STUDIES IN ORGANIC PHOTOCHEMISTRY

In Partial Fulfillment
of the Requirements for
a Bachelor of Science Degree

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Solvent Effects on Energy Transfer in Solution

Introduction

A good correlation has been established between E_T, the energy of the first excited triplet state (0-0 band of the phosphorescence spectrum in hydrocarbon glass at 77°K) of a given sensitizer and (1) the cis/trans photostationary state mixtures for olefin systems[1] and (2) the product ratio of butadiene photodimers using the sensitizer.[2] For example as the E_T of the sensitizers increases from 55 kcal/mole to 65 kcal/mole, the photostationary state in the 1,3-pentadiene system changes from predominantly trans to a nearly equal trans to cis ratio.

A similar correlation does not seem to exist between solvent effects on the E_T of the sensitizers (measured from the phosphorescence spectra at 77°K) and solvent effects on the photostationary states or dimerization product ratios in solution at 20°C. The solvent has been shown to have a significant effect on the E_T of the sensitizers. In ether-isopentane-ethanol mixture (EPA) at 77°K, benzil is reported to have an E_T of 60.6 kcal, whereas in a methyl-cyclohexane-isopentane mixture (MCIP) at 77°K, E_T = 53.7 kcal.[3] It appears, however, that at 20°C there is little or no

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1. N.J. Turro, Jr., The Triplet State as an Intermediate in Organic Photochemistry, California Institute of Technology Seminar, October 15, 1962, p. 6.

2. R.S. Liu and G.S. Hammond, J. Am. Chem. Soc., 85, 477 (1963).

3. W. Herkstroeter, unpublished results.

solvent effect on the photostationary state or on the product ratios of butadiene dimers using benzil as sensitizer.[4]

We decided to investigate solvent effects on the E_T measured in solution at room temperature of a given sensitizer and compare them with the solvent effects on the photostationary state of the cis-trans stilbene system and the butadiene photodimer ratios. Benzil and biacetyl were used as sensitizers since they phosphoresce at room temperature and are in a steep slope portion of the Saltiel plot for stilbene.

Solvent Effect on Room Temperature Emission

Room temperature emission spectra were recorded for 0.05M and 0.2M benzil and 0.05M and 0.5M biacetyl in several spectroquality solvents. The samples were degassed and sealed in vacuo. Both phosphorescence and fluorescence were observed. Energy values for the maxima were taken from spectra.

Sensitizer	Solvent	Fluorescence Maximum	Phosphorescence Maximum
Benzil	Methanol	57.1 kcal	—
"	Benzene	56.8	51.0 kcal
"	CCl_4	56.5	50.9
"	Acetonitrile	57.0	51.9
"	EtOH	57.0	—
Biacetyl	Methanol	61.6 kcal	55.4 kcal
"	Benzene	60.8	55.0
"	CCl_4	58.7	54.9
"	Acetonitrile	61.7	55.6
"	EtOH	61.8	—

4. N.J. Turro, Jr., unpublished results.

Solvent shifts were observed in the phosphorescence and fluorescence maxima. The largest phosphorescence shifts were between benzene and acetonitrile (.6 kcal for biacetyl; 1.0 kcal for benzil). We observed no concentration effects on the location of the maxima.

Solvent Effect on Isomerization of cis-trans Stilbene

Benzil and biacetyl were used as sensitizers for isomerization of cis ⇌ trans stilbene. Benzene and acetonitrile were employed as solvents. Samples were made both of cis and trans stilbene. Two tubes were charged from each sample. The tubes were degassed under vacuum and irradiated for 24 hours on the merry-go-round apparatus using a 3300 Å cutoff filter. The contents were then analyzed in the usual manner of vapor phase chromatography. Averaged values appear in the table below.

Sensitizer	Solvent	% cis
Biacetyl	Benzene	88.5%
"	Acetonitrile	89.8%
Benzil	Benzene	92.9%
"	Acetonitrile	92.4%

From Saltiel plots (sensitizer E_T's versus cis/trans photostationary states in the stilbene system) we would expect a $\frac{1}{2}$-1 kcal shift in E_T to cause a change of 3 or more in the cis/trans ratio. For biacetyl, the percent cis should be higher in benzene than in acetonitrile.[5] Experimentally we observed the opposite. This, plus the small magnitude of the effects

5. J. Saltiel, unpublished results.

on the photostationary states, lead us to conclude that there is little or no solvent effect on the photostationary state in stilbene isomerization.

Discussion

There are solvent effects on the room temperature emission spectra of benzil and biacetyl. The shifts are not as large as in MCIP and EPA glasses at 77°K, but they are definitely present. In the case of benzil there is also a large difference between the EPA and an ethanol spectrum at 77°K.[6] One possible explanation for the shifts being so large at 77°K is that we are seeing different stereochemical configurations, such as have been observed for β-naphthil.[7] This could be checked by recording emission at 77°K using solvents with different setting points and looking for temperatures at which one configuration is more favored.

For benzil we recorded phosphorescence maxima in benzene, acetonitrile and carbontetrachloride, but not in methanol or ethanol. In the case of biacetyl phosphorescence emission was recorded in all solvents except ethanol. This would indicate that biacetyl is harder to photoreduce than benzil. (We know that ethanol is a better reducing agent than methanol.) This effect might be due to lifetime differences. Also since hydrogen abstraction is much more apt to take place with $n \rightarrow \pi^*$ triplets

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6. W. Herkstroeter, unpublished results

7. W. Herkstroeter, J. Saltiel, and G.S. Hammond, J. Am. Chem. Soc., 85, 482 (1963).

than with $\pi \rightarrow \pi^*$ triplets, we can conclude that benzil and biacetyl triplets have significant $n \rightarrow \pi^*$ character. The fact that these compounds do phosphoresce at room temperature would also favor their being $n \rightarrow \pi^*$ triplets since these triplets have a shorter radiative lifetime (favors phosphorescence) than $\pi \rightarrow \pi^*$ triplets. Similarly the fact that we recorded no phosphorescence for β-naphthil in benzene at room temperature implies that β-naphthil has a $\pi \rightarrow \pi^*$ triplet, i.e., long radiative lifetime.

The question of why there is a solvent effect on the emission spectra at room temperature but not on the photostationary state cis-trans ratios or the products ratios of the photodimers of butadiene remains unanswered.

We can note a consideration. We do not know the magnitude or direction of any possible solvent effect on the substrate (ex.-solvent effect on the E_T of the stilbenes in photoisomerization). We would expect this effect to be smaller than the solvent effect on the sensitizers, but the two could be operating against each other.

Possible solvent effects on the actual energy exchange mechanism, at this time not understood, may hold the solution to our problem.

Emission of Naphthacene Impurity

Introduction

There has been some question concerning the energy of the first excited triplet state of naphthacene. A value of 56 kcal has been determined by Reid[1] from examination of the triplet to singlet emission of naphthacene (chromatographed and recrystallized in atmospheric nitrogen) in a glassy solvent at -180°C. Kasha, however, from examination of naphthacene absorption spectra, has reported the lowest lying naphthacene triplet to be at 10,250 cm^{-1} (29.3 kcal).[2] Kasha attributes Reid's value to emission from a higher excited triplet than the first.[3] It occurred to us that the anomalous naphthacene emission at 56 kcal might be caused by triplet → singlet emission from a naphthacenequinone impurity. It is known that naphthacene is quite easily oxidized and naphthacenequinone would be expected to phosphoresce quite strongly. We therefore synthesized 5,12-naphthacenequinone and examined its emission spectra.

Synthesis of 5,12-Naphthacenequinone

We synthesized the quinone by oxidation of naphthacene, following the procedure of Roitt and Waters,[4] with the exception that we used peracetic

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1. C. Reid, J. Chem. Phys., 20, 1214 (1952).

2. S.P. McGlynn, M.R. Padhye, and M. Kasha, J. Chem. Phys., 23, 593 (1955).

3. G. Viswanath and M. Kasha, J. Chem. Phys., 24,574 (1956).

4. Roitt and Waters, J. Chem. Soc., 3060-62 (1949).

acid rather than perbenzoic acid as oxidizing agent. We suspended 0.5 g of naphthacene in spectroquality CCl_3 containing 3.45 g of 40% peracetic acid. After 5 days in the refrigerator, almost all the naphthacene had dissolved and the color of the mixture had changed from orange to yellow. We washed the mixture with NaOH solution and water and then evaporated off the CCl_3. The orangish residue was redissolved in benzene and eluted through an alumina column by using 4-5 ℓ of benzene. The first band, in all probability unreacted naphthacene, was barely visible. The second band to be eluted was orange-yellow and upon concentration yielded ~.17 g of long orange-yellow needles, m.p. 296°C. The literature melting points for 5,12-naphthacenequinone are 292-293°,[5] 294°,[6] and 285°.[7] Evaporation of the benzene gave an additional .05 g of crude product (overall yield = 41%). The third band, orange-red in color, was not investigated.

Spectral Study of 5,12-Naphthacenequinone

We recorded an emission spectrum of the quinone using a medium quartz spectrograph equipped with a rotating can phosphoroscope. 10 F a Eastman Kodak plates were used. From a densitometer tracing of the photograph we obtained an E_T value of 55.6 kcal for the 5,12-naphthacenequinone.

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5. Moriconi, O'Conner, and Taranks, Arch. Biochem. Biophysics, 83, 283 (1959).

6. E. Clar, "Aromatische Kohlenwasserstoff", 233-5, Springer-Verlag, Berlin, 1962.

7. L.F. Fieser, J. Am. Chem. Soc., 53, 2336 (1931).

A similar value (55.8 kcal) was obtained from an emission spectrum using the spectrophosphorimeter (measuring the 0-0 band from the phosphorescence spectrum in hydrocarbon glass at 77°K). This agrees very well with Reid's 56 kcal value for naphthacene triplet emission. We also obtained a value of .37 ± .01 seconds for the lifetime of both the 5,12 naphthacenequinone emission and naphthacene emission in EA at 77°K. These results lead us to conclude that the 56 kcal emission recorded by Reid represented a triplet to singlet emission not of naphthacene, but rather of 5,12-naphthacenequinone, probably present in a very small amount as impurity. The fact that Reid's naphthacene was chromatographed and recrystallized under atmospheric nitrogen--and yet still contained enough 5,12-naphthacenequinone to mask the naphthacene emission--is a testimony to the easy oxidizability of naphthacene and the strength of the quinone triplet emission.

Note

Recently Herkstroeter and Lamola have shown that azulene (E_T = 37 kcal) does not quench naphthacene triplets, thus adding support to the assertion that the first triplet of naphthacene does not lie at 56 kcal.

Role of Excimers in the Photodimerization of Methyl-β-naphthyl Ether

Introduction

Methyl-β-naphthyl ether has recently been dimerized by irradiation with ultraviolet light of wavelengths shorter than 3300 Å in a variety of solvents.[1] No dimer was formed when the irradiation was carried out in the presence of benzophenone, thus leading Bradshaw and Hammond to infer that the "dimerization involves excited singlet states of the naphthyl ether."

Also, observation of fluorescence and delayed fluorescence in solutions of naphthalene in ethanol has recently been reported.[2] In both cases, the spectrum observed consisted of two bands, one with a maximum at around 3450 Å, due to emission from the singlet excited monomer, and the other, with a maximum at 4000 Å, caused by emission from a singlet excited dimer, commonly called an "excimer." In view of these results we felt it of considerable interest to investigate the possible role played by excimers in the photodimerization of methyl-β-naphthyl ether.

Singlet excimers could arise in the following three ways:

1. $A + h\nu \rightarrow A^*$
   $A^* + A \rightarrow A_2^*$
   A = β-methoxy-naphthalene
2. $A + h\nu \rightarrow {}^3A^*$
   ${}^3A^* + {}^3A^* \rightarrow A_2^{*\prime}$
3. $A_2 + h\nu \rightarrow A_2^{*\prime\prime}$.

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1. J. S. Bradshaw and G. S. Hammond, J. Am. Chem. Soc., 85, 3953 (1963).

2. C. A. Parker, Spectrochim. Acta, 19, 989-94 (1963).

It is not apparent whether or not the three excimers are identical species. In theory, however, one should be able to determine whether A_2^*, $A_2^{*\prime}$, and $A_2^{*\prime\prime}$ are the same species by observing (1) the normal and delayed fluorescence of a solution of the methyl-β-naphthyl ether and, (2) the fluorescence from a solution of the dimer.

If the equilibrium ($A_2^* \rightleftharpoons A^* + A$) is established before singlet emission in all three cases, then we should observe both monomer and dimer fluorescence in each case. If the ratio of the peak intensity of the dimer emission to that of the monomer emission is the same in the three cases, then we can assume that the identical excimer species is present in all of them. If, however, the ratio of the peak intensities differs in the three cases, this does not necessarily mean that the excimers are different. It may simply mean that an equilibrium was not established between the excimer and the excited monomer. Thus we wished to attempt to determine if the three excimers were the same species.

We were, also, interested in examining solvent effects on the excimer fluorescence and the dimerization, as well as determining a quantum yield value for the dimerization. Accordingly, we decided to observe the fluorescence and dimerization in both ethanol and benzene and attempted to determine dimerization quantum yield in one or both of these solvents.

Experimental

The β-methoxy-naphthalene was obtained commercially and recrystallized from ethanol. Absolute ethanol and spectral quality benzene were used in the preparation of all solutions. All samples were degassed and sealed in vacuo in scrupulously cleaned Pyrex test tubes. The oil diffusion vacuum pump was used to degas solutions intended for the quantum yield analysis.

Fluorescence spectra were obtained for several different methyl-β-naphthyl ether concentrations in both solvents at room temperature. The rotating can phosphoroscope was used to search for delayed fluorescence at room temperature and 0°C.

Samples of β-methoxy-naphthalene in each of the solvents were irradiated for time periods of up to several days on both the optical bench, using a 3300 Å cutoff filter, and the merry-go-round apparatus.

An attempt was made to determine the quantum yield for formation of the dimer methyl-β-naphthyl, using the benzophenone-benzhydrol actinometer system. The yield was to be determined both by ultraviolet measurements and by weighing of the precipitated product.

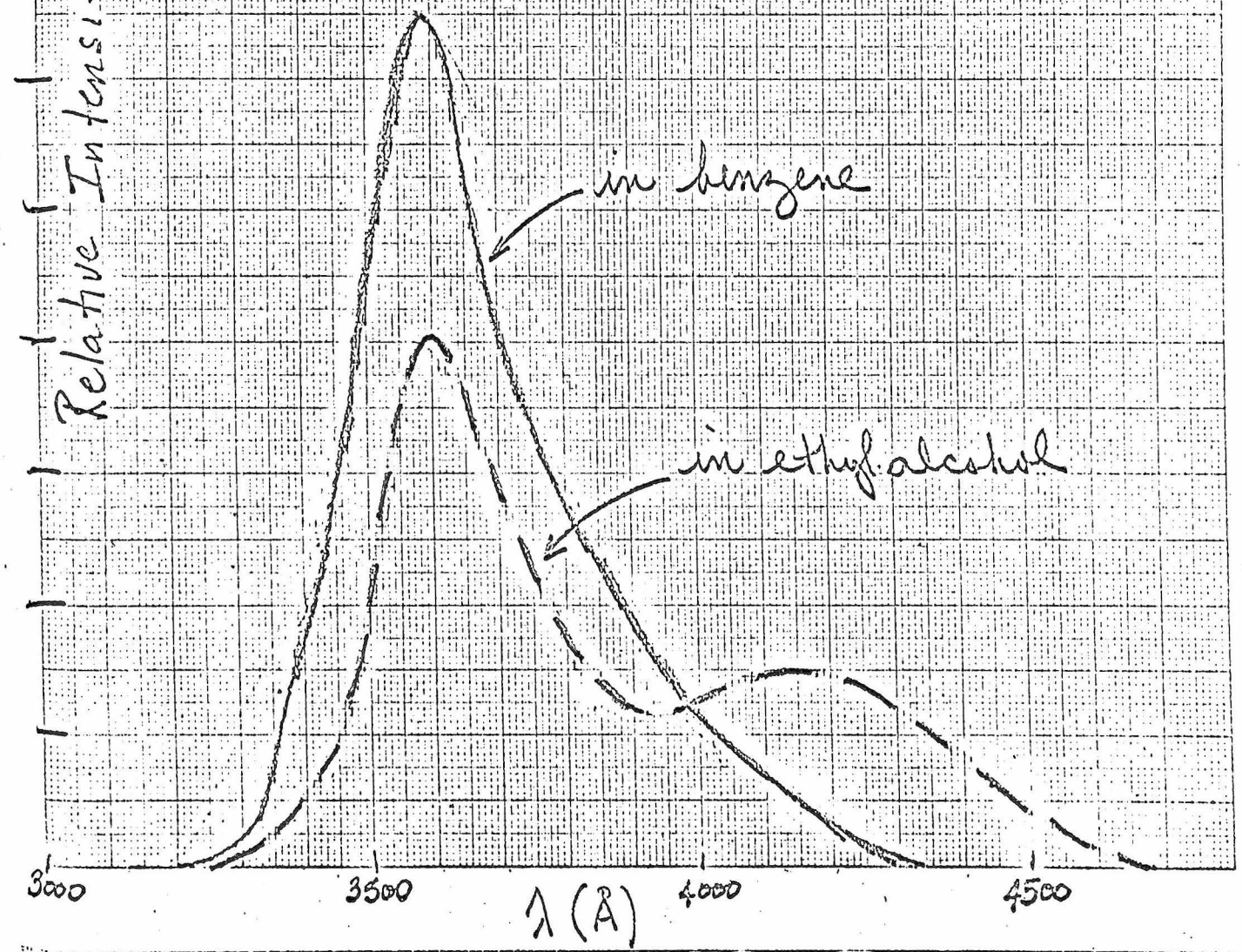
Results and Discussion

The room temperature normal fluorescence spectra of β-methoxy-naphthalene in both ethanol and benzene is shown in Figure 1 on page four. In ethanol we observed both the monomer band, centered at about 3600 Å, and the excimer band, centered at about 4150 Å. In the other case, using benzene as solvent, we observed fluorescence only from the excited monomer.

We were unable, either at room temperature or at 0°C, to observe any delayed fluorescence, even though Parker[2] has shown that this phenomena is observable with naphthalene. Consequently we expected to observe the delayed process with β-methoxynaphthalene. It is entirely possible that the delayed fluorescence was of too low intensity for our equipment to pick up. Parker's results indicated that the delayed fluorescence in naphthalene is from 1/50 to 1/100 of the intensity of the normal fluorescence. Our experimental setup, complete with the dewar filled with air or ice water, and rotating can, was such that it is very questionable whether we could have observed emission of this low intensity. Consequently, we can say only

FIGURE 1.

Fluorescence Spectrum of Methyl-β-naphthyl ether (0.03 M, 25°C., 3130 Å excitation)



that delayed fluorescence, of considerably lower intensity than the normal fluorescence, may be present. Since we could not observe any delayed fluorescence, we were unable to conclude anything about the identity of the different excimer species.

Among the tubes that were irradiated for long periods of time on either the optical bench or the merry-go-round apparatus, product was observed only in those containing ethanol as solvent. In no case was any dimerization product found in the benzene tubes. This, coupled with the absence of the excimer fluorescence band from β-methoxy-naphthalene in benzene solutions, indicates that the dimerization mechanism involves a singlet excimer. This excimer could be formed either by the complexing of an excited singlet monomer with a ground state monomer, or by triplet-triplet annihilation. The later process would give rise to the delayed fluorescence, which we have not been able to observe, but whose presence we cannot rule out. The rather large intensity, however, of normal methyl-β-naphthyl ether excimer fluorescence, at room temperature, would lead us to suspect that the predominant pathway for the production of excimers is by the association of a singlet excited and ground state monomer.

Naphthalene, itself, neither dimerizes nor shows any excimer fluorescence, delayed or normal when irradiated at room temperature. The fact, however, that both normal and delayed naphthalene excimer fluorescence are observed at lower temperatures, implies that it is not observed at room temperature because the naphthalene excimer dissociates before it can fluoresce and form the stable dimer. In the case of methyl-β-naphthyl ether, the absence of excimer fluorescence and dimerization product when benzene is used as a solvent, indicates that here, also, dissociation of the excimer competes favorably with fluorescence and dimerization. However, Bradshaw has reported that the dimer of β-methoxy-

naphthalene is formed in benzene. Since Bradshaw did not measure rates of formation of the product, there is no necessary conflict between his results and ours. We have merely shown that the rate of dimerization is higher in ethanol than in benzene and that strong excimer emission is observed in the former solvent.

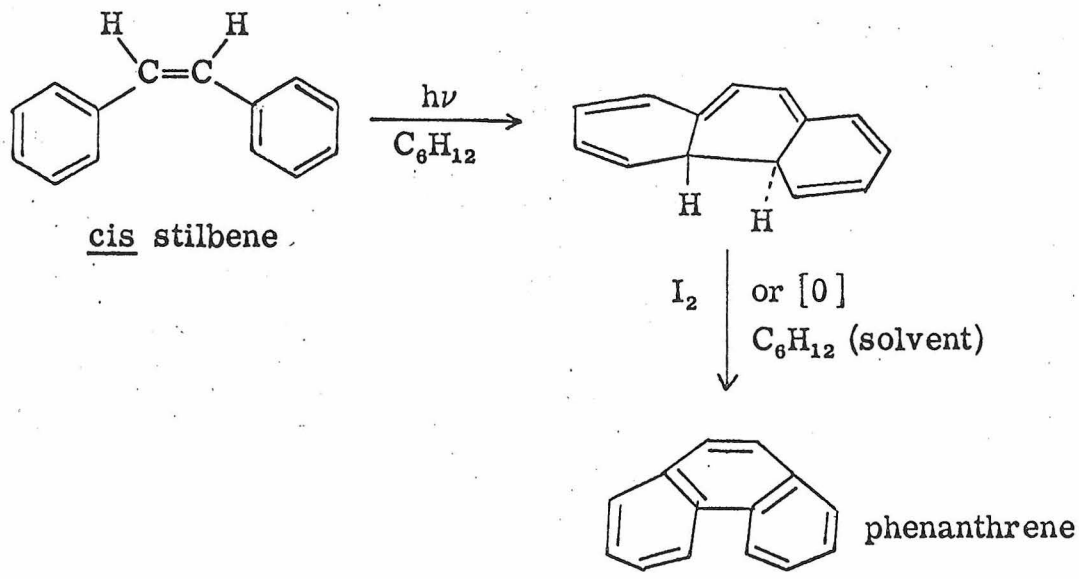
An attempt to measure a quantum yield for the dimerization in ethanol was unsuccessful because of temporary problems with available apparatus. The lamps and filter systems available, at the time, gave either too low or too variable an intensity and we were unable to obtain satisfactory actinometric results. However, given time, a quantum yield for the dimerization in ethanol should be obtainable.

A further extension of this experiment might be to attempt the dimerization of the naphthyl ether in the presence of benzophenone, using long irradiation times. Any dimerization product observed would then be the result of triplet-triplet methyl-β-naphthyl ether annihilation, giving rise to the singlet excimer, which decays to the dimer.

Attempted Photochemical Synthesis of Biphenylene

Introduction

Mallory, et al.,[1] have recently demonstrated a mechanism for the long observed photochemical conversion of stilbenes to phenanthrenes. This involves the oxidation of a dihydrophenanthrene, the initial photoproduct, to phenanthrene. This oxidation, which in the past, presumably has been caused by either dissolved oxygen or some other oxidizing agent present as an impurity, was found to be easily accomplished by the addition of a small amount of iodine. The overall reaction is then:

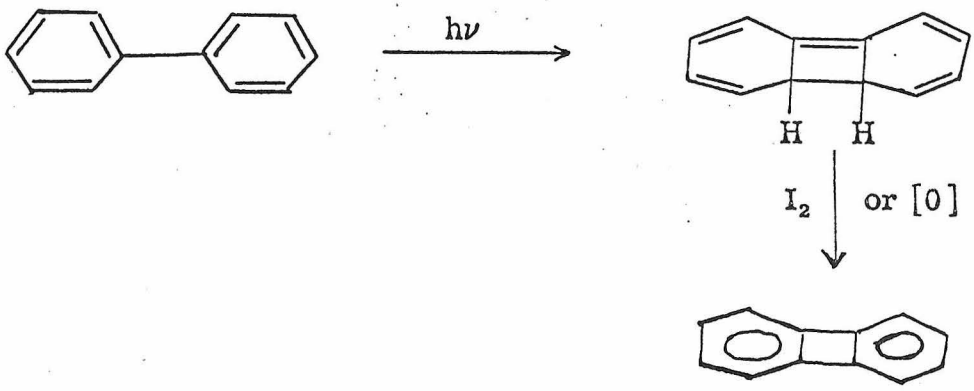


cis stilbene

phenanthrene

1. Mallory, et al., J. Am. Chem. Soc., 84, 4361 (1962).

In light of this reaction it seemed possible that biphenylene might be photochemically synthesized from biphenyl as follows:



If successful, this would be a very economical method of preparation and have commercial applications. Biphenylene, is intensely yellow, and can easily be recognized in solution.

Experimental

We irradiated two solutions of biphenyl in octane, one with a small amount of iodine and one without, for several days, while constantly bubbling air through the solutions. Octane was used primarily because of its low volatility. Ultraviolet absorption spectra were taken of both initial solutions.

Results and Discussion

Even after several days of irradiation no characteristic biphenylene color was observed. Additional ultraviolet adsorption spectra also indicated no biphenylene production.

This result is not completely unexpected, as steric and resonance considerations would lead us to suspect the conversion of biphenyl to biphenylene to be energetically much less favorable than the conversion of stilbene to phenanthrene. However, completely efficient use of the excitation

energy of biphenyl should have been adequate to lead to formation of the dihydrobiphenylene. It is entirely possible that the desired photoreaction did occur but that thermal reversion of the intermediate to biphenyl was too rapid to allow significant oxidation to occur.

Syntheses of Sensitizers or Compounds of Current Photochemical Interest

5,12-Naphthacenequinone

Introduction

The E_T (0-0 band from the phosphorescence spectrum in hydrocarbon glass at 77°K) of the first excited triplet states of benzene, naphthalene, and anthracene are ~84 kcal, ~60 kcal, and approximately 42 kcal respectively. The value recorded from naphthacene emission, however, is 56 kcal.[1] It is throught that this naphthacene value may represent emission from a higher excited triplet than the first.[2] On the other hand, since 5,12-naphthacenequinone would be expected to be a strong phosphorescence emitter with an E_T somewhere in the fifties-sixties (anthraquinone has E_T = 62.4 kcal)[3], it is possible that the 56 kcal emission of naphthacene is due to small amounts of 5,12-naphthacenequinone present as an impurity. It is known that naphthacene is quite easily oxidized. Thus we wished to synthesize 5,12-naphthacenequinone and observe its phosphorescence emission.

Experimental

We synthesized the quinone by oxidizing naphthacene, following a procedure developed by Roitt and Waters.[4] We suspended 0.5 g of naphtha-

1. A.A. Lamola, verbal communications.
2. Ibid.
3. W. Herkstroeter, unpublished results.
4. Roitt and Waters, J. Chem. Soc., (1949), 3060-3062.

cene in spectroquality CCl_3 containing 3.45 g of 40% peracetic acid. After five days in the refrigerator, almost all the naphthacene had dissolved and the color of the mixture had changed from orange to yellow. We washed the mixture with NaOH solution and water and then evaporated off the CCl_3. The orangish residue was redissolved in benzene and eluted through an alumina column by using 4.5 ℓ of benzene. The first band, in all probability unreacted naphthacene, was barely visible. The second band to be eluted was orange-yellow and upon concentration yielded ~.17 g of long orange-yellow needles, m.p. 296°. The literature melting points for 5,12-naphthacenequinone are 292-293°;[5] 294°;[6] 285°.[7] Evaporation of the benzene gave an additional .05 g of crude product (overall yield = 41%). The third band, orange-red in color, was not investigated.

9-Methylene Fluorene

Discussion

An E_T value has been obtained for fluorenone(I) from an ethyl iodide absorption spectrum.[8] Fluorenone could have either a $\pi \rightarrow \pi^*$ or an $n \rightarrow \pi^*$ triplet. It would be of interest and might give us some insight into predicting triplet energies to compare the E_T of fluorenone to that of 9-

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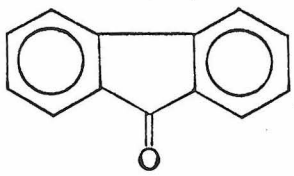
5. Moriconi, O'Connor, and Taranks, Arch. Biochem. Biophys., 83, 283 (1959).

6. E. Clar, "Aromatische Kohlenwasserstoffe", p. 233-5, Springer-Verlag, Berlin, 1962.

7. L.F. Fieser, J. Am. Chem. Soc., 53, 2336 (1931).

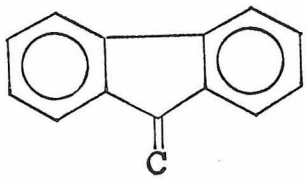
8. Jack Saltiel, unpublished results.

methylene fluorene (II), a compound which must have a $\pi \rightarrow \pi^*$ triplet. Thus we have synthesized and taken an ethyl iodide absorption spectrum of II.



I

fluorenone



II

9-methylene fluorene

Experimental

We prepared II by the reaction of phenyl 9-fluorenyl ketone (III) with alkaline formaldehyde solution.[9] III was synthesized by the action of ethyl benzoate and potassium on fluorene in the absence of solvent.[10]

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9. John G. Burr, J. Am. Chem. Soc., 74, 1717-19 (1952).

10. A. Werner, Ber., 39, 1287 (1906).