

PHOTOCHEMICAL *Z-E* ISOMERIZATION OF BENZYLIDENEPHTHALIDES: INFLUENCE OF OXYGEN ON THE COURSE OF ISOMERIZATION

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(Received October 16, 1985; in revised form January 21, 1986)

Summary

Z isomers of benzylidenephthalides were photochemically isomerized to the corresponding *E* isomers. Direct photolysis leads to a low proportion (3% - 5%) of *Z* isomers in the reaction mixture in all cases. A significant influence of the substituents on the proportion of *E* isomers was observed in the benzophenone-sensitized reaction. The influence of azulene on the sensitized isomerization of unsubstituted and 3-(4-nitrobenzylidene)phthalide in both outgassed and oxygen-saturated solutions was also studied.

1. Introduction

The photoisomerization of 2-aryl-1,3-indanediones to the corresponding benzylidenephthalides was studied by Rigaudy and Derible [1] in 1965. We have also published results in this field [2] (we obtained *E* isomers in low yields). Devaquet [3] studied the influence of the bond length and angular rotation in the C=C—C=O moiety on the energy of the excited state of the above-mentioned systems. He found that previously studied enone systems were flexible and their triplet states had very low energy. A change in the geometry of the molecule can affect the lowest triplet state of the enone. The stability, the geometry and the chemical reactivity of the different triplet states of enones are very sensitive to small changes in the relative energies of the n,π^* and π,π^* triplet states. The aim of this work was to study *Z-E* isomerization of substituted benzylidenephthalides in connection with the nature of the substituent in direct or sensitized photolysis (Fig. 1).

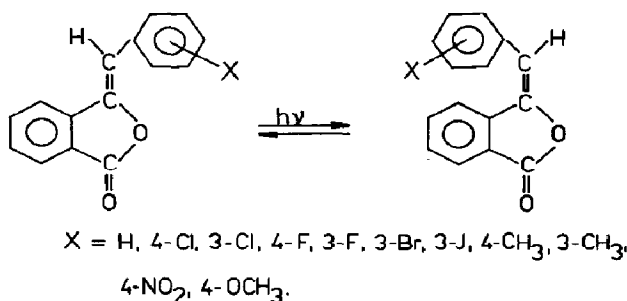


Fig. 1. Reaction scheme.

2. Experimental details

Z isomers of benzylidenephthalides were prepared according to Nathanson [4] or Hrnčiar [5]. The solvents used in all the irradiation experiments were purified in the following way. Benzene for UV (Lachema Brno) was purified on an SiO_2 column; acetonitrile (Cambrian Chemicals) and *tert*-butyl alcohol (pro analysi, Lachema Brno) were purified according to Welster *et al.* [6]. The apparatus for irradiation has been described in our previous paper [2].

The direct photoisomerization was studied under the following conditions: [benzylidenephthalide] = 10^{-3} mol l^{-1} , $\lambda = 366$ nm; in the case of sensitized isomerization, [benzylidenephthalide] = 10^{-3} mol l^{-1} , [benzophenone] = 10^{-2} mol l^{-1} , [azulene] = 0.3×10^{-3} mol l^{-1} .

Benzene was saturated with oxygen at a pressure of 101.3 kPa for 24 h. Benzene solutions of all the compounds were thoroughly outgassed (three times at a pressure of 0.014 Pa) prior to use.

In all cases the composition of the reaction mixture was determined by gas chromatography carried out with a Carlo Erba GI 450 instrument equipped with a flame ionization detector. The column, of length 120 cm and internal diameter 3 mm, was operated at a temperature of 200 - 210 °C, nitrogen was used as the carrier gas at an inlet pressure of 0.1 MPa and the stationary phase was Chromosorb W 80 - 100 mesh with (3% OV 17)–(1% QF 1).

UV spectra were measured using an NIR PE 450 spectrophotometer.

3. Results and discussion

In the electronic spectra of substituted benzylidenephthalides a band is observed at 338 nm. In accord with Loos *et al.* [7] the band at longest wavelength has been assigned to a $\pi \rightarrow \pi^*$ ($S_0 \rightarrow S_1$) transition localized in the styrene fragment [8]. The lowest singlet $n \rightarrow \pi^*$ transition of benzylidenephthalide was not experimentally determined owing to its considerable overlap with the $\pi \rightarrow \pi^*$ band.

The benzylidenephthalides in question exhibit relatively weak fluorescence and phosphorescence, in accord with results obtained by Nikolov *et al.* [8] (the *Z-p*-nitro isomer is an exception, as it did not fluoresce in polymer matrices in our experiments). Substituents have a significant effect on the π, π^* singlet-triplet splittings and consequently on the differences between the singlet and triplet energies of n, π^* and π, π^* states.

The benzylidenephthalides under study were photoisomerized with or without a sensitizer. In the direct photoisomerization ($\lambda_{\text{exc}} = 366 \text{ nm}$) the conversion of the *Z* isomer to the corresponding *E* isomer was very low (3% - 5%) and substituents altered the *Z* to *E* ratio only slightly. Both findings can be explained if it is assumed that a large proportion of singlet states is deactivated via non-emitting transitions through the n, π^* state.

Different results were obtained from sensitized photochemical isomerizations (benzophenone being the sensitizer) (Table 1). In this case, increased conversion of the *Z* isomers and a significant influence of substituents on the ratio of *Z* to *E* isomers were observed. The photostationary mixture of the *p*-OCH₃ derivative contained only 8% *E* isomer, but in the case of *p*-nitrobenzylidenephthalide 96% *E* isomer was found.

TABLE 1

Effect of substituents on the benzophenone-sensitized isomerization of benzylidenephthalides in benzene

| X | $([Z]/[E])_{\infty}$ |
|----------------------------|----------------------|
| H | 1.22 |
| <i>m</i> -Cl | 1.73 |
| <i>p</i> -F | 0.86 |
| <i>m</i> -I | 1.17 |
| <i>m</i> -F | 1.12 |
| <i>p</i> -OCH ₃ | 11.50 |
| <i>p</i> -CH ₃ | 1.85 |
| <i>m</i> -CH ₃ | 1.51 |
| <i>m</i> -Br | 1.72 |
| <i>p</i> -NO ₂ | 0.04 |

Substituents cause a change in the relative energy of the n, π^* and π, π^* triplet states. As the difference between the energies of these states becomes greater, the transmission of energy is more selective and deactivation through the triplet n, π^* state becomes feasible. Hence, as a consequence, the ratio of *Z* to *E* isomers is influenced.

This hypothesis is supported by the fact that $([Z]/[E])_{\infty}$ of unsubstituted benzylidenephthalide is proportional to the triplet energy of the sensitizer (Table 2), *e.g.* it shows a decreasing trend in the following order: acetone > acetophenone > benzophenone > anthraquinone. A similar dependence was also observed for a change in solvent polarity: benzene < acetonitrile < *tert*-butanol.

TABLE 2

Dependence of $([Z]/[E])_{\infty}$ on the energy of the sensitizer and the solvent in the isomerization of benzylidenephthalide

| Sensitizer | Solvent | $([Z]/[E])_{\infty}$ |
|---|----------------------|----------------------|
| Acetone (335 kJ mol ⁻¹) | Benzene | 95.0 |
| Acetophenone (309 kJ mol ⁻¹) | Benzene | 15.7 |
| Benzophenone (287 kJ mol ⁻¹) | Benzene | 1.22 |
| Anthraquinone (262 kJ mol ⁻¹) | Benzene | 0.92 |
| Benzophenone | Acetonitrile | 1.36 |
| Benzophenone | <i>tert</i> -Butanol | 1.65 |

We also studied the quenching of benzophenone-sensitized photoisomerization of benzylidenephthalide by azulene in outgassed as well as in oxygen-saturated benzene. Unsubstituted benzylidenephthalide and its *p*-nitro derivative were chosen as model compounds. In the case of unsubstituted benzylidenephthalide the dependence of $([Z]/[E])_{\infty}$ on the concentration of azulene was linear in outgassed as well as in oxygen-saturated solutions (Fig. 2). The slopes of the two lines are comparable: 453 mol⁻¹ for outgassed solution and 428 mol⁻¹ for oxygen-saturated solution. They

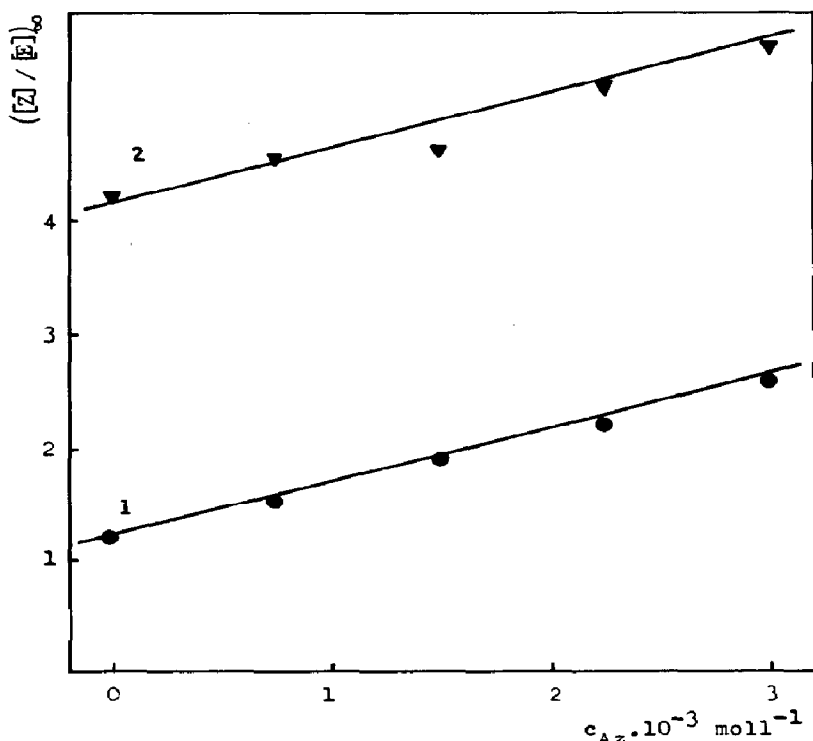


Fig. 2. Dependence of $([Z]/[E])_{\infty}$ on the concentration of azulene in the benzophenone-sensitized isomerization of benzylidenephthalide: curve 1, outgassed solution; curve 2, oxygen-saturated solution.

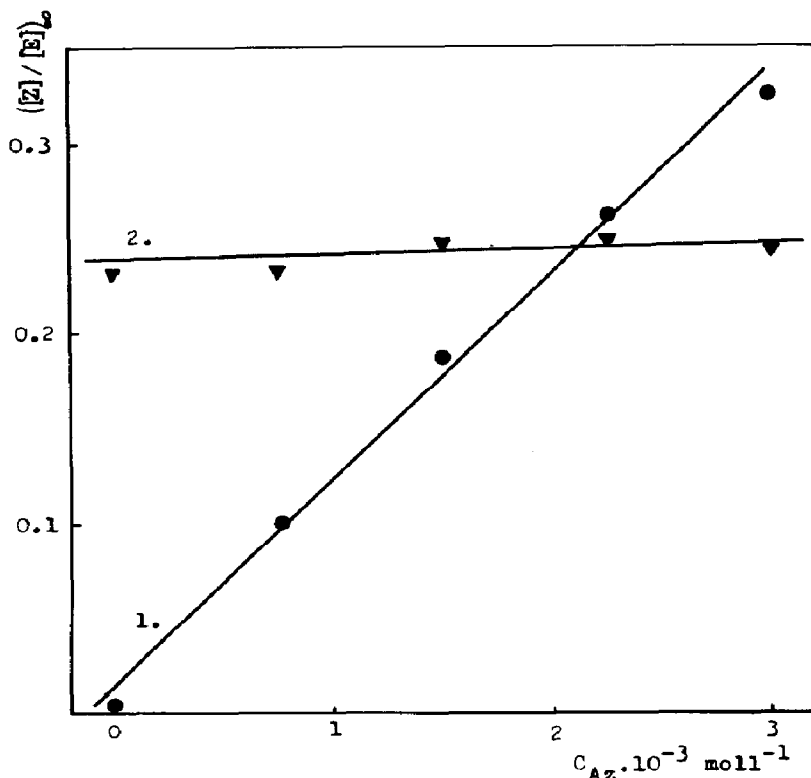


Fig. 3. Dependence of $([Z]/[E])_{\infty}$ on the concentration of azulene in the benzophenone-sensitized isomerization of *p*-nitro-benzylidenephthalide: curve 1, outgassed solution; curve 2, oxygen-saturated solution.

differ, however, in their intersection on the *y* axis (1.2 or 4.2). For the *p*-nitro derivative both lines differ in their slopes (94.4 and 0.05) as well as in their intersection on the *y* axis (0.0 and 0.2) (Fig. 3).

These results indicate that not only azulene but also oxygen takes part in the quenching of the triplet states. Saltiel and Thomas [9], however, studying the isomerization of stilbene under analogous conditions, found that the ratio $([Z]/[E])_{\infty}$ is proportional to the concentration of azulene in both outgassed and oxygen-saturated solutions. The diagrams for both dependences exhibit the same intersection on the *y* axis but different slopes.

The unequal effect of the presence of oxygen on isomerization of stilbene and benzylidenephthalides can presumably be accounted for by the presence of the $n \rightarrow \pi^*$ triplet state of the carbonyl group in the benzylidenephthalides, *e.g.* by the difference in energy between $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplets. However, one cannot exclude an exciplex of the benzylidenephthalide and azulene which is more or less quenched by oxygen. The creation of the exciplex will be affected by substitution of the benzylidenephthalide and, therefore, the quenching ability of oxygen will change with the nature of the substituent.

References

- 1 J. Rigaudy and P. Derible, *Bull. Soc. Chim. Fr.*, (1969) 3055.
- 2 A. Gáplovský, J. Donovalová and P. Hrnčiar, *Collect. Czech. Chem. Commun.*, **49** (1984) 1569.
- 3 A. Devaquet, *J. Am. Chem. Soc.*, **94** (1972) 5160.
- 4 F. Nathanson, *Chem. Ber.*, **26** (1883) 2576.
- 5 P. Hrnčiar, *Chem. Zvesti*, **14** (1960) 119.
- 6 O. W. Welster, W. Mahler and R. E. Benson, *J. Am. Chem. Soc.*, **97** (1975) 4490.
- 7 D. Loos, D. Ondrejčíková and J. Leška, *Acta Fac. Rerum Nat. Univ. Comeniana, Chim.*, **22** (1975) 65.
- 8 P. Nikolov, F. Fratev and S. Minchev, *Z. Naturforsch., Teil A*, **38** (1983) 290.
- 9 J. Saltiel and B. Thomas, *Chem. Phys. Lett.*, **37** (1976) 147.