

# MECHANISM OF PHOTOCHEMICAL REACTIONS OF ARYLVINYLENETHIOAMIDES IV: PHOTOISOMERIZATION OF PHENYLVINYLENETHIOMORPHOLIDE

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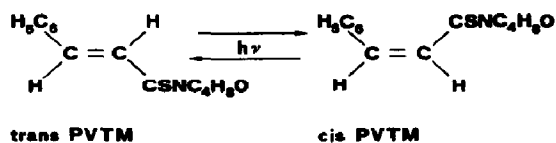
## Summary

The *cis-trans* photoisomerization of phenylvinylethiomorpholide by direct excitation and by benzophenone sensitization was investigated. Informative results regarding the mechanism were obtained from the different effect of the azulene on the direct and on the sensitized processes. The quencher did not affect the quantum yields of the direct photoisomerization which occurred presumably through singlet states, whereas it slightly increased the initial rate of the benzophenone-sensitized *cis* → *trans* photoisomerization. This latter finding was consistent with a reaction pathway involving twisting of the <sup>3</sup>*cis* state to a distorted <sup>3</sup>p state, in equilibrium with the <sup>3</sup>*trans* state, quenchable by azulene. A general scheme for arylvinylethioamide photoisomerization is proposed.

## 1. Introduction

In our previous papers the role of the aryl ring in *cis-trans* photoisomerization of arylvinylethioamides (ArCH=CHCSNH<sub>2</sub>) was evidenced and different pathways were suggested for the photoisomerization of phenylvinylethioamide (PVTa), 1-thienylvinylethioamide (TVTA) and 2-naphthylvinylethioamide (NVTA). It was shown that for PVTa [1] a singlet mechanism was operative, whereas for TVTA [2] and NVTA [3] the photoisomerization occurred by a triplet mechanism.

In the present work we have investigated the photoisomerization of phenylvinylethiomorpholide (PVTM)



with the aim of evidencing the replacement effect of the amino group by the morpholine group. PVTM provides better conditions than the previous compounds for studying sensitized reactions, on account of both its spectral characteristics and its lessened hydrogen donor capacity.

## 2. Experimental details

### 2.1. Preparation and characterization of *trans*- and *cis*-phenylvinylethio-morpholide

*Trans*-PVTM (melting point, 124 - 125 °C) was prepared in absolute ethanol from thioacetomorpholide and benzaldehyde [4]. *Cis*-PVTM (melting point, 88 - 89 °C) was prepared by irradiating solutions of the *trans* isomer in benzene with a mercury immersion vapour lamp (Hanovia 450 W) fitted with a Pyrex filter. The *cis* isomer was isolated from the irradiated solutions using preparative high pressure liquid chromatography with a 15:85 ethyl acetate:cyclohexane mixture as eluent. The IR, nuclear magnetic resonance (NMR), UV and visible spectra were consistent with those expected for the *trans* and *cis* configurations.

The more significant IR data (obtained using KBr pellets) are as follows: the stretching band of the ethylene group C=C at 1625 cm<sup>-1</sup> which is strong in the *trans* isomer and very weak in the *cis* isomer; the out-of-plane bending frequencies of the CH which appear at 970 cm<sup>-1</sup> in the *trans* isomer and at 700 cm<sup>-1</sup> in the *cis* isomer.

The NMR data (obtained in chloroform deuterated at 80 MHz) are as follows: *trans* isomer,  $\delta = 7.63$  ppm (doublet; 1 H;  $J = 14$  Hz),  $\delta = 7.3 - 7.02$  ppm (multiplet; 5 H),  $\delta = 6.58$  ppm (doublet; 1 H;  $J = 14$  Hz),  $\delta = 4.37 - 4.0$  ppm (multiplet; 4 H) and  $\delta = 3.75 - 3.5$  ppm (multiplet; 4 H); *cis* isomer,  $\delta = 7.2 - 7.04$  ppm (multiplet; 5 H),  $\delta = 6.17$  ppm (broad singlet; 2 H),  $\delta = 4.25 - 4.13$  ppm (multiplet; 2 H),  $\delta = 3.65 - 3.43$  ppm (multiplet; 4 H) and  $\delta = 3.5 - 3.37$  ppm (multiplet; 2 H). The collapse of the two protons to a broad singlet was an excellent indication of the *cis* configuration.

The *trans* isomer showed in ethanol a first shoulder at 345.5 nm ( $\epsilon = 5000$ ) due to an n- $\pi^*$  transition and two  $\pi$ - $\pi^*$  bands at 297.5 nm ( $\epsilon = 22\ 000$ ) and at 230.5 nm ( $\epsilon = 12\ 500$ ); in benzene the n- $\pi^*$  band was at 345 nm ( $\epsilon = 5000$ ) and the  $\pi$ - $\pi^*$  band was at 297 nm ( $\epsilon = 20\ 000$ ).

The *cis* isomer showed in ethanol an n- $\pi^*$  broad band at about 365 nm ( $\epsilon = 740$ ) and a  $\pi$ - $\pi^*$  band at 272 nm ( $\epsilon = 15\ 000$ ); in benzene an n- $\pi^*$  band at 385 nm ( $\epsilon = 780$ ) is visible. The extinction coefficients are in decimetres cubed reciprocal mole centimetres.

### 2.2. Apparatus

The apparatus used for irradiation and for measuring the incident light was the same as that described previously [2]. The UV and visible spectrophotometric measurements were carried out using a Perkin-Elmer 330 spectrophotometer. The IR spectra were obtained on a Perkin-Elmer 684

spectrophotometer. The NMR spectra were obtained on a Brüker 80 MHz instrument. Tetramethylsilane was used as an internal standard. The phosphorescence measurements were recorded with a Perkin-Elmer MPF-3L spectrophotometer. The chromatographic separation was carried out using a preparative Miniprep LC Jobin-Yvon apparatus.

### 2.3. Procedure

The direct photoisomerization was carried out using solutions of pure isomer in benzene and ethanol. The experimental conditions were as follows: [PVTM] =  $1.5 \times 10^{-3}$  -  $10^{-4}$  M; excitation wavelengths, 313, 333, 365 and 405 nm. The quantum yields were calculated from the initial rate of the reaction or by the method of Zimmerman *et al.* [5]. The stationary state was attained without side reactions. In all experiments carried out in the presence of quencher (azulene) or sensitizer, only benzene solutions were used. In the direct irradiation experiments in the presence of azulene, the conditions were as follows: [PVTM] =  $1.5 \times 10^{-3}$ ; [azulene] =  $(2 - 8) \times 10^{-2}$ ;  $\lambda_{exc}$  = 405 nm. In these experiments a fraction of the light was absorbed by the quencher and the quantum yields were corrected as necessary for this absorption. The sensitized photoisomerization experiments were performed under the following conditions: [PVTM] =  $(0.25 - 0.75) \times 10^{-3}$  M; [benzophenone] = 0.4 M;  $\lambda_{exc}$  = 333 nm. These conditions were chosen to achieve as small a fraction of light absorbed by PVTM as possible. The quantum yields were calculated by a method derived from the Lamola-Hammond formula [6] corrected for direct isomerization. The stationary state was calculated by extrapolation because after prolonged irradiation concomitant decomposition reactions cannot be neglected.

The experiments with combined sensitizer and quencher use were performed as follows: [*cis*-PVTM] = [azulene] =  $2.5 \times 10^{-3}$  -  $2 \times 10^{-2}$  M; [benzophenone] = 0.4 M;  $\lambda_{exc}$  = 365 nm. The quantum yields were calculated from initial conversion (within 10% of conversion) to avoid side reactions and were corrected for direct isomerization and for the fraction of light absorbed by the substrate and quencher.

All kinetics were followed spectrophotometrically in the most appropriate absorption region.

All samples in the direct and sensitized photoisomerization were deoxygenated carefully with a nitrogen stream.

### 3. Results

Under direct irradiation PVTM underwent *trans*  $\rightleftharpoons$  *cis* isomerization until a photostationary state was attained (Fig. 1). The constant isosbestic points indicated that only the isomer was formed by irradiation and that no detectable side reaction occurred. The quantum yields of the photochemical isomerization were independent of the solvent nature, benzene or ethanol, and of the irradiation wavelengths at 333, 365 and 405 nm. The following

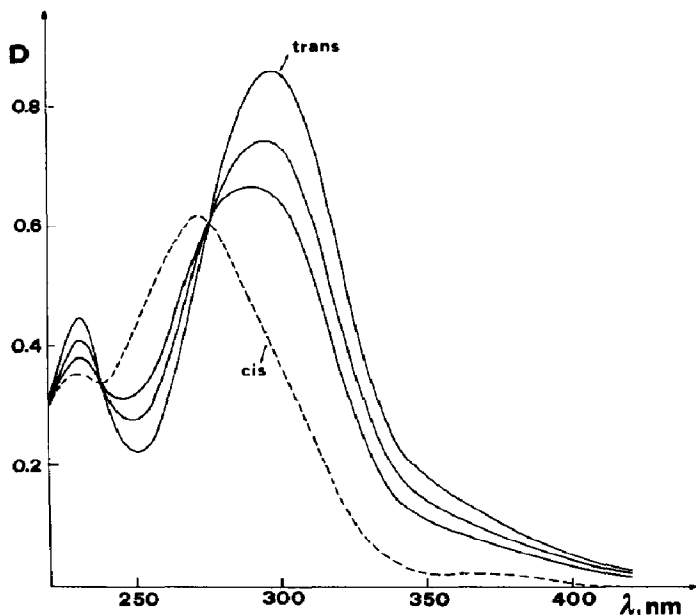


Fig. 1. Changes in the spectrum of *trans*-PVTM in ethanol by irradiation at 333 nm.

values were obtained:  $\varphi_{t-c} = 0.11 \pm 0.01$  and  $\varphi_{c-t} = 0.68 \pm 0.05$  in benzene;  $\varphi_{t-c} = 0.14 \pm 0.01$  and  $\varphi_{c-t} = 0.68 \pm 0.05$  in ethanol.

To obtain useful information about the probable reaction mechanism, through quenching of excited electronic states, we carried out some experiments of photoisomerization with benzene solutions containing azulene with a maximum concentration of  $8 \times 10^{-2}$  M. It was found that neither the *trans*  $\rightarrow$  *cis* nor the *cis*  $\rightarrow$  *trans* quantum yields were influenced by the quencher.

Benzophenone ( $E_T = 288.4$  kJ) and benzil ( $E_T = 225.7$  kJ) were effective in bringing about *trans-cis* isomerization, but with benzophenone sensitizer side reactions were negligible, whereas with the latter a photo-decomposition occurred contemporaneously.

The different behaviour of the two sensitizers was confirmed by phosphorescence quenching experiments. The benzophenone phosphorescence was quenched by *cis*-PVTM and the linearity of the Stern-Volmer plot showed that the quenching was due to energy transfer. From the slope and from the benzophenone lifetime ( $1.9 \times 10^{-6}$  s) a  $K_q$  value of  $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was obtained; therefore the process was controlled by diffusion. The analogous experiment with the *trans* isomer was not realizable, because the substrate absorbed the exciting light competitively.

The Stern-Volmer plot for quenching of benzil phosphorescence by *trans*- and *cis*-PVTM departs from linearity, deviating upwards; therefore it is probable that a chemical reaction between sensitizer and substrate occurred contemporaneously with the isomerization.

For these reasons only benzophenone was used in sensitized photoisomerization, even though it was not possible to achieve conditions of

TABLE 1

Effect of azulene on the benzophenone-sensitized *cis*  $\rightarrow$  *trans* photoisomerization of phenylvinylethiomorpholide

[azulene] $\times 10^2$ (M)	$\Phi_{c-t}^a$	$\Phi_{c-t}/\Phi_{c-t}^a$
0.25	0.43	1.89
0.50	0.44	1.87
1.00	0.45	1.84
1.50	0.46	1.80
2.00	0.47	1.76

pure sensitization. After correction for direct reaction, it was found that the quantum yields of the sensitized isomerization were dependent on the substrate concentration. Plots of  $1/\Phi_{ap}$  versus  $1/[PVTM]$  were good straight lines from which the limiting quantum yields and the energy transfer constants  $K_s$  were calculated. The values obtained were  $\Phi_{t-c} = 0.12$ ,  $\Phi_{c-t} = 0.86$  and  $K_s = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the *trans* and the *cis* isomer.

With the aim of understanding whether the inefficiency of the azulene in the direct isomerization arose from the short lifetime of the triplet state that could not be intercepted or whether it indicated that the process bypassed the triplet, we investigated the effect of azulene on the benzophenone-sensitized photoisomerization.

Attempts to obtain information about the effect of azulene on the photostationary state were unsuccessful because prolonged irradiation of the system provoked detectable side decomposition reactions.

The effect of the quencher on the sensitized *trans*  $\rightarrow$  *cis* photoisomerization has not been investigated because the relative spectral properties of the sensitizer, substrate and azulene make it difficult to achieve suitable conditions for this study. Under suitable conditions of respective concentrations and of irradiating light it is possible to investigate the effect of azulene on the initial rates of the *cis*  $\rightarrow$  *trans* isomerization. We found that the quantum yields  $\Phi_{c-t}^a$  in the presence of the quencher increased slightly with increasing quencher concentration and that the ratio between the values of  $\Phi_{c-t}$ , determined under the same experimental conditions, and of  $\Phi_{c-t}^a$  decreased (Table 1).

Under the chosen conditions the quantum yields in the absence of azulene are in the region of a value of 0.83. We therefore consider that the observed increase is due to the effect of the quencher.

#### 4. Discussion

The different effect of azulene on direct and sensitized photoisomerization leads us to assume that the direct process bypasses the triplet state in PVTM. In fact,  $\Phi_{c-t}^a$  increases with increasing azulene concentration, suggesting that the triplet states of PVTM interact with the quencher;

therefore, the invariability of the direct quantum yields in the presence of azulene is an indication that these triplet states are not populated on direct excitation. Unfortunately the PVTM is not fluorescent and therefore it is not possible to support the proposed singlet mechanism by experiments of fluorescence quenching by azulene.

The overall results are interpretable in terms of a mechanism analogous to that proposed for stilbene and substituted stilbenes [7] and for the arylvinylethioamides previously studied [2, 3]. This mechanism is described by the following equations, where S represents benzophenone and Q represents azulene:



The difference between this mechanism and that proposed for the arylvinylethioamides studied previously consists in the fact that the  ${}^3cis$  state is populated only by energy transfer and not by decay from singlet states in direct irradiation.

It should be mentioned that we have no experimental evidence for the reversibility of reaction (6) because of the impossibility of controlling experimentally the effect of azulene on the *trans*  $\rightarrow$  *cis* isomerization. Nevertheless, by assuming this reversibility, we can explain the increase in  $\Phi_{c-t}$ . In fact, on the basis of the above equations and with the assumption of a stationary state, expression (9) is valid for the *cis*  $\rightarrow$  *trans* quantum yield in the presence of azulene, after correction for the direct reaction and for the absorbed light fraction [8]:

$$\Phi_{c-t}^a = \eta_{isc} \frac{K_3[cis]}{K_3[cis] + K_2 + K_4[Q]} \frac{\alpha + K\tau[Q]}{1 + K\tau[Q]} \quad (9)$$

where  $\tau$  is the lifetime of the quenchable state  ${}^3trans$  and  $K = K_6K_7/K_{-6}$ .

Under our experimental conditions  $[cis] = [azulene]$  and the quantum yields no longer increase with increasing substrate concentration and are very close to the limiting value; therefore  $K_3[cis] \gg K_2$ ; also  $\eta_{isc} = 1$  for benzophenone. Equation (9) becomes

$$\Phi_{c-t}^a = \frac{K_3}{K_3 + K_4} \frac{\alpha + K\tau[Q]}{1 + K\tau[Q]} \quad (10)$$

where the first term  $K_3/(K_3 + K_4)$  represents the fraction  $F$  of excitation transfer to *cis*. This equation predicts an increase in  $\Phi_{c-t}^q$  with increasing quencher concentration from  $F\alpha$  at low  $[Q]$  to  $F$  at high  $[Q]$ . Because  $\alpha$  has a value very close to unity ( $\alpha = \Phi_{c-t} = 0.86$ ), the variation foreseen is very small.

From quenching experiments of benzophenone phosphorescence we found almost equal values of energy transfer constants to *cis*-PVTM and to azulene within experimental error ( $K_3 \approx K_4$ ). Therefore the ratio  $F$  is about 0.5 and the limiting values of  $\Phi_{c-t}^q$  expected are 0.43 and 0.5. The values of Table 1 fall within this range and the proposed mechanism that the  $^3cis$  state undergoes rapid twisting to a common  $^3p$  state in equilibrium with the  $^3trans$  state was supported.

In conclusion, our investigation of arylvinylethioamides supports the role of the aryl ring in the photoisomerization mechanism, which can be represented by a general scheme reaction that combines the singlet and triplet pathways (Fig. 2).

For TVTA and NVTA the pathways  $c$ ,  $d$ ,  $c'$ ,  $d'$  and  $e$  are proposed to be operating, whereas the pathway  $f$  was excluded because of the fast intersystem crossing of the  $^1p$  state to the  $^3p$  state, in equilibrium with the  $^3trans$  state, which converts to the *trans* and *cis* ground states through intersystem crossing (pathway  $h$ ) to the  $^0p$  state.

For PVTA and PVTM the pathways  $c$ ,  $c'$  and  $f$  are proposed to be operating, whereas  $d$ ,  $d'$  and  $e$  are negligible owing to the rapid twisting to the  $^1p$  state which converts to the  $^0p$  state bypassing the  $^3p$  state. When the  $^3trans$  and  $^3cis$  states are populated by energy transfer the photoisomerization follows the pathways  $g$ ,  $g'$  and  $h$  as for TVTA and NVTA.

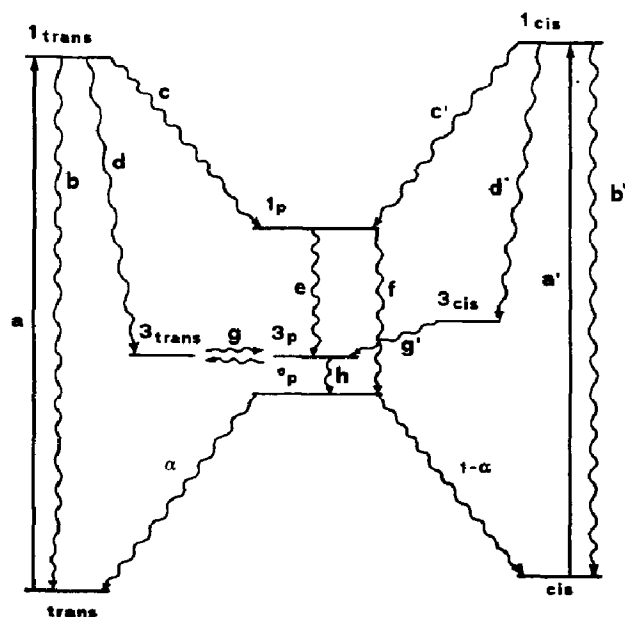


Fig. 2. General scheme of photoisomerization for arylvinylethioamides.

The  ${}^0p$  state decays to the *trans* and *cis* ground states with equal probability ( $\alpha = 0.5$ ) in TVTA, NVTA and PVTA, whereas in PVTM the decay to the *trans* ground state is much more probable ( $\alpha = 0.86$ ). This can be due to the hindrance of the morpholine group compared with that of the amino group. This large steric effect implies that the configuration of the twisted  $p$  state is closer to the *trans* configuration than to an intermediate configuration as is probable in other less hindered arylvinylethioamides.

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