

position. Since our present equipment contains only a 400 channel analyzer, search of the usual 500 c.p.s. proton range requires dividing this range into six or seven sections. A 4096 channel analyzer would be ideal for a full range search and these are just becoming available.

Acknowledgment.—We wish to thank Dr. James N. Shoolery for several helpful discussions.

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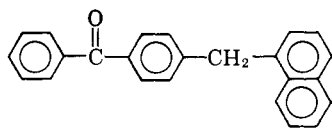
LEROY F. JOHNSON

RECEIVED FEBRUARY 4, 1963

Intramolecular Electronic Energy Transfer in 4-(1-Naphthylmethyl)benzophenone

Sir:

We have obtained evidence for intramolecular transfer of both singlet and triplet excitation in 4-(1-naphthylmethyl)benzophenone (I).¹



I

The absorption spectrum of I is virtually superimposable upon that of an equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone. That is, I contains two independent absorbing systems. I was used as sensitizer in the *cis-trans* isomerization of piperylene.²

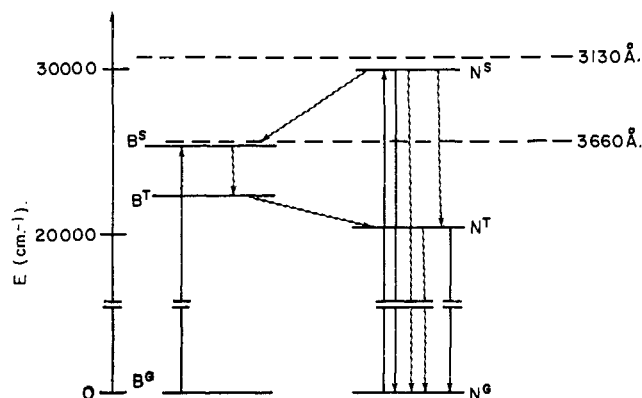


Fig. 1.—Excitation energies to the first excited singlet (S) and lowest triplet (T) states from ground (G) states of benzophenone (B) and naphthalene (N) moieties in 4-(1-naphthylmethyl)benzophenone; absorption and radiation are represented by straight arrows; wavy arrows represent radiationless processes.

Using light absorbed only by the benzophenone moiety,³ the photostationary *trans/cis* ratio obtained is 2.03 (*c.f.*, benzophenone, 1.30,⁴ and naphthalene, 2.18). Energy transfer from I to the piperylene must be taking place from a naphthalene-like triplet even though only the benzophenone moiety was initially excited.

Measurements of relative quantum yields for conversion of *cis*-piperylene to the *trans* isomer using 1-methylnaphthalene, I, and 4-methylbenzophenone, with light filtered to remove all components other than the 3130 Å. band, are given in Table I.

(1) The synthesis of I will be reported in a later paper.

(2) See G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962), for a discussion of sensitized olefin isomerizations.

(3) 1-Methylnaphthalene does not absorb at wave lengths longer than 3200 Å.; λ_{max} for the $n \rightarrow \pi^*$ transition in benzophenone lies at 3430 Å. (ϵ 132).

(4) N. J. Turro, unpublished results.

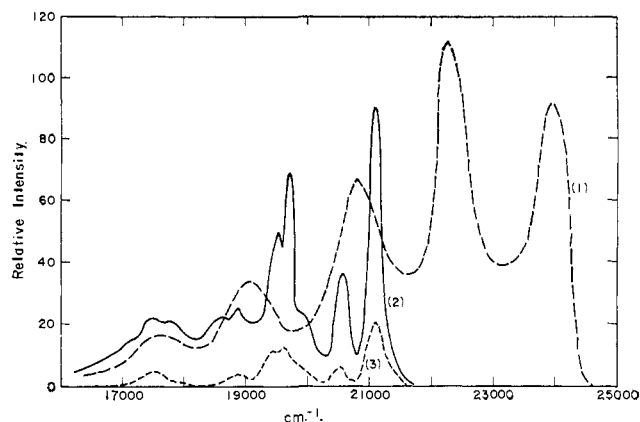


Fig. 2.—Phosphorescence from EPA solutions at 77°K.: (1) equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone, (2) 4-(1-naphthylmethyl)benzophenone, (3) 1-methylnaphthalene.

Since energy transfer from 1-methylnaphthalene triplets to *cis*-piperylene is probably as efficient as transfer from 4-methylbenzophenone triplets,⁵ the low relative quantum yield for 1-methylnaphthalene is attributed to relatively low efficiency of intersystem crossing.⁷ A sequence of intramolecular energy transfers (Fig. 1) would allow efficient intersystem crossing in the ketonic moiety to implement efficient conversion of I to naphthalene-like triplets. Spectroscopic evidence for such a sequence is clear.

TABLE I

RELATIVE QUANTUM YIELDS FOR THE SENSITIZED ISOMERIZATION OF *cis*-PIPERYLENE^a AT ROOM TEMPERATURE

Sensitizer	$\phi_c \rightarrow t$
4-Methylbenzophenone	1.00
I	0.83
1-Methylnaphthalene	0.34

^a Degassed benzene solutions containing 0.1 M *cis*-piperylene and 0.05 M sensitizer were irradiated. Relative quantum yields were obtained by comparing the amount of *trans*-piperylene produced in samples irradiated simultaneously. All incident light was absorbed and reactions were carried only to low conversion.

The only emission detected⁹ from an equimolar mixture of 1-methylnaphthalene and 4-methylbenzophenone under excitation with 3660 Å. light was that of 4-methylbenzophenone; apparently, at the concentrations employed (5×10^{-3} M) there is little intermolecular energy transfer.¹⁰ The phosphorescence spectrum of I, however, is almost identical with that of 1-methylnaphthalene (Table II) even when only the benzophenone moiety is excited.

No emission characteristic of 4-methylbenzophenone was observed from I under conditions where 0.1%

(5) Transfers exothermic by about four or more kilocalories are diffusion controlled.⁶ The lowest triplet of *cis*-piperylene lies 4 kcal. below that of 1-methylnaphthalene and 12 kcal. below that of 4-methylbenzophenone. The high concentration of *cis*-piperylene ensured that sensitizer triplets were quenched by piperylene.

(6) K. Sandros and H. Bäckstrom, *Acta Chem. Scand.*, **16**, 958 (1962).

(7) The efficiency of intersystem crossing is similar in 4-methylbenzophenone and benzophenone; the efficiency in the latter case has been judged to be unity⁴ but may be slightly lower.

(8) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(9) Emission spectra were measured in EPA at 77°K. with a photoelectric spectrophosphorimeter consisting of a Jarrell-Ash Ebert scanning monochromator (*f*/9), an EMI 9558 photomultiplier tube, a "rotating can" phosphoroscope, and appropriate recording electronics. A General Electric AH4 source was employed along with appropriate Corning glass or interference filters to isolate the groups of mercury lines near 3130 and 3660 Å. For fluorescence studies the phosphoroscope was removed.

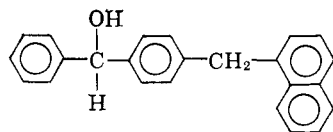
(10) A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

TABLE II
PHOSPHORESCENCE MAXIMA, EPA AT 77°K. IN CM.⁻¹

I	II	1-Methylnaphthalene
21,097	21,097	21,044
20,576	20,584	20,534
19,700	19,708	19,635
19,547	19,547	19,500

emission from benzophenone could have been detected (Fig. 2).

Apparently, efficient transfer of triplet excitation from the benzophenone moiety to the naphthalene moiety of I occurs. Singlet excitation transfer from a benzophenone to a naphthalene is unlikely since the first excited singlet level of benzophenone lies about 3000 cm.⁻¹ lower than the first excited singlet level of naphthalene. The lowest triplet state of benzophenone lies about 3000 cm.⁻¹ higher than the lowest triplet state of naphthalene and efficient triplet energy transfer can occur. Transfer of singlet excitation from the naphthalene unit to the benzophenone moiety is energetically possible and must occur with high efficiency¹¹ when I is excited with light adsorbed by the naphthalene nucleus. Fluorescence from 1-methylnaphthalene (O-O band 31,397 cm.⁻¹) is nearly ten times more intense than fluorescence from I (O-O band 31,348 cm.⁻¹). Direct involvement of the carbonyl group of I in fluorescence quenching is indicated by the fact that fluorescence of II (O-O band at 31,505 cm.⁻¹) is as intense as that of 1-methylnaphthalene.



II

The large difference between the intensities of fluorescence from I and II is attributed to loss of singlet excitation from the naphthalene nucleus of I to the ketonic part of the molecule. While the excitation is in the carbonyl-containing unit, efficient intersystem crossing to a triplet state occurs and the excitation then returns to the naphthalene unit.

Acknowledgment.—The work performed at Wesleyan University was supported by Grant No. 1467-B5 from the Petroleum Research Fund of the American Chemical Society. The work carried out at the California Institute of Technology was supported by the National Science Foundation.

(11) O. Schnepf and M. Levy, *J. Am. Chem. Soc.*, **84**, 172 (1962), and references therein.

(12) National Science Foundation Predoctoral Fellow.

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The Role of $n \rightarrow \pi^*$ Triplet in the Photochemical Enolization of *o*-Benzylbenzophenone¹

Sir:

The identification of reactive excited states in photochemistry is a subject of current interest. The $n \rightarrow \pi^*$ triplet state of the aromatic ketones has been shown to be the intermediate in intermolecular photochemical

(1) The work was presented in part at the Photochemistry Symposium in Rochester, N. Y., on March 27, 1963.

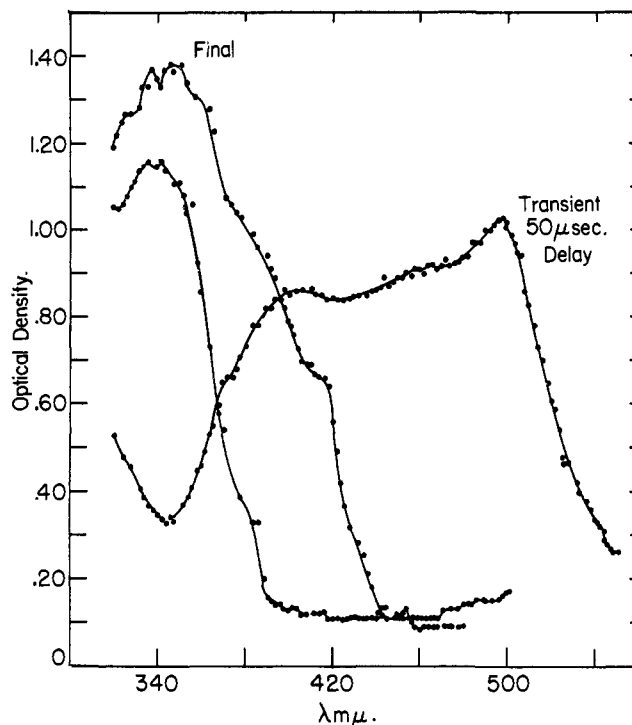
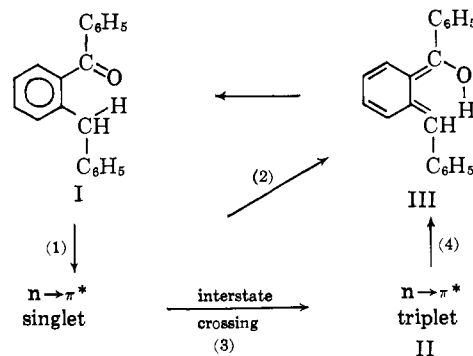


Figure 1.

reactions,²⁻⁶ while in the intramolecular type II process the singlet excited state was suggested as the reactive intermediate.⁷ *o*-Benzylbenzophenone undergoes an intramolecular photoenolization, a reaction analogous to the type II process,⁸ and the photoenol thus formed reverts back to benzylbenzophenone in a dark reaction. On the basis of the two possible reactive excited states, the photoenolization may proceed directly through the $n \rightarrow \pi^*$ singlet excited state (reactions 1 and 2) or it may proceed through the $n \rightarrow \pi^*$ triplet as the intermediate (reactions 1, 3, and 4). By flash spectroscopy we have now demonstrated that the triplet is the reactive intermediate in this intramolecular reaction.



o-Benzylbenzophenone (I), the $n \rightarrow \pi^*$ triplet state (II), and the enol (III) will all exhibit measurable electronic absorption spectra under the experimental conditions, while the $n \rightarrow \pi^*$ singlet will have too short a lifetime to be detected. The flash photolysis and spectroscopy of I were carried out in cylindrical Pyrex cells ($l = 26$ cm.) with full intensity of the flash light source

(2) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **83**, 2789 (1961), and related papers.

(3) J. N. Pitts, H. W. Johnson, Jr., and T. Kawana, *J. Phys. Chem.*, **66**, 2456 (1962).

(4) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

(5) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

(6) H. L. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(7) V. Brunet and W. A. Noyes, Jr., *Bull. soc. chim. France*, 121 (1958).

(8) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961).