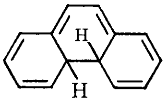
The Hexamethylstilbene–Hexamethyldihydrophenanthrene Interconversion, an Example of a Reversible Photocyclization

By K. A. MUSZKAT, D. GEGIOU, and E. FISCHER

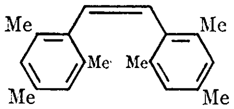
(*Photochemical Laboratory, The Weizmann Institute of Science, Rehovoth, Israel*)

ULTRAVIOLET irradiation of stilbene solutions in the absence of oxygen results in the formation, to a hitherto unknown extent, of a product assumed to be 4a,4b-dihydrophenanthrene, (I)[1–5].

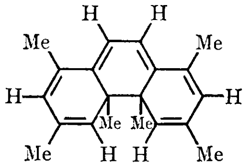
We now report results obtained by the irradiation of a solution of 1,1′,3,3′,5,5′-hexamethylstilbene (II) with 265—290 mμ light. A red product is obtained to which structure (III) is assigned on the basis of spectroscopic and chemical evidence.



(I)



(II)



(III)

This colour can be made to disappear completely either thermally, by warming above room temperature, or photochemically, by irradiating with light of wavelengths longer than about 310 mμ. In both ways *cis*-(II) is produced. The photochemical cycle *cis*-(II) ⇌ (III) seems to be largely reversible. A typical experiment is described in Figure 1 where the spectrum of a 1·3 × 10^{-4}M solution of *cis*-(II) in methylcyclohexane (curve 1) is transformed by irradiation at 275 mμ into the spectrum described by curve 2. Irradiation with visible light reverts 2 → 1. The extent of the photoconversion (II) $\xrightarrow{h\nu}$ (III) under these conditions, estimated *inter alia* from n.m.r. measurements, is about 20%. Using this value, the absorption spectrum of pure (III) was calculated by extrapolation, and is given by curve 3. A rather similar absorption spectrum was calculated for pure (I), by using a related extrapolation procedure.

The positions of the absorption peaks are as follows (approximate molar extinction coefficients in parentheses): 475 mμ (3,100), 321 mμ (7,200), 310 mμ (7,000), 245 mμ (16,000). Isosbestic points of *cis*-(II) and (III) are observed at 290 and 254 mμ.

The system (II) $\xrightarrow{h\nu}$ (III) is distinguished by the absence both of irreversible photoreactions and of oxidation by oxygen. Its thermal stability at room temperature is fair, [k(298°K) = 6 × 10^{-4} min.$^{-1}$ for the first order thermal reaction (III) → *cis*-(II)]. These three facts combine to facilitate the determination of some of the physical properties of (III) and improve the chances for its eventual isolation.

The stability of (III) towards direct and photochemical oxidation is in marked contrast to the ease with which (I) is oxidized. The reactivity of (I) is probably due to the labile allylic hydrogens in the 4a- and 4b-positions, and is removed when these hydrogens are replaced by methyl groups. This difference in chemical behaviour between (I) and

---

[1] W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Amer. Chem. Soc.*, 1963, **85**, 829.

[2] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094.

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsel, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[4] M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, 1963, **85**, 2186.

[5] The results of a detailed re-investigation of the photochemistry of the stilbene ⇌ (I) system undertaken in this Laboratory will be published shortly.

(III) thus provides additional evidence for the structures assigned above to these compounds.

The most convincing support for the correctness of formula (III) and indirectly for that of formula (I), is provided by the proton magnetic resonance spectrum of a photoreaction mixture containing about 16% of (III).

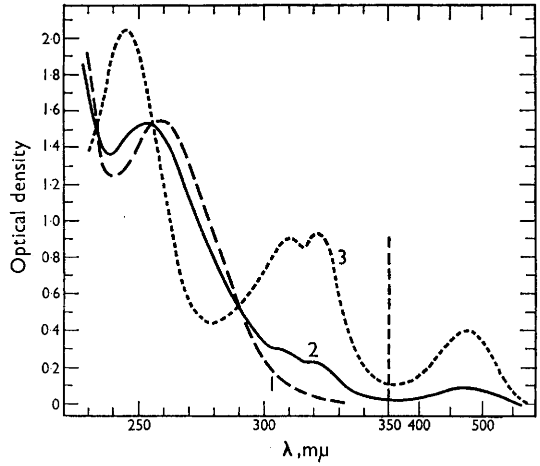


FIGURE. *Spectral changes resulting from irradiation of (II) with light as 275 mμ. Curve 1—spectrum of a* $1{\cdot}34 \times 10^{-4}$M *solution of cis-(II) in methylcyclohexane, 10 mm. cell. Curve 2—same, after irradiation. Curve 3—spectrum of pure (III), obtained by extrapolation from curve 2.*

The signals of (III) (see Table) are all sufficiently removed from those of *cis*- and *trans*-(II) to make possible a quantitative comparison of the two types of signals in the mixture of (II) and (III), and thereby also provide an independent estimate of the extent of photoconversion. The signals due to (III) disappear when the colour of the mixture is eradicated with visible light, *i.e.* after reconversion of (III) into (II).

TABLE

*P.m.r. chemical shifts of (III)**

δ, p.p.m.	Number of Protons	Assignment
1·47	6	4a, 4b methyl protons
1·68	12	1,3,6,8 methyl protons
5·35	2	9,10 protons
5·60	4	2,4,5,7 protons

* The spectrum was determined in a microcell, on a Varian Associates A–60 Spectrometer, using CCl_4 as solvent and $SiMe_4$ as internal standard.

The thermodynamic equilibrium (II) ⇌ (III) appears to be greatly in favour of (II). Compound (III) formed by ultraviolet irradiation at or below room temperature is frozen-in by virtue of the energy barrier of 23·5 Kcal/mole separating (III) from (II). This value, which is the activation energy for the first-order process (III) → *cis*-(II), was obtained from kinetic measurements in the temperature range of 40—74°C.

The quantum yields calculated[6] for (III) $\xrightarrow{h\nu}$ (II) were 0·66 at 436 and at 326 mμ, and approximately 0·4 at 313 and at 280 mμ. For (II) $\xrightarrow{h\nu}$ (III) the quantum yield was about 0·04 both at 275 and at 280 mμ. Photochemical ring closure is thus seen to be much less efficient than ring opening, possibly because of steric reasons.

(*Received, August 3rd*, 1965; *Com.* 484.)

[6] S. Malkin and E. Fischer, *J. Phys. Chem.*, 1962, **66**, 2482.