

THE INTRAMOLECULAR PHOTOCYCLOADDITION CARVONE \rightarrow CARVONECAMPHOR[†]

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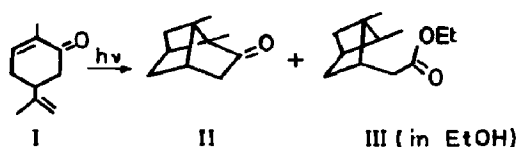
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Summary

The quantum yields of the photocycloaddition of carvone (I) to give carvonecamphor (II) have been determined in non-polar and polar solvents, under nitrogen and in air-equilibrated solutions. Quenching by oxygen was observed only in non-polar solvents: in benzene, $\Phi_{I \rightarrow II} = 0.0025$ under nitrogen and $\Phi_{I \rightarrow II} = 0.0012$ in air-equilibrated solutions. Sensitization experiments with benzophenone showed also that the reaction in benzene must proceed by triplet sensitization. A marked enhancement of the quantum yield was observed in ethanol-water mixtures compared with that in benzene and in ethanol ($\Phi_{I \rightarrow II} = 0.085$ in water-ethanol (8:2) and $\Phi_{I \rightarrow II} = 0.0088$ in ethanol). It is suggested that different excited states are involved in the photocyclization of I in non-polar (triplet state) and in hydroxylic (η, π^* singlet state) solvents on the basis of the above results and the effect of water on the absorption spectrum of I.

1. Introduction

The intramolecular photocyclization of carvone (I) to carvonecamphor (II)



was among the very first photocycloaddition reactions studied [1]. Since then, little experimental evidence has been presented concerning the photo-excited states involved in the cyclization [2 - 6]. Recently, experimental

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data obtained using laser techniques and triplet quenchers suggested that the reactive excited state leading to II is a triplet [4], possibly of π, π^* configuration [5]. The estimated lifetime of this triplet state varied: both 75 ns in degassed ethanol solutions (42 ns in cyclohexane) [5] and 350 ns in air-equilibrated ethanol solutions have been reported [6]. The product distribution was found to be intensity dependent and differences were explained tentatively in terms of multiphotonic UV photolysis [5, 6].

In this investigation the quantum yields $\Phi_{I \rightarrow II}$ of the photocyclization of I to II in solvents of different polarity, under nitrogen or in air-equilibrated solutions, and the quantum yields of the reaction photosensitized by benzophenone, were determined in an attempt to clarify the nature of the reactive electronic state involved and solvent effects operative in this reaction. Also, the reverse reaction in the dark was tried, for the first time, by using a monovalent rhodium complex as a catalyst.

2. Experimental details

2.1. Materials

I was obtained from Aldrich and purified by distillation under vacuum (8 - 10 mmHg at 60 °C). The sensitizers used were recrystallized from petroleum ether. $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ was obtained from Aldrich. All solvents used in the spectroscopic measurements were commercial spectroscopic grade materials.

2.2. Photochemical products

Solutions of I were irradiated using a Bausch and Lomb SP200 200 W high pressure mercury light source and appropriate filters. The products obtained were separated on a 6 ft \times 1/4 in 2.5% SE-30 column at 80 °C. The following retention times were obtained: α , 3.9 min; II, 5.0 min; β , 7.5 min; I, 9.6 min; III, 18.5 min. Absorption spectra were recorded by employing a Cary model 17 spectrophotometer. Mass spectra were taken using a Finigan-Mat 44 gas chromatograph-mass spectrometer on a 25 m SE-54 glass capillary column at 50 °C, and the following results were obtained. α , MS m/e (relative intensity): 150 (M)⁺, 121 (3), 119 (4), 106 (65), 91 (100), 79 (31), 65 (14), 53 (10). β , MS m/e (relative intensity): 181 (M-CH₃)⁺ probably, 150 (13), 128 (39), 121 (15), 107 (100), 93 (85), 81 (67), 67 (81), 55 (45); III, MS m/e (relative intensity): 196 (M)⁺, 167 (6), 150 (4), 122 (13), 108 (100), 93 (58), 81 (17), 67 (29), 55 (36).

2.3. Quantum yield measurements

Solutions of I and a ferrioxalate actinometer [7] were irradiated in a carousel (Baird and Tatlock Ltd., London, U.K.). The formation of II was followed by gas chromatography. The ratio of the initial slopes of the plots of the concentrations of ferrous phenanthroline (510 nm) and II vs. time gave the quantum yields in each case.

The incident light was totally absorbed by the chemical actinometer. In the case of I the amount of light absorbed was calculated. The samples were irradiated using an Osram HBO 200 W high pressure mercury lamp and appropriate filters. All photochemical experiments, except for those involving oxygen, were carried out after bubbling nitrogen through the solution. The quantum yield determinations with or without sensitizers were made at room temperature. Problems with the solubility of I (5.95×10^{-3} M) in water-ethanol solutions up to 60 vol.% in water were not met; when higher proportions of water were used extensive heating and stirring was necessary.

3. Results

3.1. Photochemical products

Solutions of I (10^{-3} M) in benzene, ethanol and ethanol-water (1:1) were irradiated for 6 h by a high pressure mercury lamp using a 365 nm or a Pyrex filter, and were subsequently analysed by gas chromatography. The sole photolysis product of I in benzene (365 nm light) was II, in accord with literature data [3]. In the case of ethanol and ethanol-water (1:1) solutions of I using 365 nm light II was mainly formed (7.5% and 61% respectively) together with a carvone or carvonecamphor isomer α (yield, below 1.2%), while by using a Pyrex filter 1-exo,5-dimethyl-*syn*-2[(ethoxy-carbonyl)-methyl]bicyclo[2.1.1]hexane (III) was formed together with a second minor constituent β (yield, below 1.5%).

3.2. Absorption spectra

The absorption spectrum of I was recorded in various solvents of different polarity. Table 1 shows the expected blue shift of the long-wavelength absorption band ($\eta \rightarrow \pi^*$) of I. Examination of Table 1 shows that water has a remarkable effect on the extinction coefficient of this band.

3.3. Quantum yields

The quantum yield $\Phi_{I \rightarrow II}$ of the photoisomerization of I to II was determined using 365 nm light, at room temperature, under nitrogen and in

TABLE 1

Solvent effect on the long-wavelength absorption band of I

Solvent	λ_{\max} (nm)	ϵ_{\max}
Cyclohexane	(336) 324	31.0
Benzene	(331) 321	35.4
Acetonitrile	318	34.8
Methanol	317	41.4
Ethanol	317	41.0
Ethanol-water (1:1)	310	55.7

TABLE 2

Quantum yields $\Phi_{I \rightarrow II}$ in ethanol at various concentrations

Concentration (M)						
5.2×10^{-3}	8.1×10^{-3}	1.1×10^{-2}	2.1×10^{-2}	4.4×10^{-2}	8.8×10^{-2}	3.8×10^{-1}
$\Phi_{I \rightarrow II}$ (365 nm light)						
0.0077	0.0068	0.0100	0.0110	0.0078	0.0100	0.0082

Mean $m = 0.0088$; probable error $Pe = 0.0009$.

TABLE 3

Variation in the quantum yield $\Phi_{I \rightarrow II}$ with solvent

Solvent	$\Phi_{I \rightarrow II}$ (air-equilibrated)	$\Phi_{I \rightarrow II}$ (under N_2)
Benzene	0.0012	0.0025
Methanol	0.0099	0.0110
Ethanol	0.0082	0.0088 ± 0.0009
Ethanol-water (9:1)	0.015	0.016
Ethanol-water (8:2)	—	0.017
Ethanol-water (7:3)	—	0.021
Ethanol-water (6:4)	—	0.026
Ethanol-water (5:5)	0.040	0.037 ^a
Ethanol-water (2.5:7.5)	—	0.071
Ethanol-water (1.8:8.2)	0.082	0.085

^aMean of five measurements.

air-equilibrated solutions. The photolysed solutions were analysed by gas chromatography. It was found that varying the concentration of I in ethanol (under nitrogen) had no effect on $\Phi_{I \rightarrow II}$ over the range of concentrations used (Table 2).

Previously, it had been found that $\Phi_{I \rightarrow II}$ was affected not so much by an increase in the polarity of the solvent but by its ability to form hydrogen bonds [3]. This observation together with the higher yield of II in ethanol-water (1:1) solutions relative to that in ethanol and the fact that $\Phi_{I \rightarrow II}$ in ethanol was found to be higher than in absolute ethanol led us to study $\Phi_{I \rightarrow II}$ in a series of water-ethanol solutions. Measurements in methanol and benzene were carried out as well for comparison. The results are summarized in Table 3.

The results of Table 3 show clearly that $\Phi_{I \rightarrow II}$ increases on increasing the water content in the ethanol. There is a tenfold enhancement in going from ethanol to ethanol containing 82 vol.% water. Determination of $\Phi_{I \rightarrow II}$ in water is not possible because of solubility problems. Table 3 shows also that while there is quenching by oxygen in the case of benzene, no such effect is observed in hydroxylic solvents.

3.4. Sensitization

The photoisomerization of I to II was sensitized effectively by benzophenone ($E_t = 68.5$ kcal mol⁻¹). Acetophenone ($E_t = 73.6$ kcal mol⁻¹) and benzil ($E_t = 53.7$ kcal mol⁻¹) were also used in these experiments, but only acetophenone was found to act as a weak sensitizer.

Using 0.0175 M benzophenone ($\epsilon_{365} \approx 70$) as the sensitizer, the quantum yield $\Phi_{I \rightarrow II}$ was studied as a function of the concentration of I in benzene (under nitrogen). The results obeyed eqn. (3), which takes the same form whether energy transfer occurs from the singlet or the triplet state of benzophenone [8].



$$\frac{1}{\Phi_{I \rightarrow II}} = \frac{1}{{}^3\Phi_{I \rightarrow II}\Phi_B} + \frac{K_2}{K_1[I]{}^3\Phi_{I \rightarrow II}\Phi_B} \quad (3)$$

K_1 and K_2 are respectively the rate constants for energy transfer to I and for spontaneous decay of excited benzophenone (B), Φ_B is the quantum yield for formation of excited benzophenone and ${}^3\Phi_{I \rightarrow II}$ is the quantum yield expected if I was present in sufficient concentration to quench all the excited benzophenone molecules. From the intercept of the plot in Fig. 1 it is found that ${}^3\Phi_{I \rightarrow II}\Phi_B = 0.0022$ (and since $\Phi_B = 1$ [9], ${}^3\Phi_{I \rightarrow II} = 0.0022$), and from the slope the ratio $K_2/K_1 = 5.1 \times 10^{-4}$ mol l⁻¹ is obtained. Assuming that the energy transfer process (eqn. (1)) is diffusion controlled ($K_1 \approx 2 \times 10^9$ l mol⁻¹ s⁻¹) [10], the lifetime of the excited benzophenone molecule must be $1/K_2 = 0.98 \times 10^{-6}$ s. This is in agreement with the reported lifetime of 3.8×10^{-6} s for benzophenone triplet in benzene [10] and excludes the short-lived (2×10^{-10} s or less) singlet of benzophenone

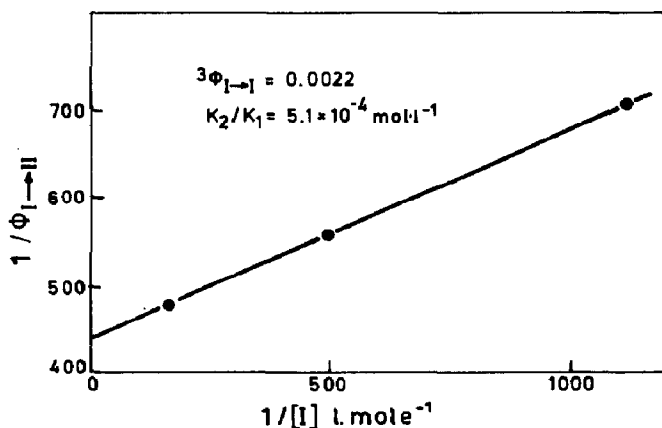
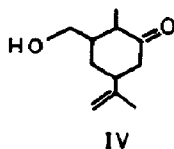


Fig. 1. Quantum yields for reaction I \rightarrow II sensitized with 0.0175 M benzophenone, extrapolated to infinite concentration of I (eqn. (3)). (${}^3\Phi_{I \rightarrow II} = 0.0022$; $K_2/K_1 = 5.1 \times 10^{-4}$ mol l⁻¹.)

[11] from being the sensitizing species. Thus, the reaction must proceed by triplet sensitization. The sensitization experiments were carried out in benzene, which is a weak hydrogen donor, since triplet benzophenone can abstract hydrogen atoms from solvents such as ethanol and may react with the compound under investigation by producing reactive radicals. Indeed, irradiation of I in methanol in the presence of benzophenone results in the product IV and not in II [12].



3.5. The reverse reaction

The reverse reaction $\text{II} \rightarrow \text{I}$ has not been previously reported in the literature. Since such photoisomerizations have been proposed as possible systems for solar energy conversion [13], an effort was made to achieve this reverse reaction. For this purpose, a monovalent rhodium complex was used as in the case of quadricyclanes to norbornadienes [14]. Thus, in one experiment II was collected in octadecane (about 5×10^{-4} M) by preparative gas chromatography and 0.12 mol.% $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ were added to the solution. The mixture was vacuum degassed (repeated freezing and thawing) and subsequently heated to 140°C in the dark for 20 h. Gas chromatographic analysis showed the partial conversion of II to I (38%), with a small new peak of an unidentified product appearing before that of I. It should be noted that II is very stable at high temperatures and heating the compound at 150°C without a catalyst for more than 20 h leaves it unchanged.

4. Discussion

According to the value of the quantum yield $\Phi_{\text{I} \rightarrow \text{II}}$ of the intramolecular photocycloaddition of I to II, which has been determined in various solvents of different polarity, under nitrogen or in air-equilibrated solutions, the formation of II is favoured in polar solvents such as ethanol ($\Phi_{\text{I} \rightarrow \text{II}} = 0.0088$ against 0.0025 in benzene). More impressive is the increase in the quantum yield in water-ethanol mixtures: $\Phi_{\text{I} \rightarrow \text{II}} = 0.085$ in water-ethanol (8:2), a value which is comparable with the quantum yield obtained by using high intensity lasers ($\Phi_{\text{I} \rightarrow \text{II}} = 0.07$ in ethanol [6]).

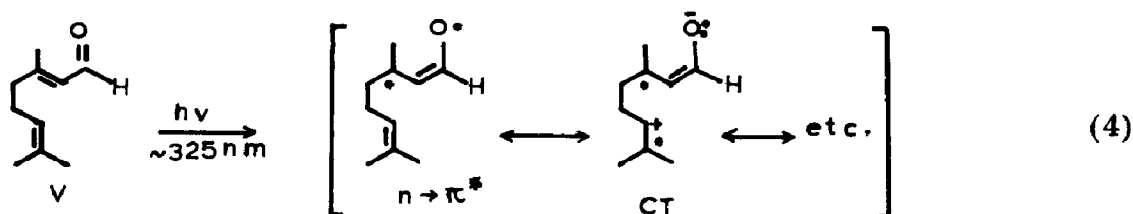
The difference between the quantum yield in benzene and that in ethanol may be explained on the basis of the proposed mechanism for the photocyclization of I, which involves its triplet state [4]. This triplet state has been reported to be observed using pulsed lasers and its estimated energy of $61.8 \text{ kcal mol}^{-1}$ was considered as indicative of a π, π^* configuration [5].

In the same study, different values for the intersystem crossing quantum yield were estimated in ethanol (0.86) and in cyclohexane (0.77), and the triplet lifetime was found to be longer in ethanol (75 ns) than in cyclohexane (42 ns). However, there is some controversy about the lifetime of the triplet state of I in the literature; a value of 350 ns in air-equilibrated ethanol solutions has also been calculated [6].

Our experimental results, however, show that oxygen quenches the photocyclization in benzene, while in methanol, ethanol and water-ethanol mixtures such an effect is not observed. The above literature data do not provide an explanation for this different behaviour; on the contrary, the observed excited intermediate presents a longer lifetime in ethanol. Thus, either this intermediate does not participate in the photocyclization of I to II or the mechanism of the reaction differs in non-polar and hydroxylic solvents.

Our photosensitization experiments with benzophenone indicate that the photocyclization of I in benzene must proceed by triplet sensitization and it appears reasonable, judging from the oxygen quenching, that a triplet precursor is involved in the direct photoisomerization in benzene.

We can refer to the structurally analogous conversion of citral (IV) to photocitral-B, for which one proposed mechanism involves the η, π^* excited state of citral mixed with some charge transfer character (eqn. (4)) [15, 16] to explain the marked enhancement of the quantum yield in ethanol and especially in water-ethanol mixtures and the lack of oxygen quenching in these cases.



The absorption spectrum of I in various water-ethanol mixtures is of considerable interest. One observes not only the expected blue shift of the $\eta \rightarrow \pi^*$ transition, but also a considerable increase in the extinction coefficient (isosbestic point, 332 nm) as the water content in the mixture increases. The increase in the extinction coefficient of the $n \rightarrow \pi^*$ transition of I may be attributed, by analogy to citral, to the mixing of the pure localized $\eta \rightarrow \pi^*$ transition with a charge transfer transition from the isolated double bond to the same antibonding π^* orbital. If these assumptions are sound then an η, π^* singlet state may be responsible for the photocyclization of I in hydroxylic solvents and especially in water-ethanol mixtures. The involvement of different excited states has also been proposed for the photodimerization of coumarin in non-polar (lowest triplet state) and polar solvents such as ethanol (lowest excited singlet state) [17]. The observation that naphthalene depresses the photoproduction of II from I

in ethanol [4] is evidence against a singlet mechanism. However, quantitative results are needed in order to confirm these observations. The intramolecular photocycloaddition of I to II has been proposed among other reactions as a possible system for solar energy storage. With this in mind, the reverse reaction in the dark was achieved for the first time by using $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ as a catalyst.

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