

SUBSTITUENT EFFECTS ON THE EFFICIENCY AND REGIOSELECTIVITY OF TETRAARYLETHYLENE PHOTOCYCLIZATION

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Summary

The photochemistry of tetraphenylethylene and seven *para* substituted derivatives has been investigated. All compounds underwent photocyclization in the presence of iodine to produce substituted 9,10-diphenylphenanthrenes. Two substituent effects were observed. The *para* substituents decrease the quantum yields for electrocyclization and simultaneously activate the substituted rings in a regiochemical sense. Thus cyclization involving the substituted ring always predominates. These results are discussed in terms of shifts in the position of the excited state funnel along the reaction coordinate and stabilization of the transition state for the cyclization reaction.

1. Introduction

The photochemical conversion of stilbene derivatives to phenanthrenes has been one of the most thoroughly studied photochemical transformations and remains a subject of great interest from both synthetic and mechanistic standpoints [1]. Factors which govern the efficiency of the cyclization reaction are still not clearly understood. Free valence [2] and Mulliken overlap population [3] treatments have been used with considerable success to evaluate the reactivities of a large number of hydrocarbon stilbene derivatives. Investigations of substituent effects have resulted in suggestions that inductive effects play a dominant role [4] and that the reaction occurs from an upper vibrational level of the electronic ground state [5]. More recently it has been suggested that the efficiency of the photocyclization is dependent upon the slope of the potential energy surface for the excited state reaction [6], a suggestion which ignores the activation energy for the cyclization reaction, which although small is nonetheless present [7].

We describe here the results of a study of the photochemistry of a series of *para* substituted tetraarylethylenes in which we have examined the manner in which substituents affect the efficiency of the photocyclization as

well as the regioselectivity in those cases in which more than one photocyclized product is possible.

2. Experimental

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are corrected. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Ultraviolet and visible spectral measurements were made using either a Beckman model 24 spectrophotometer or a Durrum model PGS spectrophotometer. Mass spectra were measured on a Hitachi RMU6E mass spectrometer. Elemental analyses were determined using an F&M model 185 carbon, hydrogen, nitrogen analyzer.

The tetraarylethylenes studied were prepared by literature methods. The compounds are shown in Table 1, together with references to their preparation. The *cis* isomer of 1,2-dianisyl-1,2-diphenylethylene (*cis*-3) was obtained from a mixture of *cis* and *trans* isomers by thick layer chromatography on silica gel (1:1, benzene-cyclohexane eluent) followed by crystallization from methanol-carbon tetrachloride and recrystallization from ethanol: melting point, 135 - 136 °C; NMR (CCl₄) chemical shift δ , 3.7 (strong (s), 6H) and 6.5 - 7.2 (medium (m), 18H); IR (KBr) absorptions, 675, 720, 1020 and 1230 cm⁻¹; mass spectrometry peak *m/e*, 392 (M⁺, base peak); analysis, (C₂₈H₂₄O₂):C,H.

Preparative irradiations were carried out by irradiating about 1 mmol of tetraarylethylene and 1 mmol of iodine in 350 ml of reagent grade benzene with a 450 W medium pressure mercury vapor lamp. The solvent was removed *in vacuo* and the photoproducts were purified by crystallization and/or column chromatography. Yields of 9,10-diphenylphenanthrenes were 50 - 70%. Satisfactory spectral data were obtained for all photoproducts[†].

Quantum yields for the disappearance of tetraarylethylene were determined in cyclohexane using potassium ferrioxalate actinometry [13]. Solutions were irradiated at 3000 Å in a Rayonet RPR-100 photochemical reactor equipped with a merry-go-round apparatus. The starting compounds

[†]Proton NMR chemical shifts: compound 4 (in CDCl₃), 3.8 (s,3H), 4.1 (s, 3H), 6.7 - 7.1 (m,4H), 7.2 - 7.4 (m,5H), 7.4 - 7.8 (m,5H), 8.3 (m,1H); compound 5 (in CDCl₃), 4.1 (s,6H), 7.2 (m,10H), 7.5 (m,4H), 8.2 (m,2H); compound 7 (in CDCl₃), 3.7 (s,6H), 4.0 (s,6H), 6.7 - 7.1 (m,8H), 7.3 - 8.1 (m,6H); compound 9 (in CDCl₃), 3.9 (s,3H), 7.1 (s,10H), 7.3 - 7.7 (m,4H), 8.1 (m,1H),8.5 - 8.7 (m,2H); compound 10 (in CDCl₃), 3.7 (s,3H), 6.7 (m,4H), 7.2 (s,5H), 7.3 - 7.7 (m,6H), 8.6 - 9.0 (m,2H); compound 12 (in CCl₄), 2.6 (s,3H), 7.0 - 7.2 (m,10H), 7.3 - 7.7 (m,5H), 8.4 - 8.8 (m,2H); compound 13 (in CCl₄), 2.3 (s,3H), 7.0 - 7.3 (m,9H), 7.4 - 7.6 (m,6H), 8.6 - 8.9 (m,2H); compound 15 (in CDCl₃), 7.2 (m,10H), 7.5 (m,5H), 8.8 (m,2H); compound 16 (in CDCl₃), 7.2 (m,9H), 7.6 (m,6H), 8.8 (m,2H); compound 18 (in CDCl₃), 7.1 - 7.9 (m,20H), 8.7 - 9.1 (m,2H).

TABLE 1
Photoproducts and product ratios of tetraarylethylenes

1:	$R_1 = R_2 = R_3 = R_4 = H$ [8]	2		
<i>trans</i> -3:	$R_1 = R_4 = H; R_2 = R_3 = OCH_3$ [9]	4	5	4/5 = 7.3
<i>cis</i> -3:	$R_1 = R_2 = H; R_3 = R_4 = OCH_3$ [9]			
6:	$R_1 = R_2 = R_3 = R_4 = OCH_3$ [10]	7		
8:	$R_1 = R_3 = R_4 = H; R_2 = OCH_3$ [11]	9	10	9/10 = 8.4
11:	$R_1 = R_3 = R_4 = H; R_2 = CH_3$ [12]	12	13	12/13 = 1.4
14:	$R_1 = R_3 = R_4 = H; R_2 = Cl$ [11]	15	16	15/16 = 1.1
17:	$R_1 = R_3 = R_4 = H; R_2 = Ph$ [11]	18	Not observed	

had the following values of $\log \epsilon$ at 3000 Å: 1, 4.09; *trans*-3, 4.03; *cis*-3, 4.07; 6, 4.07; 8, 4.02; 11, 4.07; 14, 4.07; 17, 4.15. Starting concentrations of tetraarylethylenes were approximately 1×10^{-8} M giving calculated absorbance values of about 15. Thus, essentially all of the incident light is absorbed. The solutions were also either 1×10^{-4} M or 5×10^{-4} M in iodine. The presence of iodine at these concentrations had no effect on the absorption spectra of the tetraarylethylenes in the 3000 Å region. In addition, the quantum yields were identical at both iodine concentrations for all of the tetraarylethylenes indicating that all of the dihydrophenanthrene intermediates were being oxidized. The solutions were nitrogen sparged for 30 min prior to irradiation. Concentrations of tetraarylethylene were measured directly spectrophotometrically before and after irradiation at a wavelength selected such that the absorptivity of the starting material was at least ten times that of the photoproduct. Conversions ranged between 5% and 15%.

3. Results and discussion

Upon irradiation in the presence of iodine, all of the compounds which were studied afforded the expected 9,10-diphenylphenanthrene derivatives [14]. The results of preparative irradiations are summarized in Table 1. It is apparent from these results that the *para* substituents exert an activating effect in a regiochemical sense. Thus in every case in which there are two possible products, the one resulting from cyclization involving a *para* substi-

tuted ring predominates. It is also interesting to note that both *cis*-3 and *trans*-3 gave identical mixtures of products indicating that geometric isomerization is much more efficient than electrocyclization.

Quantum yields for the disappearance of tetraarylethylene are recorded in Table 2. The same *para* substituents are here exerting a deactivating effect in that all of the compounds (with the exception of the monomethoxy derivative 6) underwent photocyclization with lower quantum efficiency than tetraphenylethylene. The decrease in quantum yield is accompanied by a corresponding decrease in singlet energy as represented by the values of ν_{\max} (Table 2).

TABLE 2
Quantum yields and absorption maxima

Compound	Φ^a	ν_{\max} (cm ⁻¹)
1	0.022 (0.001)	32 500
<i>trans</i> -3	0.016 (0.001)	31 300
6	0.0092 (0.0022)	30 900
8	0.027 (0.001)	31 800
11	0.018 (0.003)	32 400
14	0.019 (0.002)	32 200
17	0.0096 (0.0016)	31 300
<i>cis</i> -3 ^b	0.0099 (0.0025)	

^a Numbers in parentheses are average deviations. At least four runs were made for each compound.

^b This compound showed a marked dependence of quantum yield on irradiation time. The limiting quantum yield, extrapolated to 0% conversion, was 0.0046. The lower quantum yield for the *cis* isomer is consistent with the observed product ratios.

The decrease in quantum yield which accompanies a decrease in singlet energy has been noted by others. In a study of substituted stilbenes, Gusten and Klasinc made the suggestion that the cyclization occurs from a hot ground state [5]. Results reported by Laarhoven and Cuppen [15] and more recently by Filipescu *et al.* [16] indicate that the cyclization is conrotatory and therefore most likely from an electronically excited state. Muszkat and Schmidt have suggested that the efficiency of the photocyclization reaction will decrease as the slope of the potential energy surface decreases along the reaction coordinate [6]. Such an argument depends upon the absence of an activation energy for the excited state reaction. It has been shown, however, that there is an activation energy of about 3 kcal mol⁻¹ [7]. In addition, the transition state for the reaction is believed to occur early[†] and thus should be stabilized by the presence of *para* substituents.

[†] The photocyclization of the parent hydrocarbon has been described by Sargent and Timmons [14].

We feel that the substituent effects which we have described can be interpreted by examining the potential energy curve which might be expected for such a photocyclization (Fig. 1). An allowed crossing between the S_1 and S_2 surfaces may provide a funnel from which demotion to the ground state occurs [18]. Introduction of a substituent in the *para* position will lower the singlet energy of the reactant while that of the product will be expected, on the basis of both extended Hückel [6] and simple Hückel calculations, to remain essentially unchanged. This will shift the position of the excited state funnel back along the reaction coordinate towards the starting material increasing the probability of decay to regenerate starting material. This is shown in Fig. 1. This approach also provides a convenient explanation for the failure of 9,10-diphenylphenanthrene to photocyclize further to give dibenzo(g,p)chrysene. Bridging two *ortho* carbons to convert tetraphenylethylene to 9,10-diphenylphenanthrene results in a sharp decrease in the S_1 - S_2 energy gap from 24 kcal mol⁻¹ to only 3 kcal mol⁻¹ as estimated from absorption spectral data. This stabilization of S_2 might shift the funnel further in the direction of the starting material rendering demotion to give the photocyclized product virtually impossible.

The observed product ratios may also be a manifestation of the same effect. The presence of the *para* substituent will lower the activation energy for cyclization involving the substituted ring making that the preferred mode

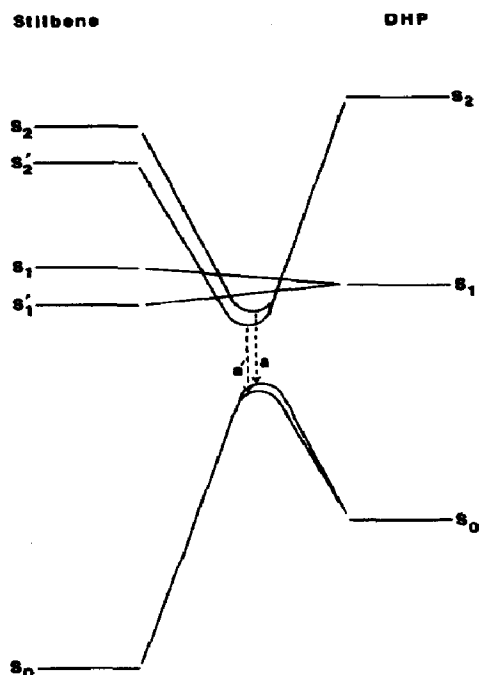


Fig. 1. State correlation diagram for the conversion of *cis*-stilbene to 4a,4b-dihydrophenanthrene (DHP). Demotion from excited to ground state occurs at point a. The primes designate states stabilized by the presence of *para* substituents.

of cyclization. This can be shown by an examination of the product ratios listed in Table 1. The substituents which should most effectively stabilize the transition state (phenyl and methoxy) are those which produce the greatest selectivity. The molecule thus "selects" the pathway with the lowest activation energy which is also the one with the lowest quantum efficiency.

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