purification. *cis*-Piperylene (Chemical Samples) was purified by preparative glpc with a silver nitrate–ethylene glycol column as described by Hammond.[24]

Quantum Yield Measurements. Quantum yield experiments were performed in a Rayonet photochemical reactor Model RPR-100 using RPR-2537 A lamps. The lamps were powered from an Isotran Model MVR 2000 constant-voltage power supply. Inside the Rayonet reactor was mounted a rotating wheel constructed from a black, anodized aluminum drum 17.8 cm in diameter by 5.7 cm thick. On the perimeter of the drum were located 30 cylindrical compartments 13 mm in diameter. Each compartment was exposed to the lamps through a slit 0.635 cm × 1.78 cm. The drum was mounted on a central shaft of a 1.78 cm aluminum rod. At the base and top of the shaft are ball bearings rigidly attached to the Rayonet reactor. The wheel was rotated at 48 rpm. The quantum yield apparatus was cooled with air which had passed through a water cooled heat exchanger. The apparatus was thermostated at 30 ± 0.1° with a temperature control mechanism employing a thermistor sensor. Calibration of the compartments of the wheel with potassium ferrioxalate actinometry demonstrated that each compartment received identical quantities of light $\pm 1\%$.

Samples (3.0 ml) of the appropriate concentrations (Table I) of 2-ethoxypyrrolin-5-one (**1**), 6-ethoxy-4,5-dihydro-2(3*H*)-pyridone (**2a**), *cis*-piperylene, and acetone in *tert*-butyl alcohol solvent were placed in oven-dried 13-mm quartz test tubes and degassed by four freeze (liquid nitrogen)–pump (2×10^{-5} mm)–thaw cycles and sealed. The concentrations of the keto imino ethers (**1** and **2a**) were such that greater than 99% of the incident light below 300 nm was absorbed. During the irradiations the lamp intensity was monitored with potassium ferrioxalate actinometry and averaged 5.7×10^{15} quanta/sec. Quantum yields were corrected for the small emission impurities above 300 nm reported for the 2537 A lamps by Southern New England Ultraviolet Co., Middletown, Conn. Analyses of product formation from the irradiation of **1** and **2a** were obtained by glpc with a 2 m × 0.64 cm column of 5% FS-1265 on 60–80 Haloport F at 140° (He, 75 cc/min) relative to external cinnamaldehyde and at 135° (He, 48 cc/min) relative to external isophorone, respectively. The quantum yields of glutarimide formation were corrected for the small amount of glutarimide formed by hydrolysis by residual water. This correction was obtained from the analysis of an unirradiated blank sample. Isomerization of *cis*-piperylene was measured by glpc with a 5 m × 0.64 cm column of 25% β,β-oxydiproprionitrile on 80–100 mesh Chromosorb P at ambient temperature (He, 46 cc/min). Quantum yields of cis–trans isomerization of piperylene were corrected for back reaction.[23] Gas chromatographic data were corrected for differences in detector response, and quantum yield irradiation times were adjusted such that no more than 10% of the starting materials were destroyed during the irradiation.

Piperylene Photostationary State in *tert*-Butyl Alcohol. A 50-ml Pyrex test tube was filled with 30 ml of *tert*-butyl alcohol solution, 2.0 g of *cis*-piperylene, and 0.50 g of benzophenone. The solution was irradiated external to a 450-W mercury lamp until the ratio of *trans*- to *cis*-piperylene did not change (12 hr) as measured by glpc with a 5 m × 0.64 cm column of 25% β,β-oxydiproprionitrile on 80–100 mesh Chromosorb P at ambient temperature. At the photostationary state the ratio of *trans*- to *cis*-piperylene was 1.34.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (GM 18349) for support of this research.

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Norrish Type II Rearrangement from π,π^* Triplet States

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*Contribution from the Research Laboratories, Eastman Kodak Company,
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Abstract: The photochemical rearrangement of 1-benzoyl-8-benzylnaphthalene (BBN) to *cis*- and *trans*-7,8-diphenylacenaphthen-7-ol has been shown to occur from the lowest triplet state which is a π–π^* state having less than 10% mixing with the lowest n–π^* state (8.9 kcal higher). The 4.7-kcal/mol activation energy for the rearrangement step is consistent with only partial localization of the excitation in the transition state. A novel quenching of the long-lived BBN triplet state has been observed with several ketones of higher triplet energy. For lack of a more precise explanation, this has been called "exciplex" quenching.

The Norrish type II rearrangement is one of the most well-studied photochemical reactions known.[3,4] The elegant work of Wagner, *et al.*, has elucidated the detailed steps of the reaction, showing that it proceeds through a reversible intermediate diradical.[5] Turro and coworkers determined many of the factors which control the multiplicity of the reactive state.[6] More recent reports showed the diverse structural variations which are possible in the Norrish type II rearrangement.[7] Almost all these studies were done with n–π^* triplets, *i.e.*, ketones in which the lowest excited state is n–π^*. A recent report by Wagner, Kemppainen, and Schott suggested that in cases where ketones with lowest π,π^* triplets undergo the Norrish type II reaction, the mechanism of the reaction involves thermal excitation of the π,π^* state to a slightly higher n,π^* state, from which reaction actually occurs.[8]

A preliminary communication on the Norrish type II photorearrangement of 1-benzoyl-8-benzylnaphthalene (BBN) through a seven-membered ring transition state was recently reported by some of us.[9] We

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(1) Author to whom correspondence should be addressed.

(2) Alfred P. Sloan Fellow, 1970–1974.

(3) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 94 (1968).

(4) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7480 (1972), and references therein.

(5) (a) P. J. Wagner and T. Jellinek, *J. Amer. Chem. Soc.*, **93**, 7328 (1971), see also ref 4; (b) P. J. Wagner and R. G. Zepp, *ibid.*, **93**, 4958 (1971); (c) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).

(6) N. J. Turro and F. D. Lewis, *Tetrahedron Lett.*, 5845 (1968).

(7) J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971).

(8) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Amer. Chem. Soc.*, **92**, 5280 (1970).

(9) A. G. Schultz, C. D. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **92**, 6086 (1970).

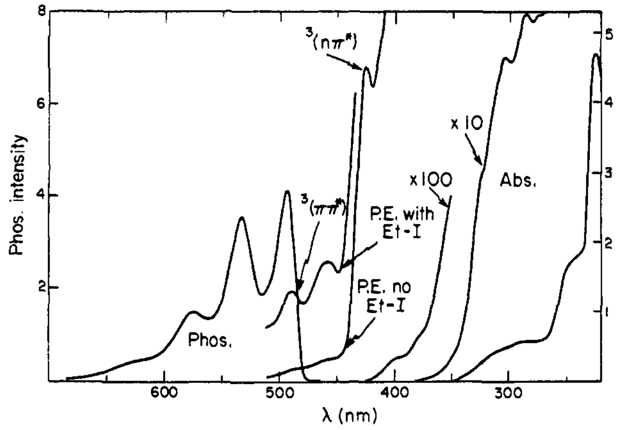


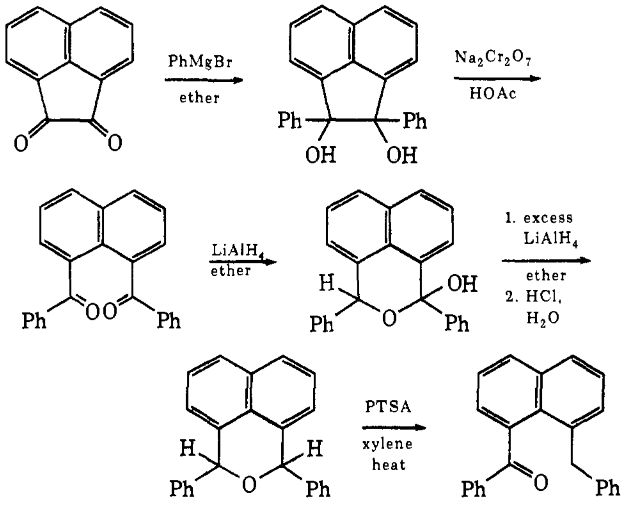
Figure 1. The absorption, phosphorescence, and phosphorescence excitation (PE) spectra of BBN. The absorption spectrum was taken in methylcyclohexane at room temperature. The $^1(n,\pi^*)$ state at 405 nm was found to shift to ~385 nm in EA. The phosphorescence and PE spectra were taken in EA (ethyl ether–isopropyl alcohol) at 77°K. Approximately 20% ethyl iodide (Et-I) was added to enhance the weak transition to the (π,π^*) triplet state.

report here the detailed measurements of the spectra, quantum yields, flash photolysis kinetics, and the mechanism of the photorearrangement of BBN.

Results and Discussion

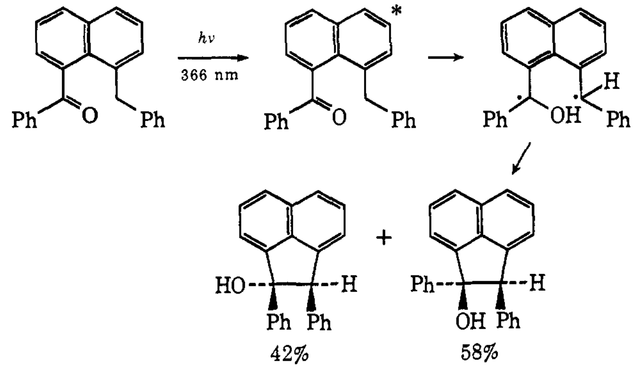
A. Preparation and Photochemical Products of 1-Benzoyl-8-benzylnaphthalene. The synthesis of BBN from benzyl chloride and 1-naphthyl phenyl ketone with aluminum chloride was reported by Dziewonski and Moszew.[10] However, in our hands this preparation gave a complex mixture of products, none of which was the desired ketone. All of the BBN used in this work was prepared from acenaphthenequinone by the method outlined in Scheme I. The mono- and dideuterated derivatives were prepared with lithium aluminum deuteride in the appropriate step.

Scheme I



Irradiation of a degassed benzene solution of BBN at 365 nm leads to the formation of two isomeric alcohols (Scheme II) in an isolated yield of 91%. (The quantum yield is discussed in the mechanism section.) The products were isolated and the product ratio was determined by preparative thin layer chromatography. The alcohols were characterized by their well-defined nmr and mass spectra as well as by their easy acid-catalyzed dehydration to the known 1,2-diphenylacenaphthylene.[11]

Scheme II



B. Spectral Properties of BBN. The solution absorption, phosphorescence, and phosphorescence excitation (PE) spectra of BBN are shown in Figure 1. The absorption spectrum shows a weak band ($\epsilon \approx 25$) at 405 nm which is assigned to the $^1(n,\pi^*)$ state. A second, stronger transition starts at ~325 nm which is very similar in position and intensity to the first transition of substituted naphthalenes.

In the S → T* absorption region, the PE spectrum of BBN shows two transitions, the lowest energy one being observed *only* with the addition of a heavy-atom solvent, ethyl iodide. This fact, along with the much higher intensity of the higher energy transition, allows us to assign the 0–0 band (488 nm) to the $^3(\pi-\pi^*)$ state.[12] These assignments are similar to those made for 2-naphthaldehyde by Kearns and Case.[12]

The energy separation between the $^3(\pi,\pi^*)$ and $^3(n-\pi^*)$ states is 3090 cm^{-1} (8.9 kcal/mol) in 2-methyltetrahydrofuran at 77°K. This large energy gap means the lowest triplet state of BBN will behave as a relatively pure π,π^* state, with little vibronic coupling to the lowest n,π^* state. The phosphorescence lifetime of BBN in 2-methyltetrahydrofuran at 77°K is 0.69 sec, calculated from the slope of Figure 2. Although quantitative measurements of the phosphorescence intensity were not made, visual comparison of **1** with 9,10-diphenylanthracene fluorescence[13] allows us to estimate that the quantum yield of phosphorescence at 77°K is high, and therefore that the natural lifetime of the triplet state of BBN is not much different from 1 sec. This is much longer than that for a pure n,π^* state (benzophenone lifetime = 0.005 sec),[14] but shorter than that of a pure π,π^* state (naphthalene lifetime = 2.3 sec),[14] which reflects the small amount of $n-\pi^*$ character the lowest triplet state of BBN must contain.

Using acenaphthene and benzophenone as models

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(10) K. Dziewonski and J. Moszew, *Bull. Int. Acad. Pol.*, 658, 660 (1929); K. Dziewonski and J. Moszew, *Rocz. Chem.*, 11, 169 (1931).

(11) W. A. Mosher, F. W. Steffgen, and P. T. Lansbury, *J. Org. Chem.*, 26, 670 (1961).

(12) (a) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, 88, 5087 (1966). (b) The assignment of the lowest triplet state is also based on lifetime and vibronic structure. See also S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, Chapter 8, for discussion of the external heavy atom effect.

(13) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc., Ser. A*, 275, 135 (1963).

(14) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 297.

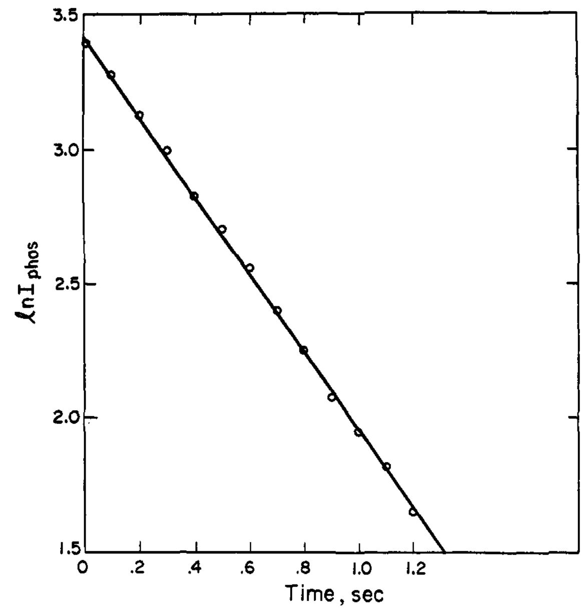

Figure 2. Plot of ln phosphorescence intensity *vs.* time. The measurement was made in 2-methyltetrahydrofuran at 77°K.

to obtain the natural lifetimes for "pure" π,π^* and n,π^* triplet states, we can calculate the amount of mixing of the two states from the measured lifetime and phosphorescence quantum yield of BBN using simple perturbation theory.[15]

The mixing coefficient C is given by[15]

$$I_1 = (1 - C^2)^{1/2}\phi(\pi,\pi^*) + C\phi(n,\pi^*) \qquad (1)$$

and calculated from

$$f_1 = f_{\pi,\pi^*} + 2Cf_{n,\pi^*}{}^{1/2}f_{\pi,\pi^*}{}^{1/2}\cos\alpha \qquad (2)$$

where α is the angle between the transition moments, f is the oscillator strength, and C is assumed to be much less than 1 ($C \ll 1$). Cos α was estimated to be on the order of $^1/_2$, and the oscillator strengths are estimated from the lifetimes. Substituting the values of the oscillator strength estimated from the natural lifetimes yields a value of 0.08 for C; thus it appears that the lowest π,π^* triplet state of BBN contains about 8% n,π^* character.

C. Mechanism of the Reaction. The quantum yield for the rearrangement of BBN in benzene is independent of concentration, suggesting the reaction is intramolecular. This is confirmed by the fact that BBN-*d* gives only monodeuterated product. The mechanism of the reaction is thus (1) excitation of BBN followed by (2) intramolecular hydrogen abstraction and (3) ring closure to products.

The rearrangement of BBN is completely quenched by the addition of small amounts (10^{-4} *M*) of *trans*-stilbene, oxygen, or 1,3-cyclohexadiene, demonstrating that the reaction occurs from the triplet state. When stilbene is used as the quencher, the quantum yield for stilbene isomerization is the same as that for benzophenone-sensitized isomerization of stilbene, indicating the intersystem-crossing quantum yield of BBN is unity. Furthermore, measurements of the lifetime of the reactive state in solution, both by flash photolysis and from Stern–Volmer plots, reveal the rearrangement occurs at a rate less than 10^4 sec^{-1}. This slow rate rules out reaction from an excited singlet state or a higher excited triplet sate of BBN.

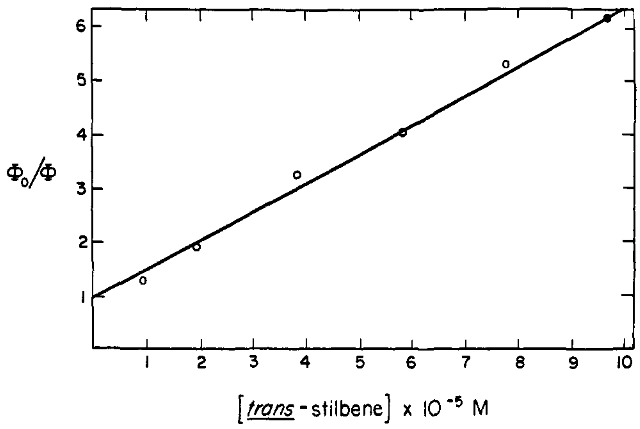

Figure 3. Stern–Volmer plot of (quantum yield)$^{-1}$ *vs.* concentration of *trans*-stilbene. The solvent was degassed benzene.

The quantum yield of rearrangement of BBN was found to be a sensitive function of the purity of the BBN, the purity of the solvent, and the method of cleaning the reaction cells. In one case, cleaning the cells with alcoholic KOH followed by insufficient rinsing gave a low value for the quantum yield, and the solution, upon standing overnight after irradiation, turned yellow. Presumably, the product alcohol had undergone base-catalyzed elimination of water to give diphenylacenaphthylene, which could function as a quencher for the BBN triplet.

Purification of BBN by zone melting proved impossible. When the contents of the tube were melted, no amount of cooling could induce a crystal to form. When the tube was opened and a seed crystal introduced, the growth of the crystalline mass down the tube was approximately 5 mm/day. The quantum yield of BBN rearrangement improved with successive slow recrystallizations from benzene–hexane until an apparently limiting value of 0.70 was achieved. It is possible that further purification might further increase the quantum yield of the rearrangement. However, it is also possible that the diradical intermediate of the reaction may revert to starting material. This could account for some or all of the inefficiency in the maximum quantum yield.

A Stern–Volmer plot of the quantum yield of BBN rearrangement in the presence of *trans*-stilbene as quencher (Figure 3) gives a value of 7.4×10^3 sec^{-1} for the rearrangement step (k_r). This value was calculated using a value of 1.2×10^9 l./(mol sec) for the rate of energy transfer from BBN to stilbene, measured by flash photolysis, and a value of $k_d/k_r = 2$, since the actual ϕ_0 value under these conditions was 0.33. This value is in excellent agreement with that measured directly by flash photolysis, but we feel the flash photolysis values are to be preferred, both because the measurement is a direct one and because the extremely dilute solutions used in flash photolysis minimize the effects of impurities in the BBN.

The rates of the rearrangement were measured directly at different temperatures utilizing flash-excitation techniques. The results are summarized in

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[15] L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill, New York, N. Y., 1935, Chapter 6.

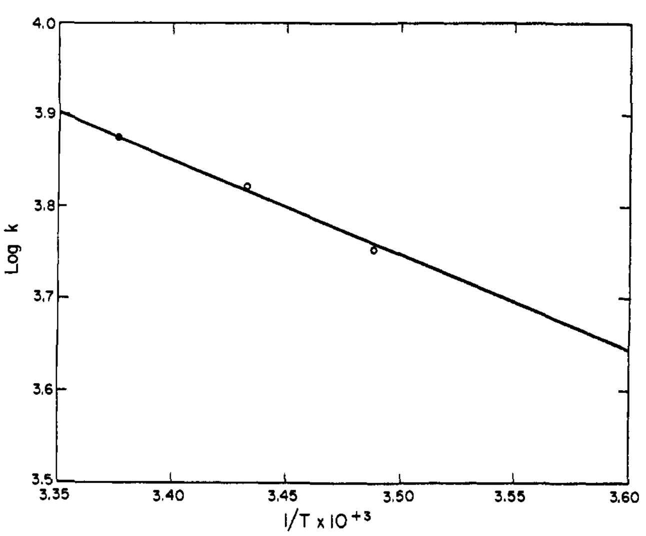


Figure 4. Arrhenius plot of the rate of rearrangement of the BBN triplet state as measured by flash photolysis.

Table I. Rate Constants for the Photochemical Rearrangement of BBN

Temp, °C	$k_d + k_r$ (sec^{-1})
13.5	5.6×10^3
18.1	6.6×10^3
23.0	7.5×10^3

Table I. The activation energy for this reaction was determined from these data and is 4.7 kcal/mol; the plot of log k *vs.* $1/T$ is shown in Figure 4. The rate constant for quenching BBN triplets by *trans*-stilbene was measured as 1.2×10^9 M^{-1} sec^{-1}, a surprisingly low value because photosensitizers having triplet energies comparable with that of BBN are known to transfer energy to *trans*-stilbene with rate constants greater than 3×10^9 M^{-1} sec^{-1}.[16] Steric constraints on energy transfer may possibly account for this observation.

The value obtained for the energy of activation for the hydrogen abstraction step in the rearrangement of BBN lies below 5 kcal/mol. Since the n,π^* – π,π^* splitting is 8.9 kcal/mol (Figure 1), and since a pure n,π^* triplet such as valerophenone shows a 5 kcal/mol activation energy,[17] reaction from the n–π^* state should require an activation energy of 13.9 kcal/mol (8.9 + 5). Clearly, the rearrangement of BBN is not occurring from a thermally excited, pure n,π^* state as suggested by Wagner.[8] The data which we have measured here are in accord with the conclusions reached by Suppan and Porter.[18] The results suggest that the substantially delocalized π,π^* triplet state of BBN with little excitation in the ketone must become partially but not totally localized on the ketone in the transition state for hydrogen abstraction. Figure 5 diagrams this situation.

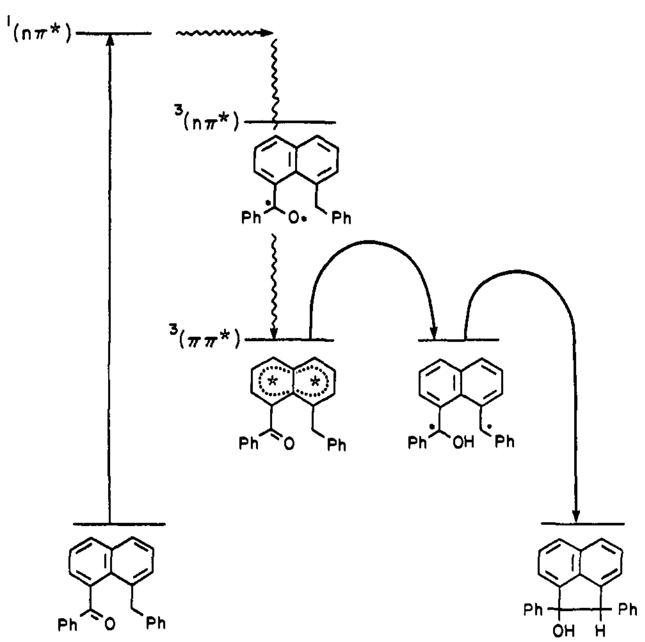
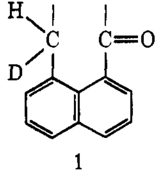


Figure 5. Energy diagram (not to scale) of the rearrangement of BBN. In the transition state the excited electron need not be localized on the carbonyl.

Table II. Rate Constants for the Photochemical Rearrangement of **1** and **2**

Temp, °C	$k_d + k_r$ (sec^{-1})	
	1	**2**
8.2		2.2×10^3
13.5	3.9×10^3	
16.7	4.5×10^3	3.0×10^3
23.0	5.3×10^3	
24.1	5.4×10^3	3.6×10^3



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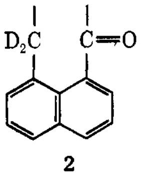

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D. Isotope Effects. Both the mono- and dideutero derivatives of BBN, shown below, were prepared by the reaction sequence of Scheme I. The rate constants for rearrangement of these partially deuterated benzoylbenzylnaphthalenes as measured by flash photolysis procedures are given in Table II. The rate constants for energy transfer to *trans*-stilbene from the triplets of **1** and **2** were measured as 1.5×10^9 and 1.7×10^9 M^{-1} sec^{-1}, respectively. The activation energies for intramolecular hydrogen abstraction by **1** and **2**, 5.1 and 4.8 kcal/mol, respectively, determined from the slopes of the plots of Figure 6, are only slightly higher and, therefore, within experimental error of this same parameter for BBN. Although one would expect a primary isotope effect in this intramolecular hydrogen abstraction, it is either absent or sufficiently small to be obscured by experimental error. However, the lowering of the rate constants ($k_d + k_r$) with increasing deuterium subtitution must be explained by an increase either in the energy or entropy of activation; the former would appear to be the more attrac-

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[16] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 4769 (1966).

[17] J. C. Scaiano, J. Grotewold, and C. M. Previtali, *J. Chem. Soc., Chem. Commun.*, 390 (1972).

[18] (a) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **62**, 3375 (1966); (b) P. Suppan, *Ber. Bunsenges. Phys. Chem.*, 72, 321 (1968).

tive rationalization, but the data are not accurate enough for an elaborate interpretation of this effect.

E. Unusual Quenching Effects. When sensitization of BBN was attempted, an unusual quenching effect was observed with certain sensitizers. For example, the isomerization proceeded normally with 10^{-4} *M* Michler's ketone, but at 0.05 *M* the reaction was entirely quenched, even though the triplet energy of Michler's ketone is 4 kcal/mol higher than that of BBN. Further experiments revealed a number of other compounds of higher triplet energy which are also effective quenchers of the reaction. The rates of the quenching reaction were determined from the slopes of plots of ϕ_0/ϕ *vs.* [quencher] and the values of k_d and k_r obtained in section C (Table III). Inspection of Table III reveals no correlation with the triplet energy of the quencher nor with the absorption coefficient of the quencher at 365 nm. This rules out quenching by simple energy transfer and by competitive absorption. Competitive absorption is further ruled out by the fact that the extent of the quenching changes with the concentration of Michler's ketone, even when Michler's ketone is absorbing over 99% of the radiation.

Table III. Quenchers and Nonquenchers for the BBN Triplet

Quenchers	k_q, l./(mol sec)	E_t, kcal/mol
2-Methylanthraquinone	$2.2 \times 10^{7\,a}$ $(8 \times 10^6)^b$	62
Michler's ketone	$1.5 \times 10^{7\,a}$	61
Thioxanthone	$6.9 \times 10^{6\,a}$ $(4 \times 10^6)^b$	65
Ethyl phenyl glyoxalate	$5.2 \times 10^{6\,a}$	62
10,10-Dimethylanthrone	$1.4 \times 10^{6\,a}$ $(0.8 \times 10^6)^b$	69
Nonquenchers		
Benzophenone		68
4-Methoxybenzophenone		68
Naphthalene		61
Fluorene		67
Dibenzothiophene		70
Acetophenone		74

[a] From Stern–Volmer plots. [b] By flash photolysis.

Another quenching mechanism which can be immediately ruled out in the cases of Michler's ketone and thioxanthone is that of the sensitizer self-quenching reaction, recently reported for both sensitizers (eq 3).[19–21] At Michler's ketone or thioxanthone

$$\text{sensitizer}^3 + \text{sensitizer} \xrightarrow{k\,=\,10^9\ \text{l./(mol sec)}} 2\text{sensitizer} + \text{heat} \qquad (3)$$

concentrations of 10^{-3}, the rate of the sensitizer self-quenching reaction in only 10^6 sec^{-1}, which is an order of magnitude less than the observed rates of quenching.

Since all the quenchers have ketone functionality, it seemed possible that quenching could occur *via* formation of a 1,3-dioxetane which would thermally revert to starting materials (eq 4).[22] Such a mechanism could also explain the sensitizer self-quenching reaction observed for thioxanthone and Michler's ketone.[19,20]

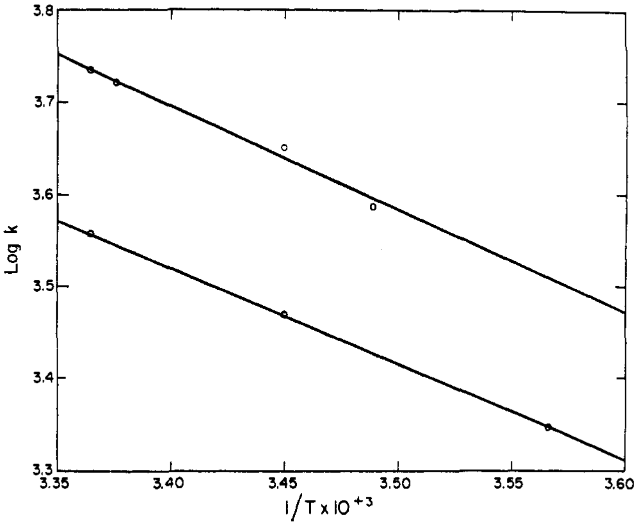
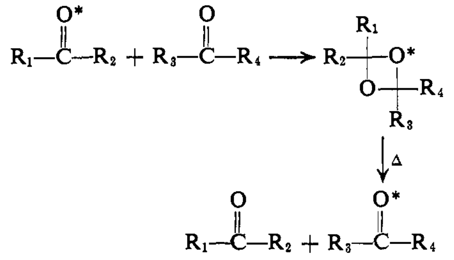


Figure 6. Arrhenius plots for mono- and dideuterated BBN (*cf.* Figure 4).



To test this mechanism, thioxanthone labeled with ^{18}O was prepared. This was irradiated in benzene with BBN and with deuterium-labeled thioxanthone. As Table IV shows, there was no ^{18}O exchange.

Table IV. Isotope Distribution of Mixtures of Thioxanthone-^{18}O and Thioxanthone-d_x or BBN in Benzene

Thioxanthone-^{18}O + thioxanthone-d_x Mass spectrum peak heights			Thioxanthone-^{18}O + BBN[c] Mass spectrum peak heights		
m/e	Before[a] irradiation	After irradiation[b]	*m/e*	Before[a] irradiation	After irradiation[b]
212	2900	2900	212	810	810
213	1900	1830	214	900	890
214	3200	3100	322	100	93
215	900	930	324	1	1
216	420	420			
217	60	78			
218					

[a] 0.03 *M* total thioxanthone. [b] Two equivalents of 366-nm radiation. [c] 0.01 *M* BBN.

A quenching mechanism for this or any other slow reaction which must be considered is the possibility of impurities that quench at a diffusion-controlled rate. The obseved quenching rates are around 10^7 l./(mol sec). This means about one part in 500 of a lower energy quencher ($k_q = 5 \times 10^9$ l./(mol sec)) would be sufficient to account for the observed quenching. Mechanisms based on impurity effects are generally difficult to eliminate unambiguously. However, in this case there are several facts which argue

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(19) T. H. Koch and A. J. Jones, *J. Amer. Chem. Soc.*, **92**, 7503 (1970).

(20) O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969).

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against the impurity mechanism. First, no special purification was done with nonquenching compounds (benzophenone, naphthalene, acetophenone, etc.). The nonquenchers were commerical chemicals which had been recrystallized once or twice from reagent grade solvents in the case of solids, or were evaporatively distilled in the case of liquids. Second, the quenching was observed with compounds from different sources and with different methods of purification. For example, commercial thioxanthone that had been simply sublimed gave the same quenching constant as thioxanthone which had been synthesized from purified thiosalicylic acid, benzene, and sulfuric acid and then recrystallized several times from various solvents, chromatographed on alumina, and finally recrystallized three times from Spectrograde ethanol. Third, in the case of ethyl phenyl glyoxalate, a carefully done gas chromatogram of the distilled liquid revealed no impurities (limit = one part/10,000). Finally, the compounds which are quenchers all have a common property that is absent in all the nonquenchers. That is, the effective quenchers all show singlet–singlet absorption below the lowest singlet state of BBN. The theoretical basis for this correlation of singlet energies with a triplet state reaction is by no means clear, but the observation of the effect weakens the case of impurity quenching as the explanation. However, it should be pointed out that in all the cases where quenching was observed, there may be a contribution to the quenching constant from any quenching impurities which may be present. While we feel, for the reasons outlined above, that such contributions are small, the values for the quenching constants in Table III may be subject to change if and when more precise measurements are made on specially purified materials. Such measurements are outside the scope of this work, and we wish to use the data of Table III only to point out that we have observed a slow quenching reaction of the triplet state of BBN, the mechanism of which, lacking further experimental data and adequate theoretical concepts, must be placed in the general class of triplet–exciplex quenching (eq 4).

$$\mathrm{BBN}^3 + \text{quencher} = (\mathrm{BBN}, \text{quencher})^* = \mathrm{BBN} + \text{quencher} + \text{heat} \quad (4)$$

This quenching mechanism was also verified by flash photolysis measurements. Measurements by this technique also demonstrated that this quenching mechanism is not unique to BBN, but also applies to 1-benzoylnaphthalene (3). Owing to overlapping triplet–triplet absorption in BBN and such quenchers as 2-methylanthraquinone, thioxanthone, and Michler's ketone, the kinetic measurements utilizing flash excitation were complicated, and corrections had to be applied carefully to the kinetic analyses; reliable rate constants were not obtained with Michler's ketone as quencher. The quencher, 10,10-dimethylanthrone, by contrast, has no triplet–triplet absorption in solution at the same wavelength as BBN and is therefore particularly suited for the quenching measurements by flash photolysis. The results are listed in Tables III and V.

Although the mechanism of this quenching is nonclassical, several recent reports of such mechanisms have come to our attention, both in the singlet[23] and triplet states,[24] with products ranging from chemical adducts and dimers to electronically and vibrationally excited states of the components of the exciplex. It is hoped that further developments in this field will lead to adequate theories to account for the details of such mechanisms.

Table V. Rate Constants for Quenching of the Triplet States of BBN and 3 by 2-Methylanthraquinone and 10,10-Dimethylanthrone as Measured by Flash Photolysis

Quencher	k_q (BBN)	k_q (3)
2-Methylanthraquinone	8×10^6	8×10^6
10,10-Dimethylanthrone	8×10^5	2×10^5

Conclusions

(1) The Norrish type II rearrangement of BBN occurs from the lowest $\pi-\pi^*$ triplet state *via* mixing with a higher n,π^* triplet state.

(2) The activation energy for the hydrogen abstraction step is consistent with only partial localization of the excitation onto the carbonyl.

(3) The long-lived triplet state of BBN and other naphthyl phenyl ketones can be quenched by the ground state of several molecules of higher triplet energy in an exciplex process.

Experimental Section

Syntheses. 7,8-Diphenylacenaphthene-7,8-diol was prepared in 82% yield by the method of Bachmann and Chu.[25]

1,8-Dibenzoylnaphthalene was prepared by adding 97 g of diphenylacenaphthenediol to a refluxing solution of 320 g of sodium dichromate in 2 l. of acetic acid. After 5 hr, the reaction mixture was cooled to room temperature and poured into 2 l. of water–ice. The resulting precipitate was filtered and washed with 10% sodium carbonate and with water. Crystallization from chloroform–hexane gave white crystals (82 g, 86% yield), mp 176–178°. Recrystallization raised the melting point to 186–188°.

1,3-Dihydro-1,3-diphenyl-1-hydroxynaphtho[1,8-*c*,*d*]pyran was prepared from 15 g of crude 1,8-dibenzoylnaphthalene in 200 ml of benzene, the mixture being dried by azeotropic distillation of water into a Dean–Stark trap. The hot solution was filtered through a 50:50 Norit–Celite pad and diluted with 200 ml of ether. Then 530 mg of $LiAlH_4$ was added and the mixture stirred for 16 hr at room temperature. Then 2 ml of saturated sodium sulfate solution was added and the mixture was stirred for 36 hr. $MgSO_4$ (5 g) was added and the mixture filtered. The filtrate was evaporated to dryness; the residue was dissolved in 25 ml of hot benzene and 60 ml of hexane was added. The product crystallized and was collected, yield 14.2 g (94%). The product was then recrystallized from chlorobenzene–heptane, mp 140–145°.

1,2-Dihydro-1,3-diphenylnaphtho[1,8-*c*,*d*]pyran was prepared from 5 g of the hydropyran in 50 ml of ether and 50 ml of benzene with 2 g of $LiAlH_4$ by stirring at room temperature for 3 days. After acid work-up, 100 ml of chloroform was added and the organic layer was dried and evaporated. The residue was recrystallized from benzene–hexane (3.9 g, 80% yield), mp 200–202°.

1-Benzoyl-8-benzylnaphthalene was prepared by refluxing equal weights of the dihydrodiphenylnaphthopyran and *p*-toluenesulfonic acid in xylene (10 ml/g) with a Dean–Stark water trap for 24 hr. After the mixture had cooled, an equal volume of benzene was added, the solution washed with sodium carbonate, and the solvent layer dried and evaporated. The resulting solid was sublimed from the melt under high vacuum, then recrystallized several times from benzene–hexane and from ethanol. The crystals formed very slowly and generally required standing overnight for good recovery: mp 139°; yield 50–70%; nmr, the benzylic protons appeared as a singlet at δ 4.17; *m*/*e* 322; ir 6.00 μ (strong), $CHCl_3$.

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Oxidation with sodium dichromate in acetic acid gave 1,8-dibenzoylnaphthalene (MMP).

The products of the rearrangement were isolated by long irradiation of 0.1 g of 1-benzoyl-8-benzylnaphthalene in 3 ml of degassed benzene. Nmr analysis of the mixture showed the starting material (12%) and the two product alcohols (88%) in a ratio of 1.4:1. Thick-layer silica gel chromatography in a benzene–solvent system resulted in the isolation of the trans alcohol, which from hexane gave white crystals: mp 110–115°; nmr singlet at δ 4.95 (CCl_4), 4.94 ($CDCl_3$), singlet at 1.75 (labile in D_2O); *m/e* 322; ir 2.92 μ (medium), 9.44 μ (strong), Nujol.

The cis alcohol was crystallized from ether and hexane to give white crystals: mp 147–148°; nmr singlet at δ 4.90 (CCl_4), 4.95 ($CDCl_3$), singlet at 2.50 (labile in D_2O); *m/e* 322; ir 2.91 (m), 3.00 sh, 9.60 μ (st), Nujol. Heating ether alcohol in acetic acid at 120° for 30 min gave 1,2-diphenylacenaphthylene.

Thioxanthone-^{18}O was prepared by adding 1 g of PCl_5 to 1 g of thioxanthone dissolved in 25 ml of methylene chloride. After the mixture had stood for several hours, red crystals of thioxanthone dichloride formed. These were collected and suspended in anhydrous ether. Then 100 μl of $H_2{}^{18}O$ (57–60%) was added followed by 5 ml of anhydrous dimethylformamide. When the mixture had changed from red to yellow, ethanol was added and the mixture warmed to dissolve the thioxanthone which was then allowed to crystallize slowly. The product was recrystallized twice more from ethanol. The mass spectrum showed mass 214 = 200 divisions, mass 212 = 180 divisions.

Thioxanthone-d_x was prepared by stirring 10 g of *o*-mercaptobenzoic acid, 100 ml of concentrated sulfuric acid, and 20 g of benzene-d_6 for 2 hr at room temperature. The mixture was poured onto ice, collected, and washed with water, dilute NaOH, and water again. The product was recrystallized three times from ethanol. The mass spectrum showed mass 212 = 130 divisions, 213 = 170 divisions, 214 = 120 divisions, 215 = 70 divisions, and 216 = 30 divisions.

Quantum yields were measured by irradiating degassed (three freeze–pump–thaw cycles with an oil-diffusion-pump vacuum), sealed Pyrex test tubes (13 × 100 mm) containing 3.2 ml of a solution of BBN in benzene in a windowed cell holder cemented to a 2-in.^{2} Corning color filter, No. 7-39. The color filter, along with a 0.52 filter, was taped to a Pyrex water jacket containing a 450-W medium-pressure mercury arc lamp. The remainder of the water jacket was covered with aluminum foil to exclude radiation not passing through the filter. The whole assembly was immersed in a 4-l. beaker filled with the thermostatically controlled temperature solution. The tube was equilibrated to the desired temperature, then placed in the cell holder and irradiated for times ranging from 15 to 30 sec. Tests showed the temperature of the solution did not change more than 0.2° during the short irradiation time. Then the tube was opened, and the contents were diluted and analyzed by uv spectroscopy in the case of pure BBN solutions, or by gas chromatography when quencher or sensitizer was present, which interfered with uv analysis. The actinometer for these measurements was the 0.1 *M* benzophenone-sensitized isomerization of 0.1 *M trans*-stilbene, for which a value of ϕ of 0.50 was used.[26,27]

The isomerization was generally carried out between 5 and 10% and was corrected for back reaction by the formula of Lamola and Hammond.[28] The extent of stilbene isomerization was measured by vpc columns packed with 10% silicon oil at 180° (thermal conductivity detector). A 50-μl sample was used in the analysis, and the peaks were cut and weighed and corrected for the 5% smaller response of *cis*-stilbene relative to *trans*-stilbene. This lamp–actinometer combination was reproducible within the limits of our measurement ($\approx \pm 2\%$).

The apparatus as described was found to produce about 10 μEinsteins of 365-nm radiation per minute per tube.

The same vpc columns were used for the BBN analysis but at 235°. The fraction lost (measured either by vpc or by nmr) was then used to calculate the quantum yield from the known lamp intensity measured by the actinometer.

Luminescence spectra were taken at 77°K in 2-methyltetrahydrofuran glass on a rotating sector phosphoriscope using two Bausch and Lomb 500-nm monochromators and a 1000-W xenon arc. The sample cells were ground and polished nmr tubes. The phosphorescence excitation spectra (PE) were taken on the same apparatus, monitoring the emission at 533 nm. Further details of this method can be found in Kearns and Case.[12] The PE spectra were corrected for xenon lines, but the phosphorescence was not corrected for phototube response. The ethyl iodide was from Eastman White Label used without purification. All absorption spectra were taken on a Cary 14 spectrophotometer at room temperature. Phosphorescence lifetimes (Figure 2) were determined by analyzing the output of the photomultiplier tube with an oscilloscope. A photograph of the oscilloscope trace was enlarged and the points in Figure 2 were measured by hand from the enlargement.

Flash photolysis measurements were carried out on an apparatus similar to that described by Calvert and Pitts.[29] The samples were contained in Pyrex cells under vacuum following degassing with four freeze–pump–thaw cycles. The decay of the triplets of BBN, **1**, and **2** was monitored at 560 nm. The output from the flash lamps was directed to the cell and passed through Corning 7-54 filters to minimize scattered light at the monitoring wavelength. The Pyrex cells had water jackets through which carefully thermostated water was passed. The temperature of the water was measured with thermocouples at the entrance and exit ports of the water jacket; there was no evidence for temperature increases in the samples following flash excitation. Porter has reported that thermal effects following flash photolysis are never important in solution reactions.[30] Even if there were small temperature increases subsequent to flash excitation in our experiments, they would be expected to be virtually uniform among the various samples. Oscillographs of triplet decay were enlarged and points on the curves were measured by hand. These points were then fitted to the best curve described by the equation

$$\frac{1}{A_t}\frac{dA_t}{dt} = \alpha + \beta A_t$$

where A_t is the absorbance of the BBN triplet at time *t*.[16] This was done by a nonlinear regression program on an IBM 360 computer, letting α, β, and the integration constant vary. The values obtained in this way for α were taken as the rate constants ($k_r + k_d$).

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