THE INFLUENCE OF SUBSTITUENTS ON THE PHOTODEHYDROCYCLIZATION OF 1,2-DIPHENYLCYCLOPENTENES I: PARA SUBSTITUENTS†

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Summary

The photodehydrocyclization of several mono-para-substituted 1,2-diphenylcyclopentenes into a phenanthrene derivative has been investigated under several conditions. It was found that the relative quantum yield of phenanthrene formation in methanol depends on the substituent when an oxidant with low efficiency (*e.g.* atmospheric oxygen) is used. In cyclohexane solution or in the presence of a more efficient oxidant, no significant substituent influence was observed. Furthermore, it has been established that the thermal ring opening of the primary photocyclization product dihydrophenanthrene (DHP) is influenced by substituents: an isokinetic relationship was found for this reaction but a linear Hammett relation was not observed. From these results it was concluded that the primary photocyclization step is not influenced by substituents. The quantum yield of product formation is influenced under conditions where thermal ring opening and oxidation of the intermediate DHP become competitive reactions (*i.e.* at low oxidation rates). The differences between the photocyclization behaviours of 1,2-diphenylcyclopentenes and stilbenes are discussed.

1. Introduction

The influence of substituents on the photodehydrocyclization of stilbene and stilbene-like compounds has been studied by several workers. Substituents may be divided into two classes by considering their particular influence on this process. (i) Substituents that induce enhanced intersystem crossing from the S_1 state to the T_1 state, *e.g.* $-NO_2$, $-Br$, $-CO(CH_3)$. Stilbenes substituted by these groups have strongly reduced photocyclization quantum yields [1] since the photocyclization proceeds from the singlet state [1 - 4]. (ii) Substituents without appreciable influence on the intersystem crossing, *e.g.* $-CH_3$, $-OCH_3$, $-F$, $-Cl$. Several workers [5, 6] have reported correlations of quantum yields or rate constants of product forma-

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†Dedicated to Professor Dr. E. Fischer on the occasion of his 65th birthday.

tion in photoreactions with substituent constants. Only those related to stilbene photocyclization will be mentioned here. Jungmann *et al.* [7] have evaluated the quantum yields of phenanthrene formation (Φ_c) of mono-substituted stilbenes in air-saturated cyclohexane as the solvent. They obtained a linear Hammett relation using σ_p constants for meta-substituted stilbenes.

For para-substituted stilbenes the quantum yield Φ_c decreased with increasing magnitude of the σ constant. On the basis of calculations by the Hückel molecular orbital method on the electronic ground state of the meta-substituted stilbenes and the UV-absorption maxima of the para-substituted *cis*-stilbenes, Güsten and Klasinc [8] concluded that the photocyclization proceeds via higher vibrational levels of the electronic ground state. In this way the relation between quantum yields and ground state substituent constants was accounted for. This conclusion is, however, in conflict with the observation that the photocyclizations proceed from the S_1 state [1 - 4].

Mallory *et al.* [9] have studied the influence of substituents (X) on the photodehydrocyclization of 1,1-diphenyl-2-(*p*-X-phenyl)ethylenes **1** into 3-X-9-phenylphenanthrenes **3** in cyclohexane as the solvent (see Scheme 1). They observed that the oxidation process is independent of the substituent X. Assuming that the rate constants of deactivation processes of **1** other than cyclization into **2** in the S_1 state are also independent of the substituent they obtained a Hammett relation for the rate constants of cyclization using σ_m values. The linear relation was ascribed to the existence of an activation barrier in the cyclization pathway of **1** (S_1) into **2** whose magnitude depends on the substituent.
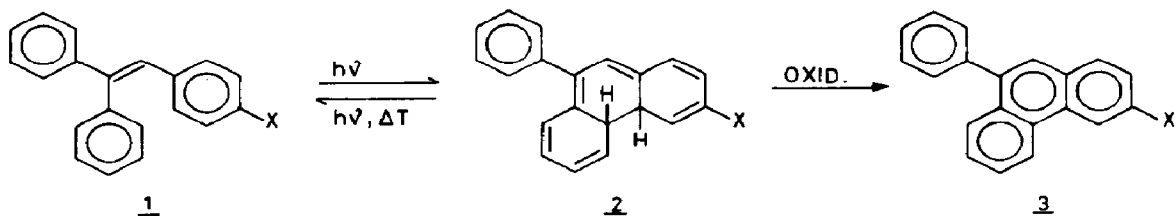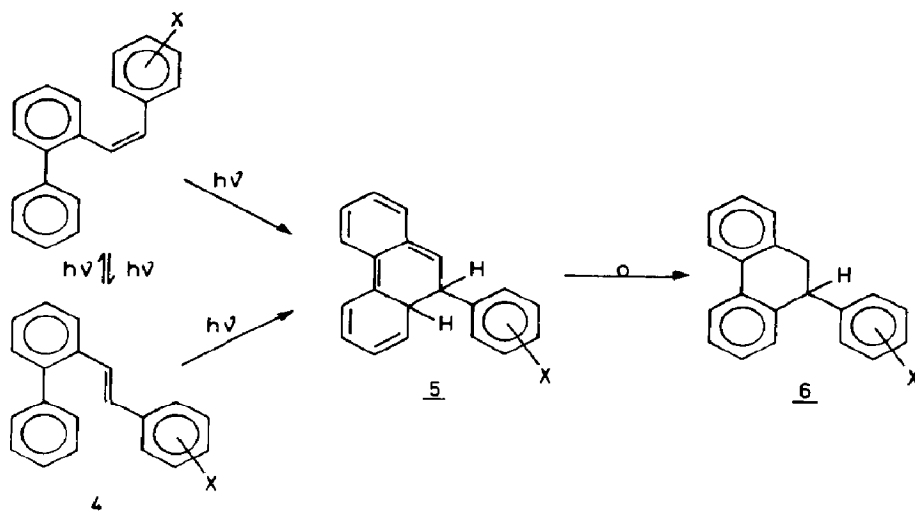

Scheme 1.

More recently the photochemistry of substituted 2-styrylbiphenyls **4** was studied by Op het Veld and Laarhoven [10].

A Hammett relation was obtained for the quantum yields of formation of the 9,10-dihydrophenanthrenes (Scheme 2). The substituents did not appear to influence the S_1–S_0 energy gap of **4** and it was supposed that the substituents affect the heights and positions of the extrema in the energy curves for ground and excited electronic states along the reaction coordinate of photocyclization. The authors argued that the correlation obtained with ground state σ values indicates that the substituent mainly affects the maximum of the energy curve of the S_0 state.

A somewhat different explanation was offered by Olsen and Buckles [11]. The decrease in quantum yield of photocyclization upon introduction

Scheme 2.

of a para substituent in tetraphenylethylene **7** (Scheme 3) was accompanied by a corresponding decrease in singlet energy (compare with Jungmann *et al.* [7]) and was ascribed to a lowering of the position of the excited state minimum relative to the ground state maximum along the reaction coordinate of photocyclization [11]. The observed predominance of the cyclization involving the substituted ring was ascribed to a lower energy of activation for that mode of cyclization.
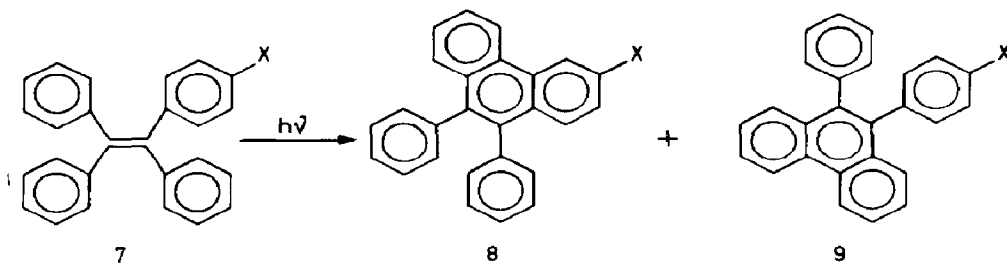

Scheme 3.

A qualitative explanation of the influence of substituents on the photocyclization of stilbene by Muszkat and Schmidt [12] was based on the use of first- and second-order perturbation effects of substituents on the energies of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), calculated by the extended Hückel method. They obtained results that were in accordance with the experimental findings [7]. More recently these authors used Mulliken electronic overlap populations [13] as a reactivity measure and obtained similar results [14]. The results, however, of analogous calculations by Op het Veld and Laarhoven [10] were not in agreement with his experimental observations.

All these authors [7 - 12, 14] have assumed that the influence of a substituent on the quantum yield of formation of the final photoproduct reflects its influence on the quantum yield of formation of the primary cyclization product. Recently, Zimmerman and Factor ascribed the successful use of ground state substituent constants in a di-π-methane rearrangement to the fact that the substituent was in a ground state moiety of the excited molecule [6]. However, such a situation cannot be expected for stilbenes, with the possible exception of distyrylbenzenes [15]. Muszkat and Schmidt have questioned [10] the applicability of their first-mentioned method [12]. Op het Veld and Laarhoven [10] and Olsen and Buckles [11] have sought a qualitative explanation of the substituent effects by considering variations in the state correlation diagrams for photocyclization. The results of Mallory et al. [9] are essentially similar, but by tentatively assuming that processes of deactivation of excited stilbene, other than photocyclization, are independent of the substituent it was concluded that the substituents influence the height of an activation barrier in the 1 (S$_1$) $\rightarrow$ 2 reaction.

In order to obtain greater insight into the effect of substituents on such photocyclizations we studied the photochemistry of substitution products of 1,2-diphenylcyclopentene 10a. Since the cyclopentene ring prevents cis–trans isomerization, one of the deactivation channels of the S$_1$ state of this stilbene system is eliminated. Furthermore, processes originating from a trans isomer do not interfere.


10a
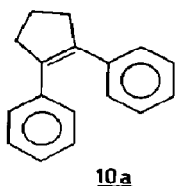
The photochemistry of the parent compound 10a has been extensively studied by Muszkat, Fischer and coworkers [3, 16 - 21].

1.1. Irradiations

The quantum yield of photodehydrocyclization of several para-substituted 1,2-diphenylcyclopentenes 10 into phenanthrenes 11 (Scheme 4) was determined relative to that of the parent compound 10a.

Irradiations were carried out at 300 nm through Pyrex in a Rayonet RPR-100 photochemical reactor equipped with a "merry-go-round" apparatus using RPR 3000 Å lamps. The solutions were 10^{-3} M in the stilbene, affording calculated absorbance values of 5 - 8 at 300 nm so that essentially all of the incident light was absorbed and the percentages of conversion were kept low (5% - 25%). Cyclohexane or methanol was used as the solvent, iodine and/or oxygen as the oxidant. In general, the corresponding phenanthrenes were the only photoproducts. Degradation products or products resulting from a (1,3) hydrogen shift in the cyclopentene ring were not observed, except when irradiating 10g.

Scheme 4.

a X = H
b X = CF₃
c X = OCH₃

d X = F
e X = Cl
f X = CH₃
g X = OH
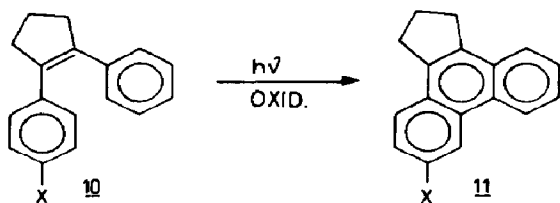
In past studies, to deduce the influence of substituents on the photo-cyclization of stilbenes, it has been assumed that the relative amounts of the final photoproducts correspond to the relative amounts of the primary cyclization products formed [7 - 13].

Mallory and Mallory [22] have reported that the use of a sufficient amount of iodine ensures effective trapping of the primary **4a,4b**-DHP which is formed. Because oxidation by oxygen is slower [3, 22, 23], we did some test runs (10^{-3} M solutions of **10a** in MeOH or cyclohexane) without iodine in an air atmosphere. After irradiation in a quartz cuvette for a few minutes the orange-yellow colour of the solution showed that not all of the **4a,4b**-DHP **12a** had been oxidized. Using the molar extinction coefficients of **10a** and **11a** (see Section 2) and the values given by Muszkat and coworkers [14, 16] for **12a**, the amount of **12a** was estimated to be approximately 5% in MeOH. Even after irradiation of an air-saturated solution some **12a** was still present (approximately 2%).
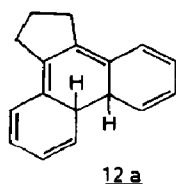
This might interfere with an accurate determination of the quantum yields. Therefore, it was decided to perform experiments in which the reaction mixtures were kept in the dark after a short irradiation until the **4a,4b**-DHP **12** had disappeared.

In a parallel series of experiments, solutions of **10a - f** were irradiated for periods of 2 min. After each period the samples were irradiated with visible light, in order to cause photoerasure of the **4a,4b**-DHP [4, 17]. Similar experiments were performed in cyclohexane; the amount of unconverted **4a,4b**-DHP in this solvent appeared to be much smaller.

The product composition of the irradiation mixtures was determined by ^{1}H nuclear magnetic resonance (NMR) and UV spectroscopy. Product

yields were obtained from the NMR spectra by integration of the cyclopentene ring proton signals, which are well separated from each other and from all other signals. Determination by UV spectroscopy was carried out by means of a computer program [24] using absorbance values at 15 - 20 wavelength points.

2. Experimental section

2.1. General methods

^{1}H NMR spectra were recorded on a Bruker WH-90 spectrometer in CDCl$_3$ solution with tetramethylsilane (δ = 0) as an internal standard. UV spectra were measured with a Perkin–Elmer 555 spectrometer. Mass spectra were recorded on a Varian MAT SM2B or Finnigan 2200 spectrometer. Melting points were determined using a Leitz melting-point microscope and are uncorrected. For column chromatography, silica (Merck, 0.063 - 0.200 mm) or alumina (Baker, aluminium oxide, neutral) was used. High performance liquid chromatography (HPLC) separations (Merck, Kieselgel 60H) were carried out on a Jobin–Yvon S.A. Miniprep liquid chromatograph (LC) fitted with a Water Associates R404 differential refractometer and a Pye–Unicam LC–UV detector. The thermal decay of 4a,4b-DHPs was followed on a Cary 15 UV spectrometer.

The procedure was as follows. An approximately 10^{-3} M solution of stilbene in MeOH was introduced into a quartz spectrophotometric cuvette which was placed in a windowed copper block surrounded by an optical Dewar flask with four quartz windows. The temperature was regulated by a stream of nitrogen through holes in the copper block and controlled by a Cryoson DR-3/TR L-4 temperature controller using a thermocouple placed against the cuvette. This equipment was originally described by Fischer [25]. The temperature was adjusted and the solution was flushed with nitrogen for 20 min and then irradiated, under nitrogen, with an external light source (Philips HPK 125W), shining through a CoSO$_4$–NiSO$_4$ filter [16], for 15 - 20 min. After irradiation, a plot of absorbance $vs.$ time was recorded. Initial absorbance values were generally about 0.8. Activation energies and entropies were determined using plots of ln(absorbance) $vs.$ time and ln k $vs.$ T^{-1} for at least four temperatures. At −30 °C the 3-substituted DHPs appeared to be stable, indicating that oxygen removal was sufficient and the measuring-light intensity was appropriate.

2.2. Synthesis

The majority of the stilbenes 10 were synthesized starting from cyclobutanecarboxylic acid as indicated in Scheme 5.

The synthesis of cyclobutyl phenyl ketone is described in ref. 26. The ketone was converted, using a Grignard reaction, into the alcohols 15 (yields 50% - 85%). These were purified by column chromatography over silica, using a hexane–chloroform gradient. On refluxing the alcohol 15 in 98% -

100% HCOOH for 8 - 12 h a mixture of isomers **16**, **10** and **17** was obtained [27]. In general, the substituted 1,2-diphenylcyclopentene **10** was the predominant product. **16**, **10** and **17** were separated and purified either by HPLC on a preparative scale or by column chromatography over alumina using hexane as the eluent. The pure fractions were used for the experiments. They were stored in a refrigerator (−20 °C) under nitrogen. The para-hydroxy-substituted stilbene **10g** was synthesized from the methoxy-stilbene **10c** using pyridine hydrochloride [28].
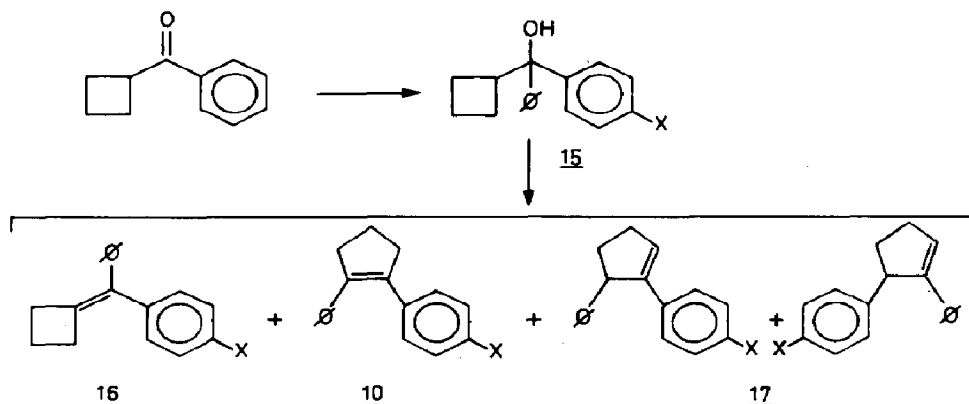
Scheme 5.

Preparative irradiations were carried out through Pyrex in a Rayonet RPR-100 photochemical reactor fitted with RPR 300 nm lamps. The 3-substituted phenanthrenes **11** were purified by precipitation from methanol, recrystallization or HPLC (silica/hexane). The physical data for the alcohols **15**, stilbenes **10** and phenanthrenes **11** are presented in Tables 1 - 3.

3. Results and discussion

In Table 4 the quantum yields for the formation of the 3-substituted phenanthrenes **11a** - f are given, relative to that of the unsubstituted phenanthrene **11a**, in 10^{-3} M methanolic solutions of **10a** - f under several oxidative conditions without subsequent photoerasure of the remaining **4a,4b**-DHP.

Figure 1 shows the formation of 3-substituted phenanthrenes **11a** - f with time in 10^{-3} M methanolic solutions of **10a** - f under an air atmosphere with photoerasure of the remaining DHP after irradiation periods of 2 min.

Table 5 and Fig. 2 show the results of similar experiments in cyclohexane. In the experiments corresponding to Fig. 1, the amount of the substituted **4a,4b**-DHP **12** present after each irradiation period (as judged from the intensity of the colour of the solution just before photoerasure) decreased with substituent in the order H, F, Cl > CF$_3$ > CH$_3$, OCH$_3$, while the quantum yield of phenanthrene formation increased in the reverse order.

TABLE 1

Physical data of alcohols 15

Phenyl substituent	^1H NMR (CDCl$_3$), δ (ppm) (TMS, δ = 0)	UV (MeOH) λ_{max} (nm) (log ϵ)	Melting point (°C)	Mass spectrum (m/e, relative intensity; e.m., exact mass; t, theory)
H	1.55 - 2.10 (m, 6H), 2.19 (s, OH, 1H), 3.41 (m, αH, 1H), 7.16 - 7.37 (m, 10H)	260 (2.63), 217 (3.86)	37.0 - 37.5	238 (M$^+$, 12), 220 (4), 210 (2), 191 (5), 183 (100), 165 (10), 152 (7), 143 (3), 133 (8), 105 (56) e.m. 238.137 ± 0.003, t 238.136
p-CF$_3$	1.60 - 2.15 (m, 6H), 2.25 (s, OH, 1H), 3.42 (m, αH, 1H), 7.2 - 7.6 (m, 9H)	257 (3.22), 219 (4.11)	69.0 - 70.0	306 (M$^+$, 7), 287 (2), 262 (2), 251 (100), 207 (2), 183 (5), 173 (28), 145 (6), 105 (4) e.m. 306.291 ± 0.003, t 306.292
p-OCH$_3$	1.7 - 2.1 (m, 6H), 2.14 (s, OH, 1H), 3.38 (m, αH, 1H), 3.76 (s, OCH$_3$, 3H), 6.7 - 6.8 (m, 2H), 7.2 - 7.4 (m, 7H)	281 (3.13), 275 (3.21), 226 (4.09), 204 (4.32)	Oil	268 (M$^+$, 18), 250 (6), 236 (5), 227 (41), 220 (22), 213 (100), 201 (19), 160 (74), 135 (54), 105 (60), e.m. 268.146 ± 0.003, t 268.146
p-F	1.55 - 2.1 (m, 6H), 2.18 (s, OH, 1H), 3.38 (m, αH, 1H), 6.84 - 7.40 (m, 9H)	271 (2.76), 264 (2.86), 206 (4.21)	Oil	256 (M$^+$, 3), 201 (100), 179 (4), 163 (2), 151 (6), 123 (23) e.m. 256.182 ± 0.003, t 256.183
p-Cl	1.8 - 2.1 (m, 6H), 2.19 (s, OH, 1H), 3.32 (m, αH, 1H), 7.15 - 7.36 (m, 9H)	268 (3.61), 222 (4.19), 206 (4.30)	47.5 - 49.0	274, 272 (M$^+$, 5, 14), 220, 218 (18, 46), 219, 217 (34, 100), 141 (18) e.m. 272.213 ± 0.003, t 272.214
p-CH$_3$	1.7 - 2.1 (m, 6H), 2.16 (s, OH, 1H), 2.29 (s, CH$_3$, 3H), 3.39 (m, αH, 1H), 7.0 - 7.4 (m, 9H)	260 (2.57), [218 (4.10)], 206 (4.27)	Oil	252 (M$^+$, 20), 197 (100), 181 (9), 165 (9), 152 (5) e.m. 252.149 ± 0.003, t 252.151
p-Br	1.6 - 2.1 (m, 6H), 2.21 (s, OH, 1H), 3.30 (m, αH, 1H), 7.1 - 7.5 (m, 9H)	260 (2.61), [218 (4.20)], 205 (4.40)	Oil	318, 316 (M$^+$, 4, 4), 300, 298 (34, 30), 263, 261 (92, 100), 185, 183 (20, 21) e.m. 318.199 ± 0.003, t 318.198

TABLE 2

Physical data of 1,2-diphenylcyclopentenes **10**

Substituent	^1H NMR (CDCl$_3$), δ (ppm) (TMS, $\delta = 0$)	UV (MeOH) λ_{max} (nm), $\lambda_{1/2\,max}$ (log ϵ)	UV (cyclohexane) λ_{max} (nm), $\lambda_{1/2\,max}$ (log ϵ)	Mass spectrum (m/e, relative intensity; e.m.: exact mass; t: theory)
H	7.13 (s, 10H)	224 (4.19), 270 (4.03), 304	225 (4.20), 274 (4.03), 304	220 (M$^+$, 45), 129 (70), 115 (58), 91 (100), 77 (39), calcd. for C$_{17}$H$_{16}$: C 92.68, H 7.32; found: C 92.82, H 7.24
p-CF$_3$	7.0 - 7.5 (m, 9H)	228 (4, 18), 282 (4.02), 308	228 (4.20), 282 (4.02), 308	288 (M$^+$, 100), 273 (34), 219 (44), 91 (73), e.m. 288.114 ± 0.003, t 288.112
p-OCH$_3$	3.75 (s, OCH$_3$, 3H), 6.90 (d, 2H, $J = 8.5$ Hz), 7.06 (d, 2H, $J = 8.5$ Hz), 7.18 (s, 5H)	232 (4.21), 276 (4.05), 306	232 (4.24), 280 (4.05), 308	250 (M$^+$, 97), 235 (23), 219 (35), 91 (100)
p-F	6.7 - 7.3 (m, 9H)	222 (4.13), 270 (3.98), 302	224 (4.16), 270 (3.99), 302	238 (M$^+$, 100), 223 (22), 139 (50), 91 (40), e.m. 238.118 ± 0.003, t 238.116
p-Cl	7.0 - 7.3 (m, 9H)	230 (4.22), 276 (4.04), 305	232 (4.27), 278 (4.05), 307	256, 254 (M$^+$, 40, 100), 251, 249 (15, 41), 219 (63), 91 (85), e.m. 254.084 ± 0.003, t 254.086
p-CH$_3$	2.29 (s, CH$_3$, 3H), 7.0 - 7.3 (m, 9H)	228 (4.20), 276 (4.05), 305	230 (4.21), 277 (4.02), 306	234 (M$^+$, 100), 219 (59), 204 (34), 91 (69), e.m. 234.142 ± 0.003, t 234.141
p-OH	4.95 (s, OH, 1H), 6.5 - 7.3 (m, 9H)	278		

All these stilbenes have a similar pattern for the protons of the cyclopentene ring in their ^1H NMR spectra: a two-proton quintet/multiplet centred at $\delta = 2.04 \pm 0.03$ with $J = 7.0 - 7.5$ Hz and a four-proton triplet/multiplet centred at $\delta = 2.89 \pm 0.03$ with $J = 7.0 - 7.5$ Hz. The remaining parts of the spectra are given in the table. All the stilbenes **10** were obtained as an oil, with the exception of **10a** (melting point, 60.0 - 61.0 °C; literature value [27], 61 - 62 °C).

The solutions of **10c** and **10f** were not visibly coloured. Similar, although generally somewhat smaller, differences in relative quantum yields were obtained upon irradiation without intermediate photoerasure of the 4a,4b-DHPs (see Table 4, air). The percentages of conversion of **10c** as well

TABLE 3

Physical data of cyclopentenophenanthrenes 11

Substituent	^1H NMR δ (ppm) (TMS, $\delta = 0$)	UV (MeOH) λ_{max} (nm) (log ϵ)	Melting point (°C)	Mass spectrum (m/e, relative intensity; e.m.: exact mass; t: theory)	Elemental analysis c: calculated (%) f: found (%)
H	7.47 - 7.94 (m, 6H), 8.61 - 8.79 (m, 2H, H_4, H_5)	300 (4.10), 288 (4.02), 278 (4.09), 270 (4.26), 254 (4.80), 212 (4.51)	150.5 - 152.5	218 (M^+, 100), 217 (39), 202 (18), 189 (4), 176 (2), 165 (3), e.m. 218.108 ± 0.003, t 218.109	c C93.54 H6.46 f C93.54 H6.48
3-CF_3	7.13 - 7.98 (m, 5H), 8.59 - 8.77 (m, H_5), 8.92 (brs, H_4)	307 (4.07), 296 (4.02), 272 (4.24), 253 (4.71), 212 (4.50)	86.0 - 87.0	286 (M^+, 100), 285 (26), 270 (6), 236 (21), 215 (44), 202 (12), e.m. 286.268 ± 0.003, t 286.266	c C75.51 H4.58 f C75.32 H4.54
3-OCH_3	4.01 (s, OCH_3, 3H), 7.01 - 7.88 (m, 5H), 8.07 (brs, H_4), 8.51 - 8.68 (m, H_5)	307 (4.04), 296 (3.97), 278 (4.24), 252 (4.70), 228 (4.42)		248 (M^+, 100), 233 (25), 217 (40), 215 (35), 202 (40), 189 (10), 124 (10)	c C87.06 H6.49 f C86.93 H6.47
3-F	6.96 - 7.89 (m, 5H), 8.27 (dd, H_4, $J_{H,F}$ = 11 Hz, $J_{H2,H4}$ = 2.5 Hz), 8.44 - 8.57 (m, H_5)	299 (4.00), 286 (3.96), 278 (4.14), 272 (4.24), 252 (4.73), 212 (4.48)	71.5 - 73.0	236 (M^+, 100), 235 (45), 220 (19), 207 (5), 183 (3), e.m. 236.158 ± 0.003, t 236.156	c C86.41 H5.55 f C86.28 H5.62
3-Cl	7.44 - 7.89 (m, 5H), 8.49 - 8.62 (m, H_4 and H_5)	305 (4.12), 292 (3.99), 280 (4.06), 274 (4.21), 254 (4.75), 216 (4.44)	95.0 - 96.0	254, 252 (M^+, 33, 100), 251 (17), 217 (73), 216 (65), 215 (68), 213 (60), 202 (65), 189 (60), e.m. 252.187 ± 0.003, t 252.188	c C80.79 H5.18 f C80.94 H4.99

TABLE 3 *(continued)*

Substituent	*^{1}H NMR* δ (ppm) (TMS, δ = 0)	*UV (MeOH)* λ_{max} (nm) (log ϵ)	*Melting point* (°C)	*Mass spectrum (m/e, relative intensity; e.m.: exact mass; t: theory)*	*Elemental analysis c: calculated (%) f: found (%)*
3-CH$_3$	2.61 (s, CH$_3$, 3H), 7.02 - 7.87 (m, 5H), 8.47 (brs, H$_4$), 8.57 - 8.76 (m, H$_5$)	302 (4.11), 290 (4.01), 280 (4.11), 272 (4.24), 255 (4.79), 224 (4.37), 214 (4.48)	96.5 - 98.0	232 (M$^+$, 100), 231 (42), 217 (42), 215 (49), 202 (20), 189 (8), 178 (4)	c C93.06 H6.94 f C93.09 H7.02
3-OH	4.32 (s, OH, 1H), 6.37 - 7.78 (m, 5H), 7.93 (d, H$_4$), 8.34 - 8.51 (m, H$_5$)	366, 350, 307, 279, 250			

All these phenanthrenes have in their ^{1}H NMR spectra a similar pattern for the protons of the cyclopentene ring: a four-proton triplet of triplet-like multiplet centred at δ = 3.33 ± 0.04 with J = 7.0 - 7.5 Hz and a two-proton quintet/multiplet centred at δ = 2.33 ± 0.03 with J = 7.0 - 7.5 Hz. The remaining part of the spectra is given in the table.

TABLE 4

Quantum yields (Φ_{rel}) for photoformation of 3-substituted phenanthrenes 11a - f in 10^{-3} M methanolic solutions of para-substituted diphenylcyclopentenes 10a - f, relative to that of **11a**, at 30 °C

Phenanthrene 11	*Oxidant*	
	Air[a] Φ_{rel}[c]	*I_2*[b]*/air*[a] Φ_{rel}[c]
a H	1.0	1.0(2.0)[d]
b CF$_3$	0.92	0.94
c OCH$_3$	1.7	1.1
d F	0.93	0.84
e Cl	0.71	1.1
f CH$_3$	1.9	1.0
g OH[e]	≈ 1.7[e]	≈ 1.1[e]

[a] $[O_2]$ = 2.1 × 10^{-3} mol l^{-1} [29].
[b] $[I_2]$ = 0.5 × 10^{-3} mol l^{-1}.
[c] Uncertainty in values of Φ_{rel} is approximately 10%.
[d] Relative to **11a** with air as the oxidant (see Table 3).
[e] Value refers to Φ of disappearance of **10g** since **11g** is not the only product (see text).
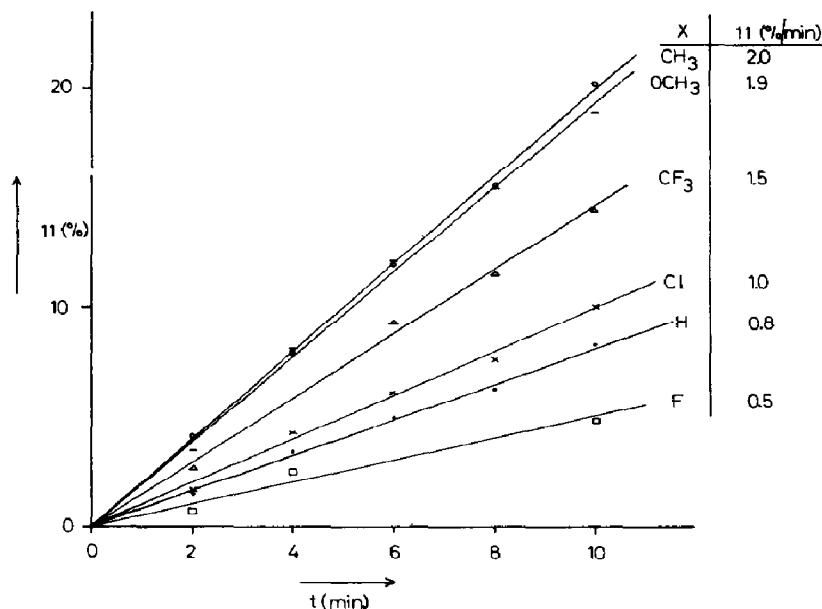
Fig. 1. Formation of phenanthrenes 11a - f with time in 10^{-3} M solutions of 10a - f in MeOH at 30 °C under an air atmosphere with photoerasure of remaining DHP after irradiation periods of 2 min.

TABLE 5

Quantum yields Φ_{rel} of photoformation of phenanthrenes 11a - f in 10^{-3} M cyclohexane solutions of 10a - f relative to that of 11a at 30 °C

Phenanthrene (11)	Oxidant		
	Air[a] Φ_{rel}[d]	I_2/air[a,b] Φ_{rel}[d]	I_2/N_2[b,c] Φ_{rel}[d]
a H	1.0	1.0	1.0
b CF$_3$	1.1	1.0	1.0
c OCH$_3$	1.1	1.0	1.1
d F	0.83	1.0	1.0
e Cl	0.95	1.1	1.0
f CH$_3$	1.2	1.2	1.1

[a]$[O_2] = 2.3 \times 10^{-3}$ mol l^{-1} [29].
[b]$[I_2] = 0.5 \times 10^{-3}$ mol l^{-1}.
[c]Nitrogen flushed.
[d]The uncertainty in values of Φ_{rel} is approximately 10%.

as 10f were almost the same in both procedures after equal irradiation periods. Thus, the differences in relative quantum yields seem to be due to incomplete oxidation of the 4a,4b-DHPs.

Oxidation by iodine may involve molecular as well as atomic iodine, since iodine in MeOH has an absorption band around 300 nm and the reaction is much faster than oxidation by oxygen [3, 22, 23]. The use of iodine
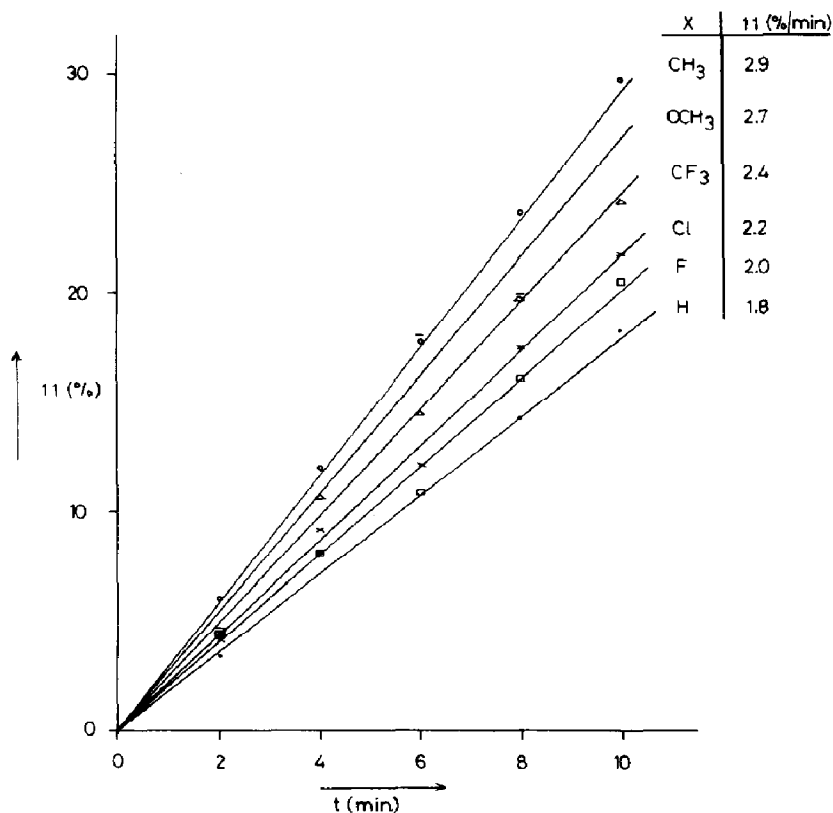
X	11 (%/min)
CH$_3$	2.9
OCH$_3$	2.7
CF$_3$	2.4
Cl	2.2
F	2.0
H	1.8

Fig. 2. Formation of phenanthrenes 11a - f with time in 10^{-3} M solutions of 10a - f in cyclohexane at 30 °C under an air atmosphere with photoerasure of remaining DHP after irradiation periods of 2 min.

as the oxidant results in nearly equal quantum yields of phenanthrene formation for all derivatives of 10 (see Table 4). Furthermore, in accordance with the (almost) absent orange-yellow colour of 12c upon irradiation in MeOH–air it was found that the quantum yield of formation of 11c in MeOH–I$_2$–air relative to that in MeOH–air was 1.3, whereas that of 11a was 2.0. (The absorption of low concentrations (below 10^{-3} M) of iodine around 300 nm does not influence the relative quantum yields given in Table 4. Irradiation of 2.2×10^{-4} M solutions of 10a, 10b and 10c in MeOH saturated with potassium peroxosulphate (K$_2$S$_2$O$_8$) as the oxidant (which does not absorb light around 300 nm) in an electronically integrating actinometer device [30] at 313 nm (bandwidth 20 nm) resulted in equal amounts of phenanthrene after absorption of equal quantities of light while no absorption by DHP could be detected.)

Comparison of the data in Table 5 (with air as oxidant) with those in Table 4 (with air) shows that the differences in relative quantum yields for the various substituents are smaller in cyclohexane. In this solvent the quantum yields of the substituted stilbenes 10b - f are comparable with that of 10a. The same conclusion can be drawn from the graphs in Figs. 1 and 2.

TABLE 6

Quantum yields of photoformation of 11a and 11c in several media (10^{-3} M in stilbene) relative to the value in MeOH/air[a] at 30 °C

Solvent/oxidant	11a Φ_{rel}[c]	11c Φ_{rel}[c]
MeOH/air	1	1[b]
MeOH/I$_2$ (0.5×10^{-3} M)/air	2	1.3
MeOH/I$_2$ (1.0×10^{-3} M)/air	1.2	—
Cyclohexane/air	3	1.9
Cyclohexane/I$_2$ (0.5×10^{-3} M)/air	4	2.6
Cyclohexane/I$_2$ (1.0×10^{-3} M)/air	4	—
Cyclohexane/I$_2$ (0.5×10^{-3} M)/N$_2$	2.7	1.7

[a] $[O_2] = 2.1 \times 10^{-3}$ M [29].
[b] $\Phi_{rel}(OCH_3) = 1.7\Phi_{rel}(H)$ (see Table 1).
[c] Uncorrected for light absorption by I$_2$.

The smaller differences were accompanied by much smaller differences in the intensity of the orange-yellow colour of the 4a,4b-DHPs, observed before photoerasure: after 2 min irradiation periods the solutions were almost colourless. Apparently in cyclohexane there are no large differences in the rates of oxidation of the DHPs derived from para-substituted stilbenes 10.

In Table 6 the quantum yields of phenanthrene formation for 10a and 10c in several media determined from NMR data are collected, relative to the value in MeOH under an air atmosphere.

The use of a 0.5×10^{-3} M solution of iodine in MeOH causes an increase in the quantum yield of phenanthrene formation compared with MeOH and air. Further increase in the iodine concentration leads to a gradual decrease in the quantum yield. This can be ascribed to light absorption by iodine. The change to cyclohexane as solvent also causes an increase in the quantum yield. The addition of iodine (transmission through 1 cm solution is 80% - 90% at the employed concentrations) in this solvent does not lead to a spectacular change in the quantum yield; in itself it is, however, a very effective oxidant (iodine under nitrogen). The high quantum yields obtained in cyclohexane with air accompany highly efficient oxidation of DHP. It has already been mentioned that (almost) no DHP was visible after the 2 min irradiation periods under these conditions.

This could also be demonstrated in another way: irradiation of a nitrogen-purged 10^{-3} M solution of 10a with 230 - 330 nm light for 20 min under a nitrogen atmosphere, followed by photoerasure of DHP by visible light, produced 1% - 2% phenanthrene in methanolic solution; in cyclohexane approximately 16% of phenanthrene was formed while no DHP was visible before photoerasure. The initial concentrations of oxygen in both solvents are nearly equal (MeOH: $[O_2] = 2.1 \times 10^{-3}$ mol l^{-1}; cyclohexane:

$[O_2] = 2.3 \times 10^{-3}$ mol^{-1} l^{-1} [29]) and deaeration may be expected to have been equally efficient.

Several variations in the interplay of rates of oxidation and of ring opening can be advanced to account for the enhanced oxidation in cyclohexane. It may be caused by HO$_2$ radicals which, according to Bromberg and Muszkat [21], are much more effective in the thermal oxidation of 12a in 2,2,4-isooctane than oxygen. Oxidation of 4a,4b-DHP by oxygen itself was shown to be faster in alcohols than in hydrocarbons [21]. Another possibility is the occurrence of a photo-oxidation of 4a,4b-DHPs. Such oxidations have been observed for some 4a,4b-DHPs [3, 16, 17, 31]. At low oxygen (and stilbene) concentrations the photo-oxidation of 12a was found to be approximately 70 times faster than its thermal oxidation in isooctane [16]. The photo-oxidation may involve excited DHP in diffusional interaction with oxygen or excitation of a complex of 4a,4b-DHP and oxygen. We have not tried to distinguish between contributions from thermal and photochemical oxidation.

From the quantum yields in the presence of iodine (especially in cyclohexane) it must be concluded that the para substituents investigated do not influence the quantum yield of photocyclization of 10a. A substituent effect on the quantum yield of photodehydrocyclization is found, however, when an oxidant with low efficiency is used. Substituents having larger $|\sigma_p|$ values generally tend to enhance the oxidation (Figs. 1 and 2).

This influence on the rate of oxidation of the DHPs 12a - f is somewhat smaller in cyclohexane than in methanol. This effect implies competing rates of oxidation and ring opening of the DHPs 12. The observation that solutions of 10 having a higher rate of conversion (10c and f) show a lower intensity of colour after a short irradiation period suggests that the substituent effect is not due to an influence on the photochemical ring opening of the DHPs. As an oxidative pathway via the electronically excited DHP does not seem to be an appropriate explanation, we studied the thermal decay of the DHPs in methanol as solvent.

The observed rate constants for thermal ring opening (k_{op}) are given in Table 7. The decay follows an Arrhenius-type equation. So the activation energies and entropies could be calculated using eqn. (1) [32].

$$k_{op} = \left(\frac{kT}{h}\right) \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(\frac{RT - E_a}{RT}\right) \tag{1}$$

It appeared that substituents at C(3) of 12 hardly influence the rate constant for thermal ring opening. The only exception is 12g (3-OH) which has a considerably higher k_{op}. Possibly a second, unidentified process takes place from this DHP (see below).

The data in Table 7 reveal an increase in the activation energy and a decrease in the activation entropy for thermal ring opening upon substitution at C(3). The same effect has been noticed [16] for substituted 4a,4b-DHPs 13 in methylcyclohexane with isohexane (substituent: H, $E_a = 73$

TABLE 7

Rate constants k_{op}, activation energies E_a and activation entropies $\Delta S^{\ddagger}$ for thermal ring opening of substituted DHPs 12 in MeOH

Substituent	$k_{op} \times 10^4$ (s^{-1})	Temperature (°C)	E_a (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	Temperature range
12a H	3.7	20	45.2	−164.4	0 - 25
a H	2.1	11			
b 3-CF$_3$	3.3	20	51.9	−142.2	0 - 25
c 3-OCH$_3$	2.6	19			
d 3-F	2.7	19			
e 3-Cl	2.7	20			
f 3-CH$_3$	3.9	20	60.0	−116.3	0 - 25
f 3-CH$_3$	1.9	11			
g 3-OH	58	22	36.4	−172.4	−15 - −22
3-Br	4.0	19			

kJ mol^{-1}, $\Delta S^{\ddagger}$ = −81.6 J mol^{-1} K^{-1}; 3-Cl, E_a = 79.5 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −66.9 J mol^{-1} K^{-1}; 3-Br, E_a = 96.2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −10.5 J mol^{-1} K^{-1} [16]). The activation energies appeared to be linearly related to the activation entropies.

From the data which refer to MeOH as the solvent, a straight line is obtained (by linear regression) with a slope of 2.44×10^{-3} K^{-1} and correlation coefficient 0.970 (without 12g the slope is 3.25×10^{-3} K^{-1}).

From the data of Muszkat and Fisher [16] a line with a slope of 2.93×10^{-3} K^{-1} and a correlation coefficient of 0.9918 is obtained. Such isokinetic relationships are usually interpreted [16] as indicating that a higher activation energy belongs to a less ordered transition state. Activation energies for substituted 12 in MeOH are found to be lower than in methylcyclohexane with isohexane (see above), which indicates a solvent influence on the transition state. The thermal ring opening presumably proceeds via excited vibrational levels of the DHP in its electronic ground state. The dependence of the activation energy on the substituent, which is unexpected from a steric point of view, might be explained by a change in the vibrational modes of the DHP and/or the polarity of the substituent.

In Table 7 rate constants for thermal ring opening at 11 °C of some substituted DHPs are given. Using the data of Bromberg and Muszkat [21] a rate constant for thermal oxidation of 12a in ethanol at 11 °C can be calculated (k_{ox} = 0.21 1 mol^{-1} s^{-1}). With an estimated oxygen concentration of 2.3×10^{-3} mol l^{-1} [29], the rate of the initiation step of oxidation at 11 °C is given by d[DHP]/dt = −5 × 10^{-4}[DHP]. The rates of oxidation and thermal ring opening are comparable in magnitude.

The similarity of the rate constants for 12a and 12f at 11 °C as well as 20 °C confirms that the substituent effect observed in Table 4 and Fig. 1 concerns the DHP oxidation.

Although the HO$_2$ radical, generated in the oxidative pathway, may cause significant oxidation of DHP in 2,2,4-trimethylpentane, no evidence has been mentioned for this process in alcohols [21].

As, after irradiation of the para-substituted stilbenes **10a, d** and **e** in MeOH under an air atmosphere the orange-yellow colour of **4a,4b**-DHP is still visible (see above), the contribution of this second, oxidative process must be very low compared with oxidation by oxygen.

Finally, separate attention should be given to the photochemistry of the *p*-hydroxy-substituted stilbene **10g**. Introduction of a *p*-hydroxy substituent in stilbene strongly reduces the photoformation of phenanthrene, and 4,4'-dihydroxystilbene is even photochemically unreactive [33]. However, 4,4'-dihydroxy-α,α'-diethylstilbene readily photocyclizes affording quantitatively the isomerized, stable DHP derivative [34]. Since **10g** resembles both systems and para substituents apparently do not influence the quantum yield of photocyclization of **10**, the formation of phenanthrene from **10g** was investigated by UV and fluorescence spectroscopy under neutral, acidic and basic conditions in MeOH. On the basis of the observed changes in the spectra upon irradiation it was concluded that under all conditions phenanthrene **11g** was formed. Irradiations in a "merry-go-round" under similar conditions indicated a rate of conversion comparable with that of **10c** (see Table 4). Phenanthrene **11g** was not the only product formed, however, under basic and acidic conditions.

Any side product possibly arises from a reaction similar to those described by Somers *et al.* [26] or to ketone formation [34]. No attempts were made to identify these products. The photoreactivity (Table 4) of the compound (**10g**) demonstrates the very small influence of the hydroxy group, compared with the influence in stilbene.

4. Conclusions

Our data have shown that the relative quantum yield of photodehydrocyclization of various mono-para-substituted diphenylcyclopentenes **10** in methanol depends on the substituent when an oxidant with low efficiency (such as air) is used. Under such conditions some para-substituted diphenylcyclopentenes (*p*-OMe, *p*-Me and *p*-CF$_3$) afford a quantum yield for phenanthrene formation that is larger than that found for the parent compound **10a**.

The quantum yield obtained for others (*p*-F, *p*-Cl) is comparable with or somewhat smaller than for **10a** (Fig. 1, Table 4). No Hammett relation is found with the substituents' σ values. Using more efficient oxidants in methanol or in cyclohexane solutions, no significant substituent influence is observed. The ring opening process of the intermediate DHPs is influenced by the substituents. No Hammett relation is found, but an isokinetic relationship between activation energies and entropies is shown. From these results, it can be concluded that the substituents have no appreciable influence on the photocyclization itself.

The photocyclization behaviour of the diphenylcyclopentenes **10** does not (completely) parallel that reported by Jungmann *et al.* [7] (and

which could be reproduced by us) for substituted stilbenes **14**. The correlation between quantum yields of phenanthrene formation from para-substituted stilbenes **14** and the maxima of their UV absorption band [8]
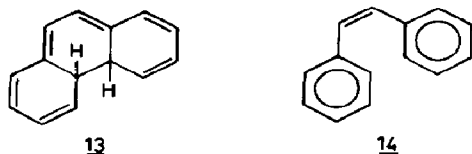
cannot be reproduced. The fluorescence band maxima in $CHCl_3$, determined using tetra(p-chlorophenyl)-$\Delta^{2,2}$-biimidazolidine [35] to remove oxygen, were very similar for all para-substituted stilbenes **10**: 410 nm for H, p-F, p-Cl, p-CF_3, p-CH_3 and 410 - 415 nm for p-OCH_3.

The relative quantum yields of phenanthrene formation from para-substituted stilbenes **14** can be influenced by an incomplete oxidation: addition of iodine to cyclohexane raises the quantum yield by a factor of 3 (Table 7). Even if this is the case the quantum yield of p-methoxystilbene **14** would still be considerably lower than that of unsubstituted *cis*-**14**. The correlation between the quantum yields of phenanthrene formation and the maxima of the UV absorption band may actually indicate an implicit correlation between the quantum yields or rate constants of deactivation (differing from cyclization) and the absorption maxima. A plausible explanation for the differences observed for the stilbenes **14** and **10** could then be a difference in the decay of the excited singlet state. For the stilbenes **14** this may take place partly via an excited twisted configuration which can be converted to the cis and trans ground states [36], whereas for stilbenes **10** such a configuration would not be attainable. This interpretation is more or less equivalent to the interpretation of Hammett relations given in refs. 10, 11 and 37 and would not be applicable to the diphenylcyclopentenes **10**.

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