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# INEFFICIENCY IN THE PHOTOISOMERIZATION OF 1,2-BIS-(4-PYRIDYL)-ETHYLENE

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We have been engaged in a study of light-induced *cis-trans* isomerization and rearrangements of the stilbazoles and bis-pyridyl-ethylenes, nitrogen containing analogs of stilbene. In the course of our work we have encountered some rather surprising phenomena.[1] The efficiency of isomerization for different compounds varies widely, depending both on number and location of nitrogen atoms. We have also observed a marked contrast between direct and sensitized reactions in several cases. In the present communication we report evidence for what amounts to a very rapid radiationless decay of excited singlet states of bis-pyridyl-ethylenes.

*Trans* 1,2-bis-(4-pyridyl)-ethylene (BPE) (Aldrich) was purified by several crystallizations from hexane. *Cis* BPE was prepared by photoisomerization of *trans* using benzil as sensitizer. The *cis* isomer was purified by repeated chromatography (alumina) and recrystallizations from hexane. Satisfactory analysis was obtained. Irradiations were carried out on degassed solutions in a "merry-go-round" apparatus[2] using the 3130 and 3660 Å lines of a medium pressure mercury lamp. Reaction mixtures were analyzed by gas chromatographic and spectral techniques. Ultraviolet spectra of *trans* and *cis* BPE are quite similar to those of their stilbene counterparts. Spectra of *trans* BPE show red shifts with increasing solvent polarity. The spectra show no sign of $n-\pi^*$ transitions. Though the *trans* isomer fluoresces, we have been unable to detect phosphorescence from either *cis* or *trans* BPE.

Both *cis* and *trans* BPE undergo fairly efficient photosensitized isomerization. The fact that benzil ($E_T$ = 53 kcal/mole) sensitizes a stationary state containing ca. 98% *cis* suggests that triplet levels for the BPE's are close to those for the stilbenes. The fraction *cis* in the benzophenone-sensitized stationary state is 0.60 ± 0.02, the same as that for stilbene.[2]

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Photoisomerization quantum yields (Table I) in both directions are somewhat low for the BPE's compared with the stilbenes or 1,2-diphenylpropenes. Studies with benzophenone as sensitizer and azulene[2,3] as quencher indicate a 50% longer lifetime for transoid triplets of BPE compared to stilbene.

TABLE I

Quantum Yields for Benzophenone Sensitized

Isomerization of 1,2-Bis-(4-Pyridyl)-Ethylenes and Stilbenes[a]

| Starting Material[b] | φ |
|---|---|
| trans BPE | 0.39 ± 0.02 |
| cis BPE | 0.21 ± 0.01 |
| trans stilbene | 0.48[c] |
| cis stilbene | 0.41[c] |

[a] Solvent, Benzene: λ - 3660 Å.

[b] Benzophenone concentration 0.05 m, olefin concentration 0.005 m, temperature 25°.

[c] Data of G. S. Hammond, et. al., J. Am. Chem. Soc., **86**, 3197 (1964).

Under direct irradiation in benzene solution at 25° both cis and trans BPE isomerize with strikingly low quantum efficiency (Table II). Degassed solutions of cis BPE gradually produce a yellow ($\lambda_{max}$ - 3430 Å), fluorescent product whose color fades rapidly when the solution is opened to air. Long term irradiation of solutions of cis produces significant quantities of trans, presumably by sensitization from the yellow product. Vpc analysis of long-irradiated solutions reveals a product having slightly longer retention time than trans. This product, which builds up rapidly in non-degassed solutions, proved to be a diazaphenanthrene.[2,4] The yellow product is probably the dihydro compound.

Solutions of trans BPE fail to undergo any change other than extremely slow formation of cis even on long term irradiation at 3130 Å. Elevation of reaction temperature to 44° produces no increase in the efficiency of isomerization. The trans to cis reaction is unaffected by changing solvent to methylcyclohexane; preliminary experiments show a very slight increase in efficiency when trans is irradiated in dimethylformamide or ethanol. Interestingly, trans 4-stilbazole, with only a single nitrogen replacing a ring carbon, undergoes efficient isomerization to *cis* in both direct[5] and sensitized reactions.

TABLE II

Quantum Yields for Direct Isomerization of 1,2-Bis-(4-Pyridyl)-Ethylenes and Stilbenes[a]

| Starting Material | $\varphi$ |
|---|---|
| *trans* BPE | 0.003 |
| *cis* BPE | $\leq$ 0.01 |
| *trans* stilbene | 0.5[b] |
| *cis* stilbene | 0.3[c] |

[a] Solvent, Benzene; Olefin Concentration, 0.005 m; 25°; $\lambda$ - 3130 Å.

[b] R. H. Dyke and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

[c] S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

The striking contrast between direct and sensitized isomerization yields indicates that the BPE's have very low intersystem crossing efficiencies ($\varphi_{isc}$). Maximum values for $\varphi_{isc}$ can be calculated by comparing the ratio $\varphi_{direct}/\varphi_{sensitized}$. This assumes that all isomerization proceeds by way of the triplet state. Values obtained by this method are 0.008 and 0.05 for *trans* and *cis* respectively.

The nearly identical absorption spectra of *trans* stilbene and *trans* BPE indicate[6] that both compounds should fluoresce with a rate constant, $k_f \approx 5 \times 10^8$ sec$^{-1}$. However, the fluorescence efficiency of *trans* stilbene exceeds that of *trans* BPE by more than two orders of magnitude. The fluorescence quantum yield, $\varphi_f$ for *trans* stilbene is 0.05[7], consequently, for *trans* BPE $\varphi_f \approx 10^{-4}$. The finding of such low efficiencies for both intersystem crossing and fluorescence demands that some new process occurs with a rate constant of ca. $10^{11}$ sec$^{-1}$. This process must be absent or slow enough to be unimportant for the stilbenes even though it results in degradation of nearly all quanta delivered to the BPE's. Interestingly, nitrogen substitution increases the lifetime of the planar triplet state while it dramatically reduces the singlet lifetime.

The phenomena reported here are probably related to the lack of emission or sensitizing properties from excited pyridine.[8] Similar energy wasting phenomena for the diazines have been attributed to decay of the initially produced singlet to a forbidden excited singlet state of lower energy. While such a process is conceivable for the BPE's, another possibility is that excited *trans* BPE singlets (as well as other pyridine and diazine derivatives) are deactivated by very rapid decay to an unstable isomer[10] which decays rapidly and specifically to *trans*. We are presently engaged in experiments to trap such products and/or verify their intermediacy.

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