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Z/*E* PHOTOISOMERIZATION OF 5-ARYLMETHYLENEHYDANTOINS AND 5-PYRIDYLMETHYLENEHYDANTOINS

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The Z/E photoisomerization of a series of 5-arylmethylenehydantoins and a series of 5-pyridylmethylenehydantoins by direct irradiation in methanol or ethanol solvent was investigated. The isomeric ratios at the photostationary state are dependent on the excitation wavelength and are related to the relative absorption coefficients of the two isomers. Measurements of quantum yields show the absence of quenching effects by oxygen or azulene, suggesting that triplet states either are not involved or are too short-lived for quenching to be observed. Preparative photoisomerization provides a route to the isomer which is not isolated or obtained only as a minor product by the usual method of synthesis.

INTRODUCTION

Preparations of 5-arylmethylenehydantoins (**1–5**) and 5-pyridylmethylenehydantoins (**11–13**) by condensation of hydantoin with the corresponding benzaldehydes or pyridinecarboxaldehydes yielded almost exclusively the *Z*-isomers.[1,2] On the other hand, condensation reactions of 1-mehylhydantoin with the same aldehydes gave mixtures of the *Z*- and *E*-isomers of the corresponding 1-methyl-substituted compounds (**6– 10**) and **14–16** respectively) with varying ratios of the geometric isomers. Thermal equilibration studies[3] confirmed the greater thermodynamic stability of the Z- over the *E*-isomers among the *N*-unsubstituted compounds, while the relative stabilities of the geometric isomers of the 1-methyl derivatives are influenced by the substituent in the phenyl ring or the position of the nitrogen atom in the pyridine ring.

We report here a study of the direct photoisomerization of these compounds which has provided a route to the thermodynamically less stable isomers. The method is efficient at ambient temperature and predominant conversion in either direction can be achieved by selection of the irradiating wavelength on the basis of the absorption characteristics of the *Z*- and *E*-forms.

RESULTS AND DISCUSSION

Preliminary experiments showed that irradiation of dilute alcoholic solutions of the *Z*-isomers of **1–5** with a medium-pressure mercury lamp and a Corning CS 9-54 glass filter resulted in substantial conversion within a few minutes to the corresponding *E*-isomers, which are not accessible by direct preparation methods. However, on further irradiation, decompositions of both forms occurred before photostationary states could be established, probably owing to absorption of the high-energy mercury emissions at 254 nm which the filter transmits to 70%. On replacing this Corning filter with a monochromator or appropriate interference filters which screen off light of low wavelengths, photoisomerization was found to proceed smoothly with little or no decomposition.

As both geometric isomers of the 1-methyl-substituted compounds **6–10** and **14–16** are available directly from preparations and their properties are well characterized, systematic studies of both *Z*→*E* and *E*→*Z* isomerization under direct irradiation are possible. The UV spectra of each pair of isomers were first recorded and their interconversions were then followed by observing spectral changes during irradiation. Figures 1 and 2 show typical spectral changes recorded during the photoisomerization of one of the compounds at two different wavelengths. That *Z*→*E* and *E*→*Z* isomerizations have occurred without significant side-reactions is evidenced by the distinct isosbestic points in the set of absorption curves and the identical photoisomerization spectra obtained on starting from either isomer. The extent of conversion at any point can be measured by the changes in absorbance at selected

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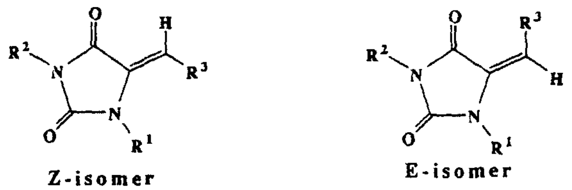
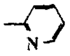
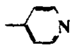
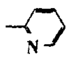
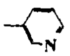
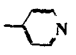
wavelengths, which may be the absorption maxima of the two isomers or one of least overlap between their absorption bands. In cases where the absorption maxima are not sufficiently well separated, high-performance liquid chromatography (HPLC) offers an alternative method of analysis of small aliquots withdrawn at different time intervals.



	R^1	R^2	R^3
(1)	H	H	C_6H_5
(2)	H	H	C_6H_4(p-OMe)
(3)	H	H	C_6H_4(p-Me)
(4)	H	H	C_6H_4(p-Cl)
(5)	H	H	C_6H_4(p-CN)
(6)	Me	H	C_6H_5
(7)	Me	H	C_6H_4(p-OMe)
(8)	Me	H	C_6H_4(p-Me)
(9)	Me	H	C_6H_4(p-Cl)
(10)	Me	H	C_6H_4(p-CN)
(11)	H	H	
(12)	H	H	
(13)	H	H	
(14)	Me	H	
(15)	Me	H	
(16)	Me	H	

Photostationary states

All the compounds studied show intense absorption maxima in the range 310–350 nm, with the *E*-isomers generally absorbing at longer wavelengths than the *Z*-isomers (Table 1). Hence the two main lines of 313 and 365 nm emitted by the medium-pressure mercury arc lamp were chosen for direct irradiation. The rates of isomerization and the equilibrium isomer ratios are found to be dependent on the excitation wavelength (Table 2). Photostationary states are related to the absorption coefficients of a pair of geometric isomers at the wavelength used.[4,5] At 313 nm, isomerization occurs readily but, because the *E*-isomer absorbs less strongly than the *Z*-isomer at this wavelength, the photostationary state favours the *E*-isomer [Figure 3(a)]. Only compound **16** does not show a strong predominance of either isomer at photoequilibrium owing to the similar molar absorption coefficients of its two isomers. At 365 nm, the absorption coefficients vary more widely among the compounds and there is also a larger difference between the values for each isomeric pair. The significantly lower absorptions of the *Z*-isomers at this wavelength are reflected by their slower conversion and their predominance at

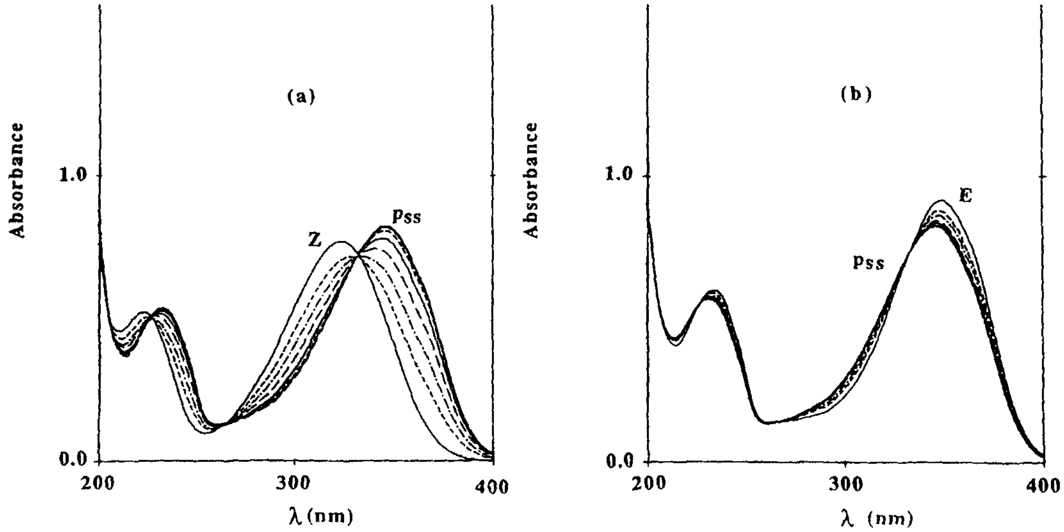


Figure 1. Changes in the electronic spectra during (a) *Z* → *E* and (b) *E* → *Z* photoisomerizations of compound **7** at an irradiation wavelength of 313 nm

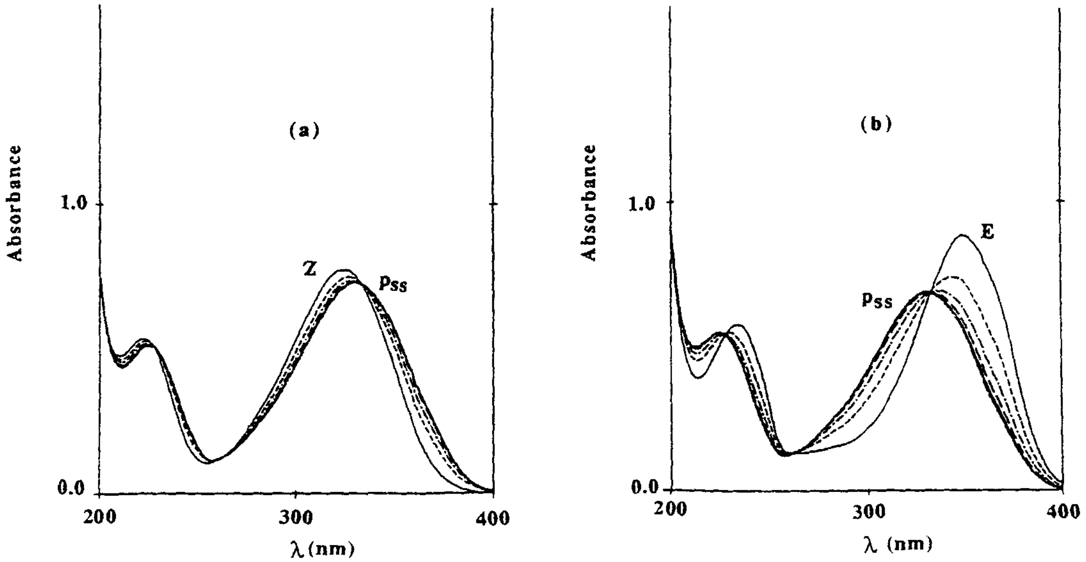


Figure 2. Changes in the electronic spectra during (a) $Z \rightarrow E$ and (b) $E \rightarrow Z$ photoisomerizations of compound **7** at an irradiation wavelength of 365 nm

the photostationary state [Figure 3(b)]. This is particularly striking for the pyridyl compounds **15** and **16**, the *Z*-isomers of which convert much more slowly than the *E*-isomers and the photostationary states show 97% enrichment in the *Z*-isomers in both cases.

Quantum yields and mechanism

At 313 nm, both quantum yields, ϕ_Z and ϕ_E, for the $Z \rightarrow E$ and $E \rightarrow Z$ photoconversion, respectively, were determined (Table 3). For the aryl compounds **6–10**, the efficiency of the $Z \rightarrow E$ conversion is slightly higher than that for the reverse change, but for the pyridyl compounds **14–16**, the quantum yields in the two directions are comparable. At 365 nm, only the quantum yields ϕ_E could be determined (Table 4) because the absorptions of the *Z*-isomers at this wavelength were too low for accurate determination of ϕ_Z.

The effect of oxygen was investigated. Quantum yields were first determined using solutions which had been purged with oxygen-free nitrogen. Measurements were then repeated for solutions aerated with oxygen and again for solutions simply degassed by ultrasonication. The results obtained under these three conditions lie within a narrow range and do not show any quenching by oxygen. A fourth set of results obtained with added azulene also failed to reveal any quenching effect. The absence of a quenching effect by oxygen or azulene, within experimental error, suggests that triplet states are not likely to be involved or are too short-lived to be quenched in the photoisomerization studied.

On irradiation, each isomer is probably first excited vertically to a singlet excited state, which then relaxes to a twisted state followed by rapid radiationless decay to either the *Z* or *E* ground states. However, the sum of the quantum yields ϕ_Z and ϕ_E at 313 nm is less than unity and all the compounds show little or no fluorescence when irradiated with light at 313 or 365 nm. This suggests that deactivation of the excited state may include other radiationless decay processes.[6]

That the facile photoisomerizations observed involve $\pi \rightarrow \pi^*$ excitation is consistent with the high intensity of the absorption bands of these compounds. The extended conjugation of the C-5—C-6 double bond, around which *Z*/*E* isomerization takes place, with an aromatic or heteroaromatic ring on one side and with the C-4 carbonyl group or the N-1 lone pair of electrons on the other side, contributes to lowering the energy of the excited state, which may be influenced by the configuration and substituent effects in the compound. At 313 nm, substituent effects are relatively small. The aryl compound **10**, with a strongly electron-withdrawing cyano substituent, and compounds **14–16**, with the electron-withdrawing pyridyl ring, give slightly higher quantum yields. This trend is more pronounced among the quantum yields measured at 365 nm, with compounds **10** and **14** – **16** showing significantly higher values than the others.

Preparative photoisomerization

The clean and facile isomerization by direct irradiation at ambient temperature and the dependence of the isomeric ratios at the photostationary state on the excitation wavelength make preparative photoisomerization feasible. On the preparative scale, a high-pressure mercury lamp was used together with appropriate filter solutions which are less precise and transmit broader bands of light compared with the monochromator or interference filters used in photostationary state and quantum yield determinations. With the $K_2CrO_4Na_2CO_3$ filter solution, which transmits a radiation band near 313 nm,[7] the *Z*-isomers of the *N*-unsubstituted compounds **1–5**, **12** and **13** could be converted to mixtures containing 30–64% of the *E*-isomers, which are not obtainable by the method of direct synthesis used. The stabilization of the ground state by intramolecular hydrogen bonding of the *Z*-isomer of the 2-pyridyl compound **11**[8,9] could contribute to its very low conversion yield of only 12% *E*-isomer. For the 1-methyl-substituted compounds **6–10** and **14–16**, preparative $E \rightarrow Z$ photoisomerizations were carried out. The *Z*-isomers of these compounds are formed as minor products from the condensations so that their isolation in a pure form is often difficult. Irradiation of the more abundant *E*-isomers, using a $CuSO_4$ filter solution, which effectively cuts off light of wavelength below 320 nm but has a high transmission of light around 365 nm,[7] resulted in mixtures containing 70–95% of the corresponding *Z*-isomers, the separation and purification of which could therefore be more readily accomplished.

Table 1. UV absorptions of compounds **1–16** in methanol at 25 °C

Compound	λ_{max}(nm)	Log ε	Compound	λ_{max}(nm)	Log ε
(*Z*)-**1**	316	4·40	(*Z*)-**10**	320	4·23
(*Z*)-**2**	332	4·45	(*E*)-**10**	342	4·33
(*Z*)-**3**	321	4·41	(*Z*)-**11**	327	4·32
(*Z*)-**4**	320	4·43	(*Z*)-**12**	316	4·36
(*Z*)-**5**	327	4·44	(*Z*)-**13**	316	4·31
(*Z*)-**6**	309	4·18	(*Z*)-**14**	321	4·19
(*E*)-**6**	334	4.24	(*E*)-**14**	330	4·18
(*Z*)-**7**	324	4·28	(*Z*)-**15**	310	4·13
(*E*)-**7**	349	4·34	(*E*)-**15**	330	4·22
(*Z*)-**8**	313	4·24	(*Z*)-**16**	308	4·15
(*E*)-**8**	338	4·32	(*E*)-**16**	330	4·11
(*Z*)-**9**	310	4·24			
(*E*)-**9**	337	4·32			

Table 2. Molar absorption coefficients (ε) and *E*/*Z* contents in the photostationary states (PSS) at 313 and 365 nm

		PSS			PSS	
Compound	ε (313 nm) ($10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$)	*E*(%)	*Z*(%)	ε (365 nm) ($10^3\,\mathrm{l\,mol^{-1}\,cm^{-1}}$)	*E*(%)	*Z*(%)
(*Z*)-**6**	1·48	69	31	0·085	29	71
(*E*)-**6**	1·30			3·53		
(*Z*)-**7**	1·75	80	20	2·86	33	67
(*E*)-**7**	0·85			18·3		
(*Z*)-**8**	1·70	74	26	0·57	21	79
(*E*)-**8**	1·22			9·06		
(*Z*)-**9**	1·71	66	34	0·57	19	81
(*E*)-**9**	1·36			6·95		
(*Z*)-**10**	1·70	59	41	1·34	16	84
(*E*)-**10**	1·26			11·7		
(*Z*)-**14**	1·45	54	46	0·83	18	82
(*E*)-**14**	1·29			2·92		
(*Z*)-**15**	1·37	55	45	0·075	3	97
(*E*)-**15**	1·23			1·82		
(*Z*)-**16**	1·38	50	50	0·22	3	97
(*E*)-**16**	1·35			2·22		

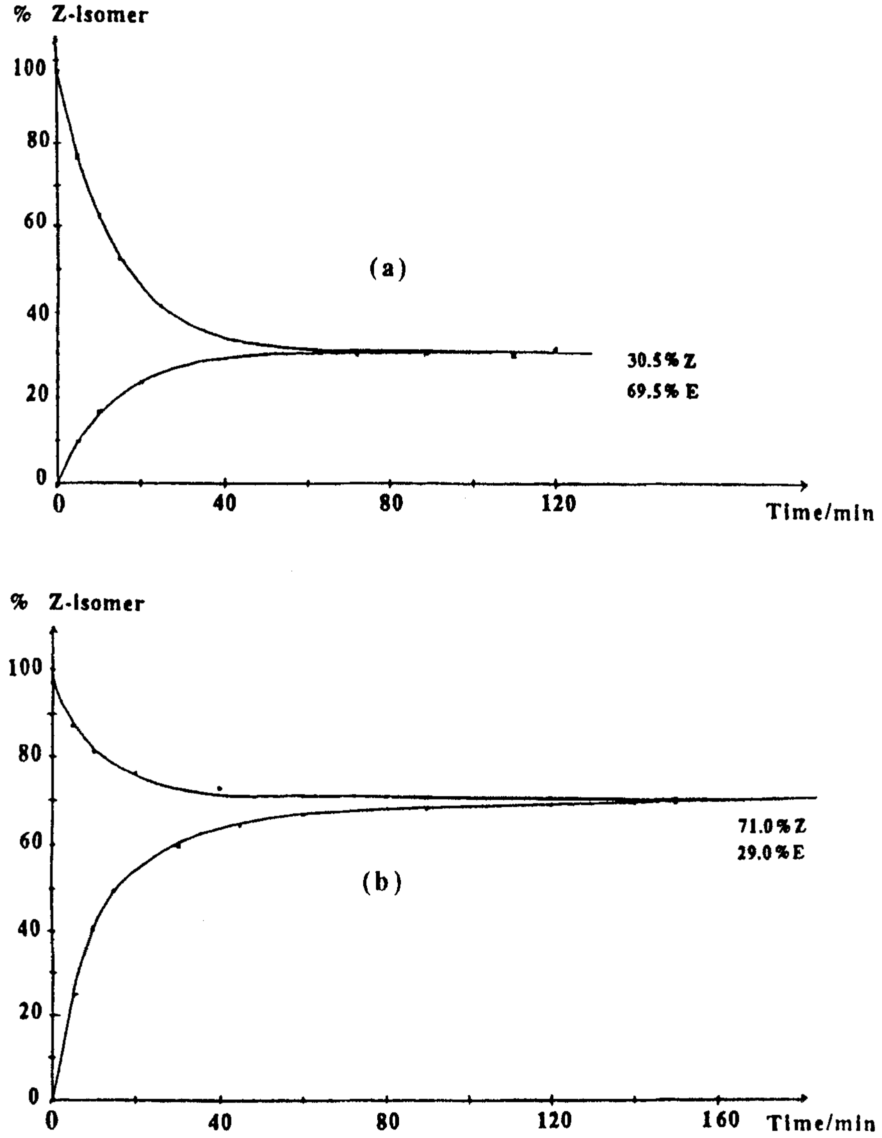


Figure 3. Changes in the percentage of *Z*-isomer during *Z*/*E* photoisomerizations of compound **6** at an irradiation wavelength of (a) 313 nm and (b) 365 nm

Photoisomerization by sunlight was attempted. From the *E*-isomers of compounds **6–10** and **14–16**, fairly satisfactory conversions to 60–80% of their Z-isomers could be achieved under strong sunlight with or without the use of the $CuSO_4$ filter solution. Conversions of the *Z*-isomers of compounds **1–5** and **11–13** required the use of the K_2CrO_4–Na_2CO_3 filter solution and gave much less satisfactory results, yielding mixtures with not more than 30% *E*-isomers.

EXPERIMENTAL

Compounds **1–16** were prepared according to published methods.[1,2] Analytical-reagent grade methanol was used as the solvent except in the preparative experiments, for which the less volatile ethanol was used.

For measurements of photostationary states and quantum yields, 10^{-5}–10^{-4} M methanolic solutions of the compounds in 1-mm quartz cells were irradiated

Table 3. Quantum yields[a] at 313 nm

	ϕ_Z				ϕ_E			
Compound	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
(*Z*)-**6**	0·33	0·37	0·39	0·36				
(*E*)-**6**					0·20	0·16	0·21	0·15
(*Z*)-**7**	0·35	0·33	0·34	0·25				
(*E*)-**7**					0·20	0·23	0·26	0·18
(*Z*)-**8**	0·31	0·33	0·38	0·33				
(*E*)-**8**					0·21	0·20	0·24	0·18
(*Z*)-**9**	0·38	0·31	0·38	0·32				
(*E*)-**9**					0·22	0·25	0·21	0·22
(*Z*)-**10**	0·38	0·33	0·37	0·36				
(*E*)-**10**					0·33	0·36	0·38	0·36
(*Z*)-**14**	0·30	0·23	0·25	0·33				
(*E*)-**14**					0·35	0·33	0·29	0·28
(*Z*)-**15**	0·35	0·34	0·27	0·35				
(*E*)-**15**					0·27	0·31	0·21	0·28
(*Z*)-**16**	0·32	0·32	0·30	0·34				
(*E*)-**16**					0·37	0·27	0·28	0·31

[a] Values measured with solutions (a) purged with oxygen-free nitrogen, (b) saturated with oxygen, (c) degassed by ultrasonication or (d) containing an equimolar amount of azulene.

Table 4. Quantum yields[a] at 365 nm

	ϕ_E			
Compound	(a)	(b)	(c)	(d)
(*E*)-**6**	0·24	0·24	0·31	0·28
(*E*)-**7**	0·21	0·20	0·19	0·20
(*E*)-**8**	0·27	0·27	0·24	0·23
(*E*)-**9**	0·35	0·29	0·30	0·33
(*E*)-**10**	0·46	0·47	0·42	0·44
(*E*)-**14**	0·43	0·44	0·48	0·38
(*E*)-**15**	0·55	0·53	0·53	0·49
(*E*)-**16**	0·57	0·54	0·51	0·53

[a] Values measured with solutions (a) purged with oxygen-free nitrogen, (b) saturated with oxygen, (c) degassed by sonication or (d) containing an equimolar amount of azulene.

with an Oriel 100-W medium-pressure arc lamp (Model 6281), using either a Bausch and Lomb ultraviolet grating monochromator (Model 33-86-01) or an Oriel interference filter [56510 (for 313 nm) or 56530 (for 365 nm)], mounted in an optical train. Potassium ferrioxalate actinometry[10,11] was used to measure the intensity of the excitation light. Each calculation of quantum yield was based on two actinometric determinations performed before and after a photochemical run. Quantum yields were determined at 5–10% conversions to obtain initial rates and minimize the effect of reverse change. UV spectral data were obtained on a Shimadzu UV-260 recording spectrophotometer. HPLC analyses were performed using a Waters liquid chromatograph and a Nova-Pak C_{18} column or a Shimadzu LC-6A liquid chromatograph and a

Table 5. Conversion yields of preparative photoisomerization

Initial compound	Yield of product (%)[a]	Initial compound	Yield of product (%)[a]
(*Z*)-**1**	56[b]	(*E*)-**6**	95[c]
(*Z*)-**2**	64[b]	(*E*)-**7**	80[c]
(*Z*)-**3**	45[b]	(*E*)-**8**	90[c]
(*Z*)-**4**	50[b]	(*E*)-**9**	95[c]
(*Z*)-**5**	60[b]	(*E*)-**10**	85[c]
(*Z*)-**11**	12[b]	(*E*)-**14**	70[c]
(*Z*)-**12**	50[b]	(*E*)-**15**	95[c]
(*Z*)-**13**	30[b]	(*E*)-**16**	80[c]

[a] Average of three experiments.
[b] % *E*.
[c] % *Z*.

Whatman Partisphere C_{18} cartridge, with methanol–water mixtures of various compositions as mobile phase.

For preparative photoisomerization, the radiation source was a Hanovia 200-W high-pressure lamp (Model 654A-0360) placed in a quartz tube. It was cooled continuously with a stream of chilled nitrogen gas during operation. Pyrex glassware was used for the filter solutions and the ethanolic test solutions of the compounds of concentration 4×10^{-3}–6×10^{-3} M. The irradiation time was about 45–60 min. The aqueous filter solutions contained 0·27 g $l^{-1} K_2CrO_4$ and 1·0 g $l^{-1} Na_2CO_3$ or 250 g l^{-1} $CuSO_4 \cdot 5H_2O$. The compositions of the irradiated mixtures were determined by HPLC or UV spectrophotometry or by integration of the well separated H-6 signals of the *Z*- and *E*-isomers in the ^1H NMR spectra.

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