis, *J. Amer. Chem. Soc.*, **95**, 1191 (1973).

obtained in 17% yield as colorless needles from benzene, mp 196–199° dec (lit.⁹ mp 194–195°).

9,10-Dihydro-9,10-dimethylantracene-9,10-dicarboxylic Anhydride (3b). A similar procedure afforded **3b**, mp 217–218° dec, as colorless crystals from methylene chloride-petroleum ether (lit. mp 215–216°;⁹ 220–221°⁴⁶).

cis-9,10-Dihydro-9,10-diphenylanthracene-9,10-dicarboxylic Acid (2c). A dispersion of 2.5 g of sodium in 75 ml of toluene was stirred overnight with a solution of 16.5 g of 9,10-diphenylanthracene in 300 ml of dry tetrahydrofuran. The acidic fraction afforded a gummy solid which was purified by trituration with methylene chloride to give 12.3 g (59%) of the *cis* diacid **2c**, mp 262–266° dec. Recrystallization of a small sample from acetic acid gave transparent crystals, mp 280° dec. Reported values¹¹ are 299, 277, and 282° dec.

9,10-Dihydro-9,10-diphenylanthracene-9,10-dicarboxylic Anhydride (3c). A mixture of 13.9 g of the diacid **2c** and 150 ml of thionyl chloride was refluxed for 4 hr and the resulting clear solution was distilled to dryness *in vacuo*. The solid residue was dissolved in the minimum amount of methylene chloride and then diluted with an equal volume of petroleum ether. The solution was concentrated on the steam bath until crystallization ensued and then set aside. From the first crop was obtained 6.05 g of pure anhydride, mp 250–258° dec. The second crop, 3.80 g, mp 205–245° dec, was recrystallized again from methylene chloride-petroleum ether to give another 1.70 g of anhydride, mp 245–257° dec, for a total yield of 7.75 g (58%). The reported¹⁰ melting point is 237°.

1,4-Dihydro-9,10-diphenylanthracene-1,4-dicarboxylic Anhydride (6). The methylene chloride solution remaining from the trituration of **2c** (above) was combined with a similar solution from another run which started with 9.9 g of 9,10-diphenylanthracene. The combined solutions were evaporated to a gum to which was added 25 ml of acetic anhydride. The solution was refluxed for 20 min and distilled to dryness *in vacuo*. The dark red residue was crystallized from methylene chloride-petroleum ether to give 0.80 g (2.5% yield based on 9,10-diphenylanthracene) of **6**, as pale orange crystals, mp 247–265° dec. Recrystallization from the same solvent mixture gave nearly colorless crystals, mp 263–271° dec.

Anal. Calcd for $C_{28}H_{18}O_4$: C, 83.56; H, 4.51; mol wt, 402. Found: C, 83.58; H, 4.77; *m/e* 402.

Preparative Photolysis of 9,10-Dihydro-9,10-diphenylanthracene-9,10-dicarboxylic Anhydride (3c). A solution of 100 mg of **3c** in 40 ml of methylene chloride in a Vycor flask was flushed with nitrogen, stoppered, and irradiated for 2 hr with 240–400-nm light from the B-H6 lamp. The pale orange solution was passed directly through a column of 10 g of grade 1 neutral alumina which was eluted with more methylene chloride. The eluate was evaporated and the residue was crystallized from ethanol to give 13 mg (16%) of 9,10-diphenylanthracene, mp 233–248°, identified by infrared and ultraviolet spectra.

Preparative Photolysis of 1,4-Dihydro-9,10-diphenylanthracene-1,4-dicarboxylic Anhydride (6). A solution of 50 mg of **6** in 40 ml of methylene chloride was irradiated for 1 hr under conditions described in the previous example. A similar work-up gave 34 mg (83%) of pure 9,10-diphenylanthracene, mp 248–249°.

9,10-Dihydro-9,10-diphenylanthracene-9,10-dicarboxylic Acid Bis-acetic Anhydride (4). A mixture of 1.0 g of the diacid **2c** in 10 ml of acetyl chloride was refluxed for 16 hr and evaporated to dryness *in vacuo*. The white solid was trituated with ether to afford 0.84 g (70%) of **4**, mp 168–170° dec. $\lambda_{max}^{n_{D_2O}}$ 5.52 and 5.77 μ .

Anal. Calcd for $C_{32}H_{24}O_6$: C, 76.18; H, 4.80. Found: C, 75.99; H, 4.79.

cis-2,3-Diphenylsuccinic Anhydride (7). A suspension of 2.00 g of *meso*-2,3-diphenylsuccinic acid in 20 ml of acetyl chloride was refluxed for 8 hr and then evaporated to dryness *in vacuo*. The residue was trituated with ether to give 1.70 g (91%) of the *cis* anhydride as colorless crystals: mp 169–172° (lit. mp 156°;⁴⁷ 160–170°⁴⁸) $\lambda_{max}^{CH_2Cl_2}$: 252 nm (ϵ 380), 258 (420), 264 (340), 268 (200).

trans-2,3-Diphenylsuccinic Anhydride (9). One gram of *meso*-2,3-diphenylsuccinic acid was heated in an oil bath at 240–250° for 1 hr. Crystallization of the resulting yellow oil from methylene chloride-petroleum ether afforded 0.36 g (39%) of pale yellow crystals, mp 114–116.5°. Recrystallization from ether-petroleum ether gave pale yellow prisms of *trans* anhydride: mp 115–117°

(46) A. H. Beckett and R. G. Lingard, *J. Chem. Soc.*, 588 (1961).

(47) E. V. Dehmlow, *Chem. Ber.*, **100**, 3260 (1967).

(48) R. Buchan and M. B. Watson, *J. Chem. Soc. C*, 2465 (1968).

(lit. mp 115–116,⁴⁹ 118°⁴⁷), $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 252 nm (ϵ 480) 258 (540), 264 (460), 268 (300).

Reaction of *meso*-2,3-Diphenylsuccinic Acid with Acetic Anhydride. A solution of 1.0 g of *meso*-2,3-diphenylsuccinic acid in 10 ml of acetic anhydride was refluxed for 3 hr and the excess solvent was removed by distillation at reduced pressure. The resulting oil, which could not be crystallized, was dissolved in 2:1 ether-petroleum ether and chromatographed over 20 g of grade 1 neutral alumina. The first fractions afforded a total of 100 mg (11%) of 3,4-diphenyl-5-methyl-2(5*H*)-furanone (10) as colorless crystals, mp 136–140°. Two recrystallizations from ethanol raised the melting point to 140–142°; $\lambda_{\text{max}}^{\text{max}}$ 5.76 and 6.11 μ ; $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 282 nm (ϵ 12,000).

Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2$: C, 81.58; H, 5.64; mol wt, 250. Found: C, 81.92; H, 5.65; m/e 250.

The nmr spectrum (CDCl_3) clearly showed the CH_3CHO group as a doublet (3 H) at τ 8.55 and a quartet (1 H) at τ 4.53.

Instrumental. The light source for the qualitative and preparative photochemical studies was a 1000-W General Electric B-H6 high-pressure mercury arc equipped with a Corning 9863 nickel oxide filter transmitting at 240–400 nm. Quantum yields were determined by the method of Hatchard and Parker⁵⁰ using a 12-W Hanovia low-pressure mercury lamp. The 254-nm line was isolated by the use of a chlorine filter.

Fluorescence and phosphorescence spectra were run on a Perkin-Elmer (Hitachi) MPF-2A fluorescence spectrophotometer. Fluorescence measurements were made on room temperature solutions in 1-cm² quartz cells. Phosphorescence measurements were made at 77°K in 2 mm i.d. quartz cells using the phosphorescence accessory of the spectrophotometer. Phosphorescence lifetimes were measured from polaroid prints of the oscilloscope display showing the decay of the phosphorescence signal as a function of time following extinction of the exciting light.

A single bottle of methylene chloride (Baker analyzed reagent) was the source of solvent for all solutions used for comparative dynamic photoluminescence measurements since solvent background luminescence variations were large relative to measured emission from 6. From the RCA No. 6217 photomultiplier (S10 photocathode) in Figure 7, the anode current was measured with a Keithly Model 414 Linear picoammeter, with the ammeter output connected simultaneously to a Tektronix Type 531A oscilloscope (Type 1A1 Plug-in preamplifier) and to a Bausch and Lomb V.O.M.-5 strip chart recorder. Thus rapid signal changes during short time intervals could be observed *via* the oscilloscope, and slower rates of change over longer time intervals could be followed by the chart recorder or the picoammeter meter.

A dark current compensating device could be switched into the input circuit when desired. In order to assure linearity in the photodetector signal, photomultiplier anode current was kept below 20 μA (usually below 10 μA).

The sample holder consisted of a thin (0.5 mm) brass plate, with a rectangular aperture (5 mm wide and 10 mm high) in the plate designated as "sample area." The long dimension of the aperture was perpendicular to the plane defined by the two optic axes in Figure 7 and the center of the aperture coincided with the point of the intersection of the two optic axes. This sample holder could be

rotated through 360° about an axis parallel to the long side of the aperture, and bisecting the short sides.

Lenses at (1) in the detection section shown in Figure 7 developed a 1:1 image of the vertical center line of the sample area onto the photomultiplier cathode. For most experiments the blue transmitting filter at (2) consisted of a combination of two Corning standard glass filters, Color Specification No. 3-73 and 5-58. For several experiments an interference filter (Baird-Atomic, Type B-2) having peak transmission of ~55% at 449 nm, and full bandwidth at half-intensity of 8.5 nm, was used at (2).

Since a relatively narrow wavelength range of radiation near 300 nm was desired for photoexcitation, medium-pressure mercury arcs were used at (3). Initial experiments utilized a General Electric H85A3/UV lamp with the long dimension of the lamp perpendicular to the plane of Figure 7. A ground silica window at (4) acted as a diffuser and a secondary source. The quartz lenses at (5) developed a 1:1 image of the diffuser onto the sample holder. The filter cell at (6) was filled with basic potassium chromate solution (0.2 g of K_2CrO_4 /l. of 0.05 *N* NaOH) replaced daily. Exciting radiation incident on the sample holder had the following wavelength distribution: 88% at 313 nm, 9% at 302 nm, 2% at 297 nm, and ~1% at 334 nm.

The H85A3/UV lamp was driven by a voltage stabilized 60-cycle ac source, and the temporal intensity profile thus consisted of 120 pulses/sec. While this fluctuating excitation presented no problem for slow luminescence changes, a small asymmetry between alternate pulses introduced jitter in measurements over short time intervals. Therefore, a General Electric S-4 sunlamp, operated in the dc mode, was used at (3) for measurement of luminescence signals from samples during initial periods of photoexcitation (and also for some long term periods). Spectral distribution of output from the GE S4 lamp impinging on the sample holder was essentially the same as for the H85 lamp.

Mounting arrangements for the S4 lamp made use of the diffuser plate at (4) inconvenient, and so it was removed. Thus lenses (5) imaged the arc in front of the sample holder, and a diverging beam of exciting radiation impinged on the sample holder. At this location in space the beam was larger than the sample area, and no effect of arc wander was observed. Electrical power for the S4 lamp was supplied by a Kepco Model PR-310-2M regulated dc supply, and current through the lamp was controlled at 0.75 A (voltage drop of about 130 V across the lamp after a warm-up period).

Absolute intensity at the sample area using the GE H85 lamp plus diffuser was of the order of 1 mW/cm², while with the GE S4 lamp and no diffuser the intensity was higher (several milliwatts/cm²).

The manually operated shutter at (8) required about 20 msec to open. Angle between optic axes of excitation section and detection section is 40°.

While neither the excitation section nor the detection section exhibited short term (minutes) fluctuations, there sometimes was a slow drift over hours and days. In order to allow comparison between measurements at different times, a sample of Corning glass (Code 014, Color Specification No. 0-54), in a mount allowing reproducible positioning in the sample holder, was used as a reference for calibration. When irradiated by the excitation section, this glass exhibited blue luminescence unchanged under prolonged irradiation at ~300 nm and little influenced by temperature variations around 25°. Measurements of signal from this reference sample were made at the beginning, during, and at the end of a set of experiments. They were used to correct other measurements to a standard set of conditions when necessary.

(49) R. Anschutz and P. Bendix, *Justus Liebig's Ann. Chem.*, **259**, 61 (1890).

(50) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).