(0.05 ml) and anhydrous HF (1.5 ml) were added. The colorless solution turned brown-red within several minutes. It was kept at room temperature for 60 min whereupon the hydrogen fluoride was evaporated in a stream of dry nitrogen gas. The residue was triturated with dry ether and the solvent was removed by centrifugation. The powder which had sedimented was dried under vacuum (1 mm).

Final removal of the *p*-nitrobenzyl-protecting group was effected by catalytic hydrogenation. The dry powder was dissolved in acetic acid (90%, 5 ml), 100 mg of 5% Pd on $BaSO_4$ was added, and the hydrogenation was carried out for 2 days at atmospheric pressure. An additional amount of catalyst (100 mg) was added and the hydrogenation was continued for another 2 days. The yellow solution became gradually colorless during the reduction. The catalyst was then filtered and washed with 85% acetic acid. The filtrate and washings were combined and evaporated to dryness under vacuum (1 mm). The residue was dissolved in a few milliliters of water and lyophilized to give a colorless solid preparation of crude bradykinin (48 mg). The crude nonapeptide yielded on acid hydrolysis (6 *N* HCl, 22 hr) a molar amino acid ratio of Arg, 2.05; Phe, 1.98; Pro, 2.98; Ser, 0.96; and Gly, 1.00. The homogeneity of the product obtained was checked by paper electrophoresis (pH 1.5, 3.5, and 6.5) and by paper chromatography using *n*-butyl alcohol–acetic acid–water (4:1:1), 80% pyridine, or 1-propyl alcohol–water (2:1) as developers. Comparison of the patterns obtained, using ninhydrin and Sagakuchi reagents, respectively, with the corresponding patterns given by an authentic sample of bradykinin (kindly supplied by Dr. Sakakibara) revealed that the crude bradykinin synthesized contained traces of arginine and *p*-toluidine and probably traces of unreduced nonapeptide ester. Final purification was effected on IRC-50 ion-exchange resin which had been equilibrated with 1 *M* acetic acid according to Merrifield.[6]

The pure bradykinin obtained (31 mg) yielded on acid hydrolysis: Arg, 2.12; Phe, 1.85; Pro, 3.05; Ser, 0.90; and Gly, 1.10. Its biological activity as assayed by the guinea pig ileum contraction test,[8] or by the Edery sensitization test,[9] was found identical with that of an authentic sample of the biologically active nonapeptide.

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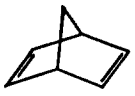
Communications to the Editor

Mechanisms of Photochemical Reactions in Solution. LIV.[1] A New Mechanism for Photosensitization

Sir:

In this and the accompanying report[2] we report what we believe to be the first clearly documented cases of photosensitized reactions in which the act of energy transfer apparently involves conversion of electronic to vibrational energy. The work is closely related to our studies of quenching of the fluorescence of aromatic compounds by substances having no low-lying excited singlet states.[3]

Since we have found that conjugated dienes are effective quenchers, a logical extension of the study was to look for reactivity in bicycloheptadiene (**1**). The compound contains two centers of unsaturation which interact strongly even though they are not in direct conjugation.



1

2

We find that **1** quenches the fluorescence of naphthalene with a rate constant of 1.3×10^7 l. mole^{-1} sec^{-1}. This rate is slightly slower than quenching by piperylene (3.4×10^7 l. mole^{-1} sec^{-1}) but is faster than quenching by cyclohexene or cyclopentene ($\sim 5 \times 10^6$ l. mole^{-1} sec^{-1}). In the course of the study we checked to determine whether or not quenching was accompanied by formation of quadricyclene (**2**) since the isomerization **1** → **2** has been accomplished by both direct excitation[4] and triplet energy transfer.[5] No detectable reaction occurred.

To our considerable surprise, we find that **2** *is a very reactive quencher and that quenching is accompanied by isomerization of* **2** *to* **1** *with an efficiency of about 50%.* The rate constant for the quenching reaction was measured by observing the reduction in the intensity of naphthalene fluorescence in the presence of varying concentrations of quadricyclene.

$$\frac{\tau_0}{\tau} = 1 + k_q\tau[Q] \qquad (1)$$

The value of k_q is 3.2×10^9 l. mole^{-1} sec^{-1}. With the concentration of **2** of 0.6 *M* the quantum yield for the production of **1** is 0.52 ± 0.01.

We visualize the mechanisms of quenching and isomerization are as shown in eq 2–6. $A^{*(1)}$ is an exciplex[6]

$$S \xrightarrow{h\nu} S^{*(1)} \qquad (2)$$

$$S^{*(1)} \xrightarrow{k_i} S^{*(3)} \qquad (3)$$

$$S^{*(1)} + 2 \xrightarrow{k_q} A^{*(1)} \qquad (4)$$

$$A^{*(1)} \xrightarrow{k_1} S + 1 \qquad (5)$$

$$A^{*(1)} \xrightarrow{k_2} S + 2 \qquad (6)$$

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(4) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

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(6) The term "exciplex" is intended to be nonspecific as to the kind of binding forces involved. We are inclined to believe that weak attractions are generated by exciton interaction and possibly by charge transfer, since we expect the ground state of the complex to be essentially nonbonding. However, we have no way to rule out the possibility that localized bonds between the partners may be formed and eventually broken again. Specifically, a Schenck mechanism[7] cannot be entirely ruled out.

formed by weak interaction of the excited sensitizer with quadricyclene. Reactions 5 and 6 are two paths for nonradiative decay of the exciplex. Both nonradiative processes must be very fast since no new fluorescence is observed in the presence of the quencher. Reactions 5 and 6 may involve a common first step, production of a vibrationally excited form of **2**, which then partitions between relaxation paths that produce **1** and **2**. The internal conversion reaction must depend in a critical way on coupling between the vibrational modes of the quencher and the electronic excitation of the complex. This conclusion is compelled especially strongly by comparison of the behavior of **1** and **2**. We presume that the binding energy of an exciplex containing **1** would be lower than that of the exciplex from **2**, since the singlet excitation energy of **2** is higher than that of **1**. However, **1** is much less efficient as a quencher and undergoes no significant chemical change when it does quench naphthalene singlets. If the entire 90 kcal mole^{-1} energy available in excited naphthalene singlets were transferred to the quenchers, the latter would be endowed with energy far in excess of that required to produce the transition state involved in the thermal isomerization of **2** to **1**.[8] A common species cannot be produced from the two isomers during the quenching process.

We have observed a number of other cases of singlet sensitization in cases in which the energy acceptor has no known excited singlet states lying below the lowest excited singlet of the sensitizer. Many other aromatic hydrocarbons sensitize the conversion of **2** to **1** in parallel with quenching of fluorescence,[10] and the accompanying report[2] shows that sensitized isomerization of sulfoxides can follow the same mechanism. An especially interesting example is the sensitized *cis–trans* isomerization of the 1,2-diphenylcyclopropanes. In early reports we have shown that the reaction can be effected using sensitizers having low triplet excitation energies[11] and that the use of an optically active napththalene derivative as a sensitizer leads to considerable asymmetric induction.[12] We now find that sensitization by naphthalene and its derivatives requires interaction between substrates and the excited singlet states of the sensitizers. The demonstration follows the same lines as those described above. The quantum yield for the sensitized reaction, although lower than in the sensitized conversion of **2** to **1**, quantitatively parallels quenching of the fluorescence of the sensitizers. Furthermore, piperylene, which can be isomerized by naphthalene by the triplet mechanism, has only a very weak quenching effect on the sensitized isomerization of the diphenylcyclopropanes; however, 2,5-dimethyl-2,4-hexadiene, a much more powerful singlet quencher than piperylene,[3b] quenches the isomerization of the diphenylcyclopropanes very stongly.

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(13) National Institutes of Health Postdoctoral Fellow, 1967–1968.

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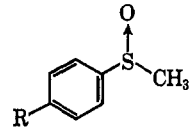
Mechanisms of Photochemical Reactions in Solution. LV.[1] Naphthalene-Sensitized Photoracemization of Sulfoxides

Sir:

Mislow, *et al.*,[2] first observed that the pyramidal inversion of some aryl alkyl sulfoxides could be effected photochemically using naphthalene as a sensitizer. Reinvestigation of these results has lead to a rather different mechanism from the one originally proposed.[3]

The energy levels of **1** have been determined spectroscopically. The first excited singlet state of racemic **1a** is placed at about 113 kcal mole^{-1} based on the



1a, R = CH_3
b, R = Br
c, R = OH

maximum of the ^1L_b band[4] occurring at 2530 Å. The energy of the first triplet state of racemic **1b** was determined from the weak and structureless phosphorescence in an ether–alcohol glass (1:2 by volume) and the structured singlet–triplet absorption spectrum of this compound in chloroform solution. The phosphorescence and singlet–triplet absorption are mirror images and place the triplet state at 79 kcal mole^{-1}. These results imply that electronic energy transfer from either the singlet or the triplet state of naphthalene to the sulfoxide to produce the corresponding excited state of the latter is highly endothermic (by 23 and 18 kcal mole^{-1}, respectively) and should not occur at any appreciable rate.

The possibility of ground-state complex formation between racemic **1b** and naphthalene has been ruled out on the basis of the absorption spectrum of a mixture which shows no anomalous bands in the 2400–3500-Å region. Irradiation of degassed solutions of naphthalene and either **1b** or **1c**, with light absorbed only by naphthalene (λ 3130 Å), led to formation of new products, but the quantum yield was only 1% of that for sensitized racemization. The only isolated products were the corresponding sulfides.

These observations limit the mechanisms to be considered for the sensitized racemization of **1**. Other results from this laboratory[5] suggested that the mechanism

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(5) Reference 1 and references cited therein.