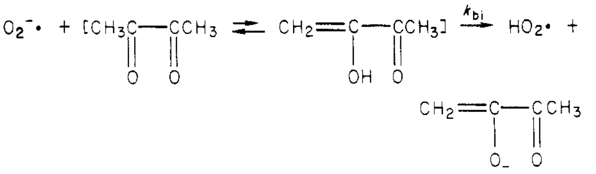
by $O_2^{-}\cdot$ from the enol tautomer with disproportionation of $HO_2\cdot$ (eq 5 for 2,3-butanedione).

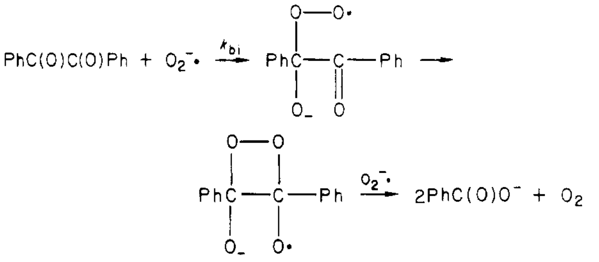


$$O_2^{-}\cdot + [CH_3C(O)C(O)CH_3 \rightleftharpoons CH_2{=}C(OH)C(O)CH_3] \xrightarrow{k_{bi}} HO_2\cdot + CH_2{=}C(O^{-})C(O)CH_3 \quad (5a)$$

$$HO_2\cdot + HO_2\cdot \xrightarrow{fast} H_2O_2 + O_2 \quad (5b)$$

An analogous interpretation has been given for the deprotonation of 1,3-diketones by KO_2/18-crown-6 ether in benzene.[10] The resulting enolates are reported to be resistent to oxidation by O_2 and $O_2^{-}\cdot$.

Benzil. The absence of α-hydrogens precludes enolization of benzil (PhC(O)C(O)Ph). Hence, it does not have significant protic character and cannot induce disproportionation of $O_2^{-}\cdot$ via transfer of a proton. The reaction stoichiometry, kinetics, and products for the facile $O_2^{-}\cdot$-benzil process (Table I) are consistent with nucleophilic addition to a carbonyl carbon as the primary step, followed by cyclization on the second carbonyl carbon to give a dioxetane radical (eq 6). In the presence of excess $O_2^{-}\cdot$ the latter is reduced and dissociates to give two benzoate ions and O_2 (Table I). Such a dioxetane closing has precedent for the unsaturated carbons of vinyl peroxy radicals.[11] However, the present system involves a radical addition to a carbon-oxygen double bond, which is believed to be a novel process.



(6)

The chemistry for the $O_2^{-}\cdot$-benzil reaction appears to be analogous to that for the oxygenation by $O_2^{-}\cdot$ of dehydroascorbic acid (an α,β-tricarbonyl) to give threonate ion and oxalate.[6] For the latter system a mechanistic path similar to eq 6 has been proposed on the basis of the reaction stoichiometries, kinetics, and products (the rate constant (k_{bi}) in DMF is 3.3×10^4 M^{-1} s^{-1}).

The earlier suggestion[5] that $O_2^{-}\cdot$ reacts by electron transfer to benzil is not consistent with the respective reduction potentials in DMF (benzil, $E^{\circ\prime} \approx -1.2$ V vs. SCE; $O_2/O_2^{-}\cdot$, $E^{\circ\prime} \approx -0.8$ V) and the rapid reaction rate. Also, initial formation of benzil anion radical via electron transfer would lead to a diversity of products via subsequent reactions with O_2, $O_2^{-}\cdot$, and the media. The observed 2:1 $O_2^{-}\cdot$-benzil reaction stoichiometry with the exclusive quantitative production of two benzoate ions and one O_2 molecule and facile second-order kinetics are consistent with the initial nucleophilic addition to carbonyl carbon that is outlined by eq 6.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-8212299. We are grateful to Professor Julian L. Roberts, Jr. (University of Redlands) for assistance with the kinetic measurements by means of the rotated ring-disk electrode technique.

Registry No. O_2^{-}, 11062-77-4; 2,3-butanedione, 431-03-8; 2,3-pentanedione, 600-14-6; ethyl pyruvate, 617-35-6; benzil, 134-81-6.

---

(10) Frimer, A. F.; Gilinsky-Sharon, P.; Aljadeff, G. *Tetrahedron Lett.* 1982, *23*, 1301.

(11) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 698.

Photochemical Behavior of 2-Phenylbenzoxazole. Synthesis of 1,3-Diazetidine via the Intermolecular $[2_\pi + 2_\pi]$ Cycloaddition of Two Carbon-Nitrogen Double Bonds

Jacques Roussilhe, Evelyne Fargin, André Lopez, Bernard Despax, and Nicole Paillous*

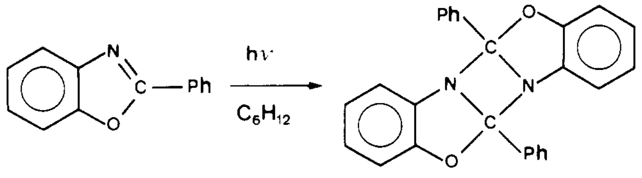
Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique, ERA au CNRS No. 264, Université Paul Sabatier, 31062 Toulouse Cedex, France

Received December 1, 1982

The photochemical behavior of 2-phenylbenzoxazole (1) in cyclohexane solutions is investigated. In concentrated solutions, photodimerization of 2-phenylbenzoxazole is observed ($\phi \simeq 0.08$). In dilute solutions, this reaction is no longer efficient, and only a very slow reaction with cyclohexane takes place, leading to photoaddition and photosubstitution products with a low quantum yield ($\phi < 1.5 \times 10^{-3}$). Photosensitization and quenching experiments as well as heavy-atom effects indicated that the two reactions derive from different excited states. The photodimerization occurs from the singlet excited state and the reaction with the solvent from the triplet state. Photodimer 2 is stable in the solid state at room temperature but reverts to 1 quantitatively in solution. The rate of the cycloreversion reaction can be enhanced either by catalysis or by irradiation. The activation barrier determined by UV measurements was found to be 90 kJ mol^{-1}. By use of microcalorimetric experiments, the molar enthalpy of reversion was found to be -116 kJ mol^{-1}. For application of this new system to light energy conversion, the recycling capacity of the interconvertion process as well as the heterogeneous catalysis of the thermal reversion was studied.

Although the photochemical behavior of compounds containing C=N double bonds is now being extensively investigated, it has not developed as rapidly as the photochemistry of carbonyl compounds.[1-3] The reason gen-

Scheme I



1

2

erally invoked is the poorer reactivity of the excited C=N double bond due to its rapid decay processes. In the benzoxazole series, in particular, many 2-aryl-substituted compounds are highly fluorescent.[4] As these compounds can be prepared by irradiation of benzisoxazoles,[5-9] they could be assumed to be fairly stable under UV light.

Only photochemical studies related to benzoxazoles which are not 2-substituted have been reported. These compounds give rise to intermolecular reactions involving the hydrogen atoms in the 2-position in the heterocycle. So, irradiation of benzoxazole leads to an oxidative coupling reaction in the presence of oxygen.[10] In the case of phenanthro[9,10]oxazole a photoalkylation occurs at the 2-position.[11]

In this paper we report the photochemical behavior of a 2-aryl-substituted compound, 2-phenylbenzoxazole.[12] Unexpectedly, we found that 2-phenylbenzoxazole undergoes a photodimerization reaction involving two C=N double bonds. Although cycloaddition reactions between two C=C double bonds or between a C=C and a C=N double bond are well-known, the occurrence of such a reaction between two C=N bonds is much more unusual. Only one example concerning fluoro imines has been reported by Margaretha.[13]

Results

According to the concentration of the medium, the irradiation of 2-phenylbenzoxazole induces two different reactions.

Photodimerization of 2-Phenylbenzoxazole in Concentrated Medium. Photolysis of degassed concentrated solutions of 2-phenylbenzoxazole in cyclohexane was carried out at 20 °C in Pyrex tubes with 300-nm UV lamps.

The irradiation of 1 ($c = 10^{-1}$ M) for 6 h led to the selective formation of a photoproduct which precipitates in the medium. The compound so obtained (80% conversion) proved to be a dimer as shown by elemental analysis and DCI mass spectrometry. The photodimerization process may involve either the C=N double bond or the double bonds of the aromatic rings. The IR spectrum of dimer 2 exhibits a drastic decrease in the intensities of both $\nu_{C=N}$ (1620 cm^{-1}) and $\nu_{N=C-O}$ (1550 cm^{-1}) vibrations, thus demonstrating the participation of the C=N double bond. The phenyl groups, however, do not seem to be concerned, no high-field signal being detected in the ^{1}H NMR spectrum. Thus, it can be concluded that dimer 2 results from a [2 + 2] cycloaddition between two C=N bonds.

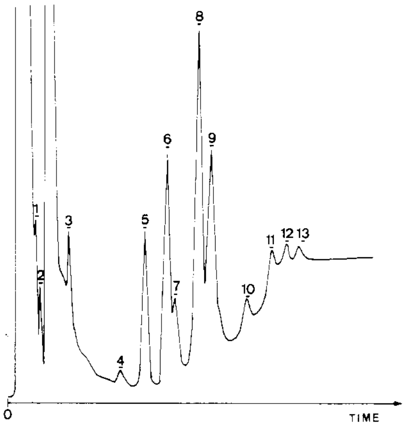


Figure 1. VPC analysis of irradiation mixture of 2-phenylbenzoxazole in cyclohexane solution ($c = 5.10^{-3}$ M, $t = 280$ h).

To discriminate between a head to head and a head to tail photodimer, 2-phenylbenzoxazole, ^{13}C labeled on the carbon atom in the 2-position, was synthesized. The ^{13}C NMR spectrum of the corresponding photodimer only exhibits a singlet ($\Delta\nu_{1/2} = 6$ Hz) at 123.3 ppm for the two labeled carbon atoms (the ^{13}C in 2-phenylbenzoxazole being at 163.6 ppm). The magnetic equivalence of the two ^{13}C atoms is consistent with a 1,3-diazetidine structure, since for a 1,2-diazetidine two signals corresponding to vicinal coupling would be expected ($J_{^{13}C-^{13}C} \simeq 30\text{–}50$ Hz)[14] (Scheme I).

Reaction with the Solvent in Dilute Medium. The photodimerization is efficient as long as the medium is concentrated enough ($\phi \simeq 0.08$, $c = 10^{-1}$ M). In a dilute medium ($c < 10^{-2}$ M) this reaction is no longer observed even though the 2-phenylbenzoxazole still absorbs all the light. Irradiation of a solution of 1 in cyclohexane (5×10^{-3} M) for 280 h gives a mixture of 14 new products, with a very poor quantum yield ($\phi_{total} < 1.5 \times 10^{-3}$). Analysis by VPC/mass spectrometry of the mixture (Figure 1) indicates that these compounds result from an interaction with the solvent (except for the first three compounds which were not analyzed). The most abundant photoproduct 8 (28% of all the photoproducts) results from the addition of a molecule of cyclohexane to 2-phenylbenzoxazole (m/e 279). Compounds 4–7 and 9 (52%) correspond to the substitution of a hydrogen atom of the substrate by a cyclohexyl group (m/e 277). Compounds of higher molecular weights (10–13) are also obtained but in very low yields. Most likely, the substitution products result first from an addition of solvent on either of the two phenyl rings followed by a rearomatization of the whole molecule due to presence of air after opening the sealed tubes (Scheme II). Such additions are uncommon although some of them have already been observed in aromatic series.[15-19]

---

[1] Wettermark, G. "The Chemistry of the Carbon Nitrogen Double Bond"; Patai, S., Ed.; Wiley-Interscience: New York, Chapter 12, p 565. Beak, P.; Messer, A. "Organic Photochemistry"; Chapman, O. L., Ed.; Marcel Decker, New York, 1969; Vol. II, p 117.

[2] Pratt, A. C. *Chem. Soc. Rev.* **1977**, *6*, 63.

[3] Padwa, A. *Chem. Rev.* **1977**, *77*, 37.

[4] Reiser, A.; Leyshon, L. J.; Saunders, D.; Mijovic, M. V.; Bright, A.; Bogie, J. *J. Am. Chem. Soc.* **1972**, *94*, 2414.

[5] Ferris, J. P.; Antonucci, F. R.; Trimmer, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 919.

[6] Ferris, J. P.; Antonucci, F. R. *J. Am. Chem. Soc.* **1974**, *96*, 2014.

[7] Goth, H.; Schmidt, H. *Chimia* **1966**, *20*, 148.

[8] Heinzelmann, W.; Marky, M. *Helv. Chim. Acta* **1974**, *57*, 376.

[9] Grellman, K. H.; Tauer, E. *J. Photochem.* **1977**, *6*, 365.

[10] Grellman, K. H.; Tauer, E. *Tetrahedron Lett.* **1974**, 375.

[11] Maeda, M.; Iwase, Y.; Kojima, M. *J. Heterocycl. Chem.* **1976**, *13*, 221.

[12] Roussilhe, J.; Despax, B.; Lopez, A.; Paillous, N. *J. Chem. Soc., Chem. Commun.* **1982**, 380.

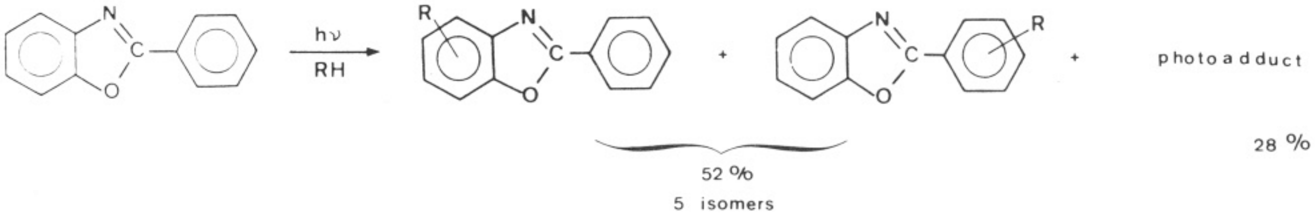
[13] Margaretha, P. *Helv. Chim. Acta* **1982**, *65*, 290.

[14] Breitmaier, E.; Voelter, W. "^{13}C NMR spectroscopy"; Verlag Chemie: Weinheim/Bergstr., Germany, 1974; p 98.

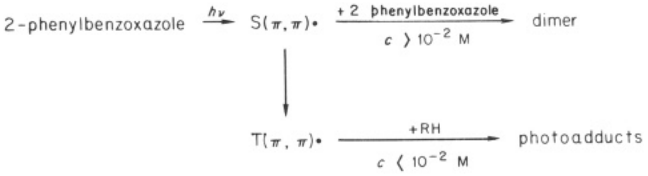
[15] Caplain, S.; Castellano, A.; Catteau, J. P.; Lablache-Combier, A. *Tetrahedron* **1971**, *27*, 3541. Caplain, S.; Catteau, J. P.; Lablache-Combier, A. *J. Chem. Soc. D* **1970**, 1475.

[16] Lamotte, M.; Risemberg, S.; Pereyre, J.; Joussot-Dubien, J. "Polynuclear Aromatic Hydrocarbons"; Jones, P. W., Lever, P.; Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1979; p 159.

Scheme II



Scheme III



Excited States. UV spectrophotometric investigations[20] as well as theoritical calculations[21] have demonstrated that the first excited state of 2-phenylbenzoxazole has a π,π^* character. Moreover, the relative positions of the lower excited states $S(\pi,\pi^*)$, $T(\pi,\pi^*)$, and $T(n,\pi^*)$ have been defined by Reiser.[4] In contrast to the situation reported for benzoxazole, it is likely that the π,π^* singlet state of 2-phenylbenzoxazole lies between the n,π^* triplet state and the π,π^* triplet state. The latter triplet state is the lowest excited state.[22] Its energy can be expected to be around 267.5 kJ. It is known from El Sayed's work[23] that for nitrogen heterocycles no spin–orbital coupling occurs between singlet and triplet states of the same electronic configuration. Consequently, in the case of 2-phenylbenzoxazole, the intersystem crossing ought to be slow. This agrees with the high fluorescence quantum yield of this compound ($\phi = 0.78$).

Considering these energy data, we carried out various experiments using benzophenone as sensitizer ($E_T = 286.3$ kJ) and naphthalene ($E_T = 254.5$ kJ) or *cis*-piperylene ($E_T = 243.7$ kJ) as quenchers. The quantum efficiencies of the reaction at an early stage (conversion <10%) were measured. ϕ_0 is the quantum yield of the formation of the photoproducts without additives and ϕ the yield of the same products after addition of sensitizer or quencher. It should be noted that in concentrated solutions ($c = 10^{-1}$ M) selective irradiation of benzophenone ($c = 2 \times 10^{-2}$ M) at 350 nm only gave photosubstitution products and no photodimer. The distribution of the photoproducts is rather the same as in direct irradiation in dilute medium. In the same way, irradiation of concentrated solutions of 2-phenylbenzoxazole containing piperylene or naphthalene (in such ratios that no more than 1% of the light was absorbed by the quencher) was carried out at 300 nm. In all cases only very small variations of the quantum yield of photodimerization were observed (ϕ_0/ϕ varying between 1.05 and 1.14).

The effect on the reaction rate of a heavy atom which enhances intersystem crossing was also investigated: addition of xenon to a concentrated solution of **1** (10^{-1} M) clearly decreases the rate of dimerization ($\phi_0/\phi = 5.25$) while at low concentrations (10^{-2} M) xenon increases the rate of photoreactions with the solvent ($\phi_0/\phi = 0.72$). From all these results, it can be concluded that the photodimerization involves the singlet excited state of 2-phenylbenzoxazole while the photoreaction with the solvent derives from the triplet state (Scheme III).

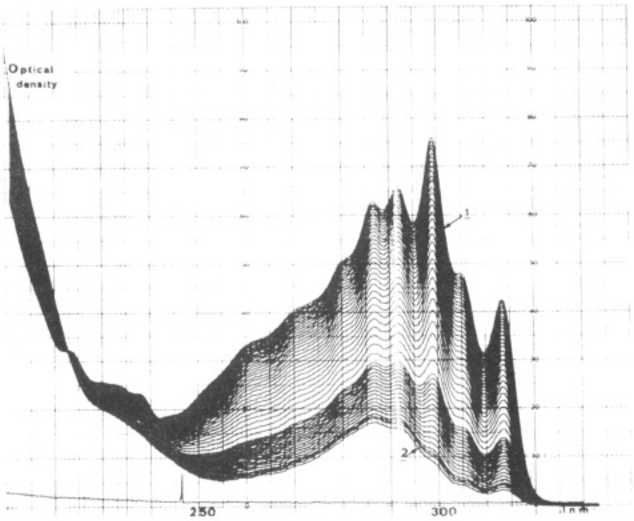


Figure 2. Spectral changes of a solution of photodimer **2** in cyclohexane at 30 °C.

Table I. Effect of Temperature on the Decomposition Rate Constant and on the Half-Life of Photodimer 2 in Cyclohexane Solution

temp, °C	$10^{-5}k_d$, s^{-1}	$t_{1/2}$, h
20	0.73 ± 0.02	26.2
25	1.36 ± 0.04	14.2
30	2.64 ± 0.09	7.3
35	4.05 ± 0.09	4.7

Stability of Photodimer 2. The photoproduct we mainly studied is the photodimer of 2-phenylbenzoxazole, the yield of other photoproducts being negligible even under the best conditions. At room temperature, photodimer **2** appears to be stable indefinitely but reverts to 2-phenylbenzoxazole on being heated to its melting point (mp 178 °C). In solution, this reaction occurs at lower temperatures. The first-order rate constants of reversion were determined at various temperatures by UV spectrophotometry (Figure 2). The results are summarized in Table I. From these data, we find the thermally induced conversion of **2** into **1** to be associated with an activation energy of 89.9 ± 6.3 kJ mol^{-1}, the Arrhenius preexponential factor being 2.6×10^{10}.

The conversion of dimer into monomer can be drastically enhanced by proton catalysis. Addition of traces of trifluoroacetic acid or *p*-toluenesulfonic acid to a benzene or cyclohexane solution of **2** gives **1** almost instantaneously. This effect is in agreement with Mackay's studies showing that the cleavage of diazetidines may be facilitated by the

---

[17] Lamotte, M.; Lapouyade, R.; Pereyre, J.; Joussot-Dubien, J. *C.R. Hebd. Seances Acad. Sci. Ser. C* **1980**, *290*, 211.

[18] Lamotte, M.; Lapouyade, R.; Pereyre, J.; Joussot-Dubien, J.; *J. Chem. Soc., Chem. Commun.* **1980**, 725.

[19] Joussot-Dubien, J.; Lamotte, M.; Pereyre, J. *J. Photochem.* **1981**, *17*, 347.

[20] Nurmukhametov, R. N.; Gobov, G. V.; Pushkina, L. N. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1967**, *41* (7), 831.

[21] Bazyl, O. K.; Gruzinskii, V.; Danilova, V. I.; Kopylova, T. N.; Maier, G. V. *Opt. Spectrosc.* (*Engl. Transl.*) **1980**, *48* (2), 147.

[22] Olszowski, A.; Romanowski, H.; Ruziewicz, Z. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1973**, *21* (4), 381.

[23] El Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834.

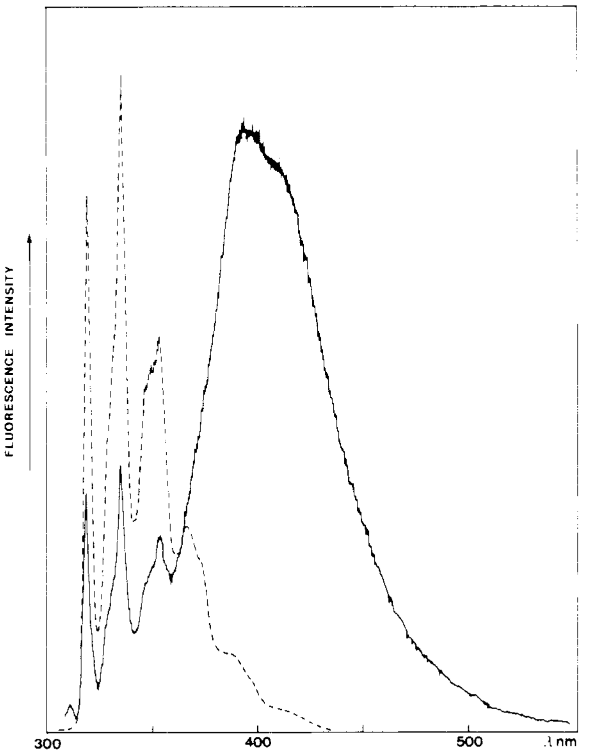


Figure 3. Fluorescence spectrum of the cleaved photodimer **2** in methylcyclohexane glass at 77 K (—); spectrum obtained after melting the glass at room temperature and refreezing at 77 K (···).

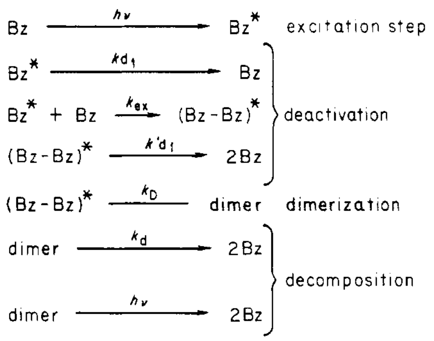
protonation of nitrogen atoms.[24]

The decomposition of photodimer **2** may also be induced photochemically. Irradiation at 300 nm of a solution of **2** gives **1** very rapidly. In spite of this photochemical reversion, the yield of photodimerization is very high. This result can be explained by the low absorption coefficient of the dimer ($\epsilon_1/\epsilon_2 = 12$ at 300 nm) and its low solubility which causes its precipitation, thus preventing it from being further irradiated.

Mechanism. The photodecomposition of dimer **2** allowed us to observe the formation of a 2-phenylbenzoxazole excimer. No excimer could be detected by studying the fluorescence of increasingly concentrated solutions of 2-phenylbenzoxazole. But it was easily observed by the method of Chandross.[25] The dimer in a methylcyclohexane matrix at 77 K (10^{-5} M) was cleaved by excitation at 285 nm in situ in the spectrofluorometer. After several minutes of irradiation, a fluorescence excimer appeared at wavelengths ($\lambda_{max} = 395$ nm) longer than those of the fluorescence of 2-phenylbenzoxazole ($\lambda_{max} = 325$ nm) and grew in intensity for about 15 min, after which it remained constant. The spectrum obtained after warming the glass at room temperature and refreezing it at 77 K was identical with the spectrum of 2-phenylbenzoxazole in methylcyclohexane (Figure 3). Moreover, the excitation spectra related to the short-wavelength and long-wavelength emissions are identical. This is evidence that the long-wavelength fluorescence is that of an excimer. So we can postulate the intermediacy of an excimer in the photodimerization process. However, we cannot completely discard the possibility of competition between excimer and photocyclomer formation.

Taking into account all the previous data, we postulate that the most likely mechanism is as shown in Scheme IV.

Scheme IV



Light Energy Conversion System. The photochemical formation of a highly strained compound which can easily revert to the starting material may be of possible use in the conversion of radiant energy to heat. In order for the system to be of interest, one of the most important conditions is that the energy stored per mole must be high.

The molar enthalpy of decomposition of **2** in a benzene solution was determined by microcalorimetric measurements. So as to make the thermal jump clear, the rate of decomposition was enhanced by proton catalysis. Addition of dimer to a benzene solution of CF_3COOH rapidly releases -142.0 ± 0.5 kJ mol^{-1}. This value is not only related to the molar enthalpy of decomposition ΔH_S but has to be corrected by taking into account the molar enthalpy of dissolution of the dimer ($+27.2 \pm 0.3$ kJ mol^{-1}) and the molar enthalpy of interaction between CF_3COOH and the resulting monomer. This latter value (-26.8 ± 0.1 kJ mol^{-1}) was determined by adding CF_3COOH to a benzene solution of 2-phenylbenzoxazole and taking into account the molar enthalpy of dissolution of CF_3COOH into benzene. The corrected value of the stored molar enthalpy is given in eq 1. The molar enthalpy competes favorably with the

$$\Delta H_S = -142.0 - 2(-26.8) - 27.2 = -116 \pm 1 \text{ kJ mol}^{-1} \quad (1)$$

molar enthalpies reported for other currently proposed reversible reactions. The energy storage of one of the most attractive interconversion processes, the norbornadiene $\rightleftarrows$ quadricyclene system, lies around -110 kJ mol^{-1}.[26]

Another requirement for the practical use of such a system is long-term recyclability. It implies that the extent of side reactions is low enough under our conditions. Attempts were made to determine the maximal number of cycles which can be performed until the concentration of 2-phenylbenzoxazole is too low for photodimerization to occur (i.e., residual concentration of $1 \simeq 10^{-2}$ M). Eighty repeated photochemical and thermal cycles were achieved under these conditions. Taking into account that the material balance was 90%, we calculated the maximal number of cycles to be about 1770. The byproducts formed in these experiments are the products previously detected by irradiating **1** in a dilute medium. Since these products arise from the triplet state, their formation may be slowed down by addition of a quencher such as pyrene ($E_T = 203.5$ kJ). Under these conditions, the material balance after 80 cycles is 94%, and the recycling capacity of the material may be increased to 2880. The total energy finally converted was calculated to be about 8.4×10^4 kJ kg^{-1}.

To promote further application of this work, we have also begun to look ahead to other aspects of the development. In particular, investigations are underway into polymeric catalysts for the thermal back-reaction. We have

---

[24] Mackay, D.; Pilger, C. W. *Can. J. Chem.* **1974**, *52*, 1114. Mackay, D.; Wong, L. L. *J. Chem. Soc., Chem. Commun.* **1974**, 621.

[25] Chandross, E. A. *J. Chem. Phys.* **1965**, *43*, 4175.

[26] Kabakoff, D. S.; Bunzli, J. C. G.; Oth, J. R. M.; Hammond, W. B.; Berson, J. A *J. Am. Chem. Soc.* **1975**, *97*, 1510.

shown that addition of polysulfone sulfonic acid can enhance the rate of thermal decomposition of photodimer 2.

Conclusion

The investigation of the photochemical behavior of 2-phenylbenzoxazole provided one the the first examples of a [2 + 2] involving two CN double bonds. This photodimerization reaction is a new method to obtain 1,3-diazetidines.

The interconversion between 2-phenylbenzoxazole and its photodimer has potential application in the field of solar energy. Due to the very low efficiency of the photochemical side reactions and of the high value of the molar enthalpy stored by the dimer, this system merits further consideration. The problems to be overcome to obtain a practical system mainly concern the enhancement of the photodimerization quantum yield and the shift of the required wavelength toward the red. Presently, the photodimerization is performed at 300 nm so that solar light cannot be used. Work is in progress in our laboratory to synthesis new compounds meeting these requirements.

Experimental Section

General Remarks. Elemental analyses were performed at the CNRS Central Microanalytical Laboratory, Villeurbanne. Melting points were determined on a Kofler block and are left uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Cameca 250-MHz spectrometer. Chemical shift values are reported in parts per million with internal tetramethylsilane as a reference. Infrared spectra were obtained from KBr pellets with a Perkin-Elmer Model 683 spectrophotometer. UV spectra were determined with a Beckman Acta IV UV-visible spectrophotometer. Emmission spectra were recorded on an Aminco SPF 500 (corrected spectra) spectrofluorometer. For low-temperature measurements, solutions of dimer in methylcyclohexane were placed in quartz tubes (~ 3 mm i.d.) and immersed in liquid nitrogen in a quartz Dewar flask. VPC analyses were performed with an Intersmat Model 16 C 112F gas chromatograph (flame-ionization detection). The column (1.5 m × 3 mm) consisted of 10% SE-30 on Chromosorb PAW 80-100. Peak integrals were measured by means of an LTT Icap Model 5 electronic integrator. Mass spectra were obtained by using a Ribermag R10-10 GC/MS system. DCI experiments were carried out on the same instrument with ammonia as ionization gas.

Synthesis of 2-Phenylbenzoxazole. 2-Phenylbenzoxazole was prepared in a one-pot synthesis, as already reported,[27] which was adapted from a method described for the synthesis of polybenzoxazoles by the Battelle Institute.[28] For the synthesis of the ^{13}C-labeled 2-phenylbenzoxazole, ^{13}C-labeled benzoic acid with an isotopic purity of 86% was converted to benzoyl-^{13}C chloride and then reacted with *o*-aminophenol.

General Procedure for Irradiation. This procedure was followed unless otherwise noted. Cyclohexane (Merck spectroquality) was used without further purification. Aliquots (4.0 mL) of the solutions were transferred to clean dry Pyrex tubes (diameter 14 mm). They were degassed by three freeze–pump–thaw cycles (pressure less than 10^{-5} torr) and the tubes then sealed under vacuum. Irradiation experiments were performed with a Rayonet RPR 100 reactor equipped with 16 mercury lamps (λ = 300 or 350 nm) and with a merry-go-round sample holder. Light intensities were monitored with potassium ferrioxalate[29] or cyclohexanone/2-propanol actinometry.[30] Due to the high molar extinction coefficient of 2-phenylbenzoxazole ($\epsilon_{299} = 28.2 \times 10^3$) all the directly irradiated solutions absorb entirely the 300-nm UV light whatever their concentration.

Table II. Influence of Quenchers in Concentrated Medium

[phenyl-2 benzoxazole], mol L^{-1}	quencher	[quencher], mol L^{-1}	ϕ_0/ϕ
5×10^{-2}	piperylene	1.6×10^{-3}	1.14
10^{-1}		2.5×10^{-3}	1.06
10^{-1}	naphthalene	7.5×10^{-2}	1.05
10^{-1}		2.5×10^{-2}	1.09

Photolysis of 2-Phenylbenzoxazole in Concentrated Solution. During photolysis of concentrated ($c \geq 10^{-2}$ M) solutions of 2-phenylbenzoxazole in cyclohexane a precipitate was formed. It was decanted by sonication and centrifugation. At the end of the irradiation, the tubes were opened. The precipitate was easily isolated by filtration, purified by benzene washing, and dried under vacuum. The chemical yield for a 10^{-1} M solution after 6 h of irradiation reached 80% (20% of starting material being unchanged); mp 178 °C. Anal. Calcd for $C_{26}H_{18}N_2O_2$: C, 78.98; H, 4.65; N, 7.17; O, 8.20. Found: C, 78.58; H, 4.63; N, 7.15; O, 8.10. Due to the (thermal) lability of the compound, mass spectroscopy was carried out by desorption in a chemical-ionization plasma (NH_4^+, T_{source} = 80–100 °C, desorption current intensity 30–100 mA). Under these conditions, the mass spectra showed an (M – H^+) ion at *m/e* 391 (16%), corresponding to a dimer structure, and a base peak at *m/e* 195, corresponding to 2-phenylbenzoxazole. The peak at *m/e* 391 disappeared after a short while, and the mass spectrum then showed strictly the same fragmentation pattern as for 2-phenylbenzoxazole: ^1H NMR (300 scans; C_6D_6 isotopic purity ≥99,9%) δ 7.83 (m, 2 × 2 H, H_{meta}) 7.02 (m, 2 × 2 H, H_{ortho}), 6.91 (m, 2 × 1 H, H_{para}) 6.82 (m, 2 × 1 H, H_4 or H_7), 6.65 (m, 2 × 2 H, H_5 and H_6), 6.47 (m, 2 × 1 H, H_7 or H_4); ^{13}C NMR (13 000 scans; C_6D_6 isotopic purity 99%) δ 123.3 (C2, s, $\Delta\nu_{1/2}$ = 6 Hz).

Photolysis of 2-Phenylbenzoxazole in Dilute Solution. Aliquots (8 mL) of 5×10^{-3} M cyclohexane solutions of 2-phenylbenzoxazole were irradiated for 280 h. The tubes were opened and the yellow solution was evaporated to dryness at room temperature and redissolved in chloroform. VPC/MS analyses revealed the presence of numerous photoproducts [photoproducts (average relative abundance) *m/e*]: **1–3** (3.1), not analyzed; **4** (1.6), 277; **5** (13.2), 277; **6** (14.1), 277; **7** (3.4), 277; 8 (27.8), 279; **9** (19.7), 277; **10** (3.0%), 367; **11** (6.5%), 285; **12** (5.6%), 390; **13** (1.9%), not analyzed.

Benzophenone-Sensitized Photolysis of 2-Phenylbenzoxazole. Benzophenone was purchased from Prolabo and used without further purification. Aliquots (4 mL) of a cyclohexane solution of 2-phenylbenzoxazole (2 mL, 2×10^{-1} M) and benzophenone (2 mL, 2×10^{-2} M) in a Pyrex tube were degassed as described. The tubes were irradiated at 350 nm on a merry-go-round sample holder immersed in an acetone bath in order to completely avoid light irradiation at 300 nm. Under these conditions, the 2-phenylbenzoxazole present in the mixture absorbs only 1% of the light at 350 nm. The temperature of the system was controlled by cold water circulation. After 29 h of irradiation, no precipitate was observed. The irradiated mixtures were evaporated to dryness at room temperature and redissolved in chloroform. The photoproducts were identified by comparison of their retention times with mixtures formed by direct irradiation in dilute medium. This analysis showed that the main photoproducts were the same and were obtained in the same ratio. Owing to the small quantities formed, the quantum yields were not determined.

Quenching Experiments. Piperylene was purchased from Fluka and used without purification. Naphthalene was obtained from Merck and was recrystallized. Irradiations were performed at 300 nm. The relative concentrations of the quenchers and 2-phenylbenzoxazole were selected such that the quencher absorbed no more than 1% of the incident light. Therefore the ratios ϕ_0/ϕ are uncorrected in terms of the relative absorptions of the quencher and 2-phenylbenzoxazole. Solutions of 2-phenylbenzoxazole were added to solutions containing the various quenchers and then degassed as described earlier. The precipitate was carefully filtered off, washed, and dried. Table II summarizes the experimental data.

---

(27) Despax, B.; Paillous, N.; Lattes, A.; Paillous, A. *J. Appl. Polym. Sci.* **1982**, *27*, 225.

(28) Bellman, G. G.; Groult, A. M.; Arendt, J. M. Ger. Offen 2 330 452, 2 330 542.

(29) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(30) Moore, W. M.; Ketchum, M. *J. Am. Chem. Soc.* **1962**, *84*, 1369.

Table III. 2-Phenylbenzoxazole[a] Recycling

quencher (concn, mol L^{-1})	recovd 2-phenylbenzoxazole after 80 cycles, %	global yield after cycle, %	theoretical no. of cycles
none	100 (not irradiated)		
none	90.1	99.87	1770
pyrene (3.5×10^{-3})	93.8	99.92	2880

[a] [2-Phenylbenzoxazole] = 0.1 M in all cases.

Heavy-Atom Effect. Xenon was purchased from "L'air Liquide". Cyclohexane solutions of 2-phenylbenzoxazole were first bubbled with xenon. After three freeze-pump-thaw cycles, the tubes were sealed under 1 atm of xenon. For the irradiated 10^{-1} M solution of 2-phenybenzoxazole, the precipitate was filtered off, washed, and dried as described earlier. For the irradiated 10^{-2} M solution, the recovered 2-phenylbenzoxazole and the photoproducts were measured by VPC with pyrene as an internal standard.

Recycling Capacity of the Chemical Components. The irradiations of 10^{-1} M solutions of 1 were carried out for 2 h by following the general procedure. The average conversion was about 50%. The thermally induced reversion was then performed at 70 °C. Eighty photothermal cycles were achieved under these conditions. The same procedure was repeated after adding a cyclohexane solution of pyrene (3.5×10^{-3}M) to the solution of the dimer. The quantity of 2-phenylbenzoxazole recovered in these experiments was compared to the initial quantity of 2-phenylbenzoxazole. These measurements were performed by VPC analysis after adding the same quantity of pyrene to each sample. The chemical yield of starting material recovered after one cycle (and then the maximal number of cycles) was calculated from the yield of 2-phenylbenzoxazole unchanged after 80 cycles (Table III). The total energy converted after 2880 cycles was determined by computing the energy released for each cycle, the latter decreasing as the formation of byproducts increases.

Thermodynamic Measurements. The thermally induced reversion of 2 → 1 was studied by following the increase of absorbance of a cyclohexane solution of 2 (1 mg of 2 dissolved in 100 mL of solvent) by using a constant temperature bath (Figure 2). The first-order rate constant was determined by using the least-squares Guggenheim method[31-33] on a Tektronix 4051 microcomputer. In the kinetic measurements, the infinity spectrum agreed with that of authentic 2-phenylbenzoxazole. The effect of temperature was determined by obtaining the rate constant at various temperatures. The activation energy (E_a) and the preexponential factor (A) were derived from the Arrhenius equation $\ln K = \ln A - E_a/RT$ (correlation coefficient ≤ 0.997).

Microcalorimetric Measurements. Microcalorimetric measurements were carried out in an L.K.B. 8700-1 calorimeter with 100-mL cells. The dissolution reaction of Tris (tris(hydroxymethyl)aminomethane)[34] in a 0.1 M HCl solution was used for calibration. The data were treated as described in Wadso's original paper.[35] Molar enthalpies were obtained with benzene as the solvent. The benzene was dried by passing it through a column of 3-Å molecular sieves and stored over molecular sieves of the same pore size. Samples were weighed on a Mettler balance with an accuracy of 1×10^{-6} g. The cells were filled and sealed under a dry inert atmosphere.

Acknowledgment. We thank Prof. Reisse for allowing us to perform the microcalorimetric measurements in his laboratory at the University of Brussels.

Registry No. 1, 833-50-1; 2, 82461-25-4; cyclohexane, 110-82-7.

---

(31) Guggenheim, E. A. *Philos. Mag.* **1926**, 1, 358.
(32) Detar, D. F. "Computer Programs for Chemistry"; W. A. Benjamin: New York, 1968, Vol. 1.
(33) Hogg, J. L. *J. Chem. Educ.* **1974**, *51*, 109.
(34) Hill, J. O.; Ojelund, G.; Wadso, I.; *J. Chem. Thermodyn.* **1969**, *1*, 111.
(35) Wadso, I. *Sci. Tools*, **1966**, *13*, 33.

Transformations of Cyclopropanol Intermediates. 5. Preparation and Reactions of 1-Hydroxy-1,5α-cyclocholestan-7-one

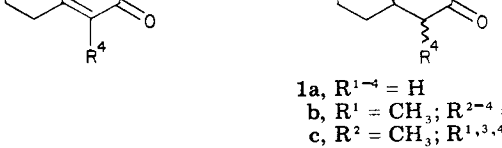
Joel R. Christensen and William Reusch*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received January 4, 1983

Cholest-5-ene-1,7-dione, a new polyfunctional steroid, gave 1-hydroxy-1,5α-cyclocholestan-7-one (**6**) on dissolving metal reduction. Acid- and base-catalyzed isomerizations of **6** were studied and the results compared with corresponding reactions of the parent cyclopropanol **1a**. The chief rearrangement products from **6** were the cis and trans 1,7-diketo steroids **10** and **11** and the ring-A spiro epimers **12** and **13**. Surprisingly, no B-norsteroid products were obtained despite the isolation of an isomer of **6**, 7-hydroxy-5,7β-cyclocholestan-1-one (**14**), from the base-induced reaction of **6**. Ring-cleavage reactions of reduced derivatives of **6** and **14** were also examined.

Dissolving metal reduction of the Wieland-Miescher ketone and several methyl homologues thereof invariably gives cyclopropanols having structure 1 (eq 1).[1] The course of acid- and base-catalyzed ring-opening reactions of these cyclopropanols is sensitive to the location and orientation of substituents.[2] For example, reaction of the parent system **1a** with potassium hydroxide in aqueous methanol gave a mixture of the isomeric bicyclic diketones **2a**, **3a**, and **4a**, whereas the analogous 7-methyl epimers **1b** and **1c** were transformed under similar conditions with remarkable selectivity (eq 2).



(1)

1a, $R^{1-4} = H$
b, $R^1 = CH_3$; $R^{2-4} = H$
c, $R^2 = CH_3$; $R^{1,3,4} = H$
d, $R^3 = CH_3 R^{1,2} = H$
e, $R^4 = CH_3$; $R^{1-3} = H$

To explore the course of these synthetic transformations

---

(1) W. Reusch, K. Grimm, J. Karoglan, J. Martin, K. Subrahamanian, Y.-C. Toong, P. S. Venkataramani, J. Yordy, and P. Zoutendam, *J. Am. Chem. Soc.*, **99**, 1953 (1977).
(2) W. Reusch, K. Grimm, J. Karoglan, J. Martin, K. Subrahamanian, P. S. Venkataramani, and J. Yordy, *J. am. Chem. Soc.*, **99**, 1958 (1977).

0022-3263/83/1948-3741$01.50/0