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Laser photoisomerization of methyl α-arylcinnamates; effect of chloro substitution

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Abstract

An investigation of the 308 nm laser photochemistry of methyl α-phenylcinnamate (**1a**) and a series of *p*-chloro-substituted derivatives is reported. Dilute solutions of (*E*)-**1a** or (*Z*)-**1a** undergo photoisomerization, but also form ring closure products analogous to those observed during the photolysis of *cis*-stilbene. The photostationary state (PSS) compositions (*E*/*Z*) were determined by analytical high performance liquid chromatography (HPLC). The PSS values are not dependent on the laser power or the presence of oxygen. However, they are unusually rich in the *E* isomer compared with the PSS of alkyl cinnamates (over 70% *E* compared with about 50% *E* for alkyl cinnamates). *p*-Chloro substitution on the α ring causes a small increase in the *E* content of the PSS, whereas *p*-chloro substitution on the β ring leads to a dramatic reduction in the *E* content of the PSS (28% *E*). Possible explanations for these results are discussed.

1. Introduction

Photochemical *E* to *Z* isomerization has been the subject of intense research for several decades [1–4]. Much of this work has been concerned with the photochemistry of stilbene and its derivatives. The photoisomerization of cinnamic acids and alkyl cinnamates has also received considerable attention [5–28]. By contrast α-arylcinnamates have largely been neglected. In this paper, we examine the photoisomerization process for a series of substituted methyl α-arylcinnamates.

The UV photochemistry of alkyl cinnamates is fairly well established. The only photochemical process in dilute solution is singlet-mediated *E* to *Z* isomerization [12, 14, 16–19], leading to a photostationary state (PSS) mixture with a composition of the order of 45% *Z* to 55% *E* in a variety of solvents [14, 16–19].

The situation is rather different for α-arylcinnamates. In addition to *E* to *Z* photoisomerization, UV irradiation of air-saturated solutions of methyl α-phenylcinnamate results in an irreversible ring closure reaction analogous to that observed with stilbene under similar conditions [24–27]. Although the ring closure reaction has been examined in some detail for methyl α-phenylcinnamate [24–28], little work has been done on the photoisomerization reaction of this molecule. In addition, no attempt has been made to examine the influence of reaction conditions (for example, solvents and oxygen) or of phenyl ring substituents on the photoisomerization of methyl α-phenylcinnamate. The latter is of particular interest as the relationship between ring closure and isomerization in the stilbene system has recently been re-examined [29–31]. With these points in mind, we undertook the present study.

2. Experimental details

2.1. Materials

The structures of the methyl α-arylcinnamate (**1**) isomers are shown in Scheme 1. They were prepared by the Horner–Wadsworth–Emmons modification of the Wittig reaction [32, 33].

(*E*)-Ethyl cinnamate (purity, better than 99%, Merck) and 9-cyanophenanthrene (Aldrich) were used as received. Solvents (Rathburn or Merck) were of high performance liquid chromatography (HPLC) grade.

2.2. Laser apparatus and photolysis technique

Samples were typically excited with pulses (308 nm, approximately 10 ns) provided by a Lumonics 510 excimer laser operating with an XeCl mixture. Average unattenuated pulse energies were about

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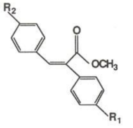


(Z)- methyl α-arylcinnamate

$R_1 = R_2 = H$ (Z)-1a

$R_1 = H$ $R_2 = Cl$ (Z)-1b

$R_1 = Cl$ $R_2 = H$ (Z)-1c

$R_1 = R_2 = Cl$ (Z)-1d

Scheme 1.

40 mJ per pulse (Scientech 365 power/energy meter).

The unattenuated laser beam initially passed through a mask containing a hole (1 cm×1 cm). About 10% of the resulting beam was redirected at right angles to the original beam by a quartz beam splitter. It was then defocused by a quartz lens (focal length, 10 cm). The sample cuvette was positioned about 30 cm beyond the focal point of the lens. A mask containing a hole (1 cm×2 cm) was placed immediately in front of the cuvette. Typically the average laser energy reaching the sample was between 0.5 and 1 mJ per pulse.

Continuously stirred, air-saturated methanol solutions of cinnamate esters (about 10^{-4} M) were irradiated in quartz cuvettes (1 cm×1 cm) (Perkin–Elmer). In several experiments samples were deoxygenated by the freeze–pump–thaw method. In either case, the samples were subjected to varying numbers of laser pulses to give particular values of incident laser energy E_L, where E_L = (average laser pulse energy) × (number of laser pulses).

2.3. Analytical techniques

The *E* and *Z* isomers of **1a**, **1b** and **1d** were separated with an LDC Analytical Consta Metric 3200 analytical HPLC system operating with a 10 cm C-18R reverse phase column. The mobile phase was methanol–water (57% to 43%) pumped at 1.0 ml min^{-1}. For **1c** the isomers were separated on a 10 cm silica column using *n*-hexane–CH_2Cl_2 (70% to 30%) as the mobile phase (flow rate, 0.15 ml min^{-1}). In the latter system the photolyses were performed in methanol, the methanol was rotoevaporated and the residue was redissolved in CH_2Cl_2 for analysis.

HPLC detection was by absorption with excitation at 254 nm. Ester retention times and concentration response factors were calibrated against authentic samples.

UV–visible absorption spectra were measured with a Perkin–Elmer Lambda 17 UV–visible spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Brucker AC-250P instrument.

2.4. Lamp photolysis, separation and identification of ring closure products

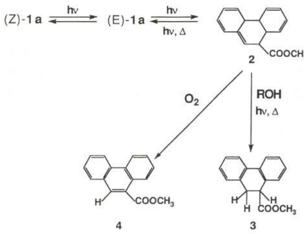
A 500 mg mixture of (*E*)-**1a** and (*Z*)-**1a** in 100 ml of air-saturated methanol was photolysed, with stirring, in a preparative photochemical reactor (Hanau, Heraeus model) for 13 h. A water-cooled, high-pressure mercury lamp was used as the excitation source. Its emission was filtered through Pyrex.

Samples were taken during the course of the photolysis and examined by analytical HPLC (conditions as described above). This confirmed that the reaction products under lamp photolysis conditions were the same as those obtained with the laser.

At the end of the photolysis period the reaction mixture was passed over a silica column and eluted with CH_2Cl_2. The resulting mixture was separated by preparative HPLC (Waters, model Prep-LC 500A) over a silica column with CH_2Cl_2–*n*-hexane (5.5:4.5) as the mobile phase. Two of the resulting fractions contained over 50% of the injected material. These were further separated on preparative thin layer chromatography (TLC) plates with CH_2Cl_2–*n*-hexane (6:4). Two pure materials (other than (*E*)-**1a** and (*Z*)-**1a**) were isolated in this way and their proton NMR spectra were obtained.

The material with the shorter analytical HPLC retention time has been identified as methyl 9,10-dihydro-9-phenanthroate (**3**) (Scheme 2). The proton NMR spectrum of this material shows a doublet of doublets at 3.14 ppm and a second doublet of doublets at 3.35 ppm, which can be assigned to the two geminal hydrogens on C-10. Furthermore, the spectrum exhibits a triplet at 3.91 ppm for the hydrogen on C-9 and a singlet at 3.64 ppm for the methyl ester group. The identity of this material was confirmed by co-injection of an authentic sample of **3** into the chromatograph together with a photolysed sample of **1a**.

The material with the longer retention time has been identified as methyl 9-phenanthroate (**4**) (Scheme 2). Apart from a singlet at 4.05 ppm



Scheme 2.

TABLE 1. Absorption characteristics of the methyl α-arylcinnamate isomers and several other olefins in methanol

Olefin	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})
(*E*)-**1a**	283	16700
(*Z*)-**1a**	286	20600
(*E*)-**1b**	288	19000
(*Z*)-**1b**	290	22000
(*E*)-**1c**	284	16000
(*Z*)-**1c**	290	19000
(*E*)-**1d**	288	17000
(*Z*)-**1d**	295	19000
(*E*)-Methyl cinnamate	277	24000[a]
(*Z*)-Methyl cinnamate	269	10715
cis-Stilbene	276	9830
trans-Stilbene	312	37200

[a]Methyl cinnamate data from ref. 18.

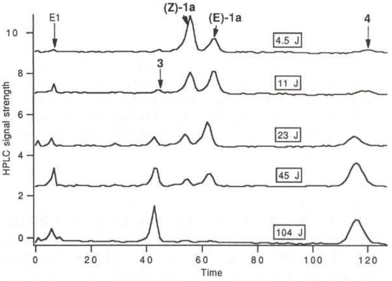


Fig. 1. Reverse phase HPLC traces obtained during the 308 nm laser photolysis of 1.0×10^{-3} M (*Z*)-**1a** in air-saturated methanol. Average pulse energy $E_P = 30$ mJ per pulse. Traces were obtained at different levels of incident energy ($E_L = E_P \times L_P$) between 4.5 and 104 J as indicated (see text for explanation of E1). Signal strength in arbitrary units; time in seconds.

assigned to the methyl ester group, the proton NMR spectrum of this material reveals resonances only in the aromatic region between 7.6 and 8.9 ppm. This spectrum was identical with the spectrum of an authentic sample obtained by the acidic alcoholysis of commercially available 9-cyanophenanthrene [34]. The identity of this material was confirmed by co-injection of an authentic sample of **4** into the chromatograph together with a photolysed sample of **1a**.

3. Results

The absorption bands of all the esters in dilute methanol solutions are broad and lack vibrational structure. The absorption spectral data are given in Table 1.

Figure 1 shows the HPLC traces obtained when a 1.0×10^{-3} M methanol solution of (*Z*)-**1a** was photolysed using the incident laser energies (E_L) indicated. The average laser pulse energy was 30 mJ per pulse. Clearly *Z* to *E* isomerization occurs, but in addition three other product peaks are observed.

Two of the "side" products, **3** and **4**, formed during the photolysis of **1a** have been positively identified as described above. The HPLC "peak" eluting immediately after injection (E1 in Fig. 1) appears to represent a mixture of several polar species (as judged by their short retention times). Because this peak does not represent a pure compound and the retention times of the species that make up this peak are similar, it is expected that they would be difficult to separate, and no attempt was made to identify them.

Figure 2 shows the behaviour of (*E*)-**1a** and (*Z*)-**1a**, as well as that of **3** and **4**, in the range of E_L up to 5 J. The pulse energy was 0.6 mJ per pulse and the initial ester concentration was 1.0×10^{-4} M. The *y*-axis data are the ratios of the HPLC concentrations of the various substances to the sum of the concentrations of the *E* and *Z* ester peaks. The esters rapidly reach a point (between about 0.5 and 1 J) at which their relative composition remains constant corresponding to the PSS. By contrast the amounts of **3** and **4** continue to increase over this entire energy range in accordance with the irreversible formation of these products. If irradiation is prolonged the total isomer concentration is reduced, eventually leading to the complete conversion to products other than *E* and *Z*. However, the relative concentration of *E* to *Z* remains constant at the PSS value throughout.

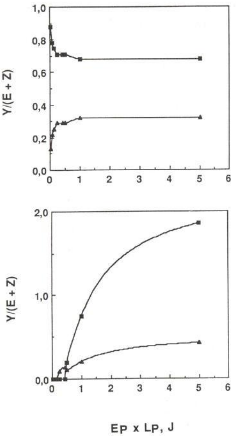


Fig. 2. Concentrations of various species Y relative to the sum of the concentrations of (*E*)-**1a** and (*Z*)-**1a** as a function of the incident laser energy during 308 nm photolysis of 1.0×10^{-4} M (*E*)-**1a** in air-saturated methanol. Y: (*E*)-**1a** (upper figure, squares); (*Z*)-**1a**, (upper figure, triangles); **3** (lower figure, squares); **4** (lower figure, triangles).

When samples of (*Z*)-**1a** were irradiated in air-saturated hexane or dichloromethane, photoisomerization was also observed. In addition, the formation of a species corresponding to **4** was indicated by the HPLC data. No other products were formed. In degassed hexane only *Z* to *E* photoisomerization was observed.

The PSS compositions obtained are given in Table 2. The PSS for **1a** was the same regardless of whether the starting isomer was *E* or *Z*. It was also independent of the laser pulse energy between 0.6 and 30 mJ per pulse, the initial ester concentration and the solvents tested.

In order to verify that our laser photolysis technique was providing reliable PSS data, a series of air-saturated 1×10^{-4} M methanol solutions of (*E*)-ethyl cinnamate were photolysed at 308 nm. The photolysis resulted in the formation of (*Z*)-ethyl cinnamate only and the PSS was found to contain 56% *E* which is in excellent agreement with literature values [18].

Photolysis of chloro-substituted esters **1b–1d** in air-saturated methanol with 308 nm excitation leads to a behaviour comparable with that observed for esters **1a**. PSS values were also obtained for **1b–1d** (Table 2).

In addition to the isomers of **1b–1d**, photolysis also resulted in the irreversible formation of products analogous to **3** and **4** (as well as additional products in some cases). We postpone a detailed examination of these other products until a later date.

4. Discussion

4.1. Absorption spectroscopy

The broad featureless absorption bands observed for both the *E* and *Z* α-arylcinnamates resemble those of *cis*-stilbene which is non-planar [1–4]. In terms of absorption coefficients, esters **1a** to **1d** resemble alkyl cinnamates in that there is a relatively small difference between ϵ_Z and ϵ_E (a factor of two or less) [18]. This contrasts with the stilbene system for which ϵ_{trans} is six times greater than ϵ_{cis} at 313 nm.

(*E*)-Alkyl cinnamates are planar in the solid state [35, 36], whereas the phenyl rings of the (*Z*)-esters are believed to lie about 45° out of the enone plane [37]. In solution, the *Z* isomers of the alkyl cinnamates typically show a blue shift of 8 to 10 nm relative to the *E* isomer, which may be attributed to this reduction of phenyl overlap with the enone. However, no such blue shift is seen in our systems. Rather, we see a weak red shift. In most cases the *E* and *Z* isomers have, considering the broadness of the peaks, the same value of λ_{max} indicating a very similar degree of delocalization in both forms.

Methyl substitution of methyl cinnamate at the α position causes a blue shift of λ_{max} of both the *E* and *Z* forms relative to the corresponding methyl cinnamate bands [18]. Presumably the α-methyl group interacts with the phenyl group inhibiting planarity of the π system. By contrast, the effect of α substitution with a phenyl group in the case of **1** results in a pronounced red shift relative to methyl cinnamate. This indicates that, in spite of a lack of planarity in this sterically crowded molecule, there is significant delocalization of electrons over the entire π system. A similar effect is observed on β-phenyl substitution of methyl α-methylacrylate. The λ_{max} value of methyl α-methylacrylate is about 210 nm [38], whereas that of (*Z*)-methyl α-methylcinnamate is shifted by nearly 50 nm to 258 nm. Thus, although the α-methyl group may inhibit the planarity of methyl α-methylcinnamate relative to methyl cinnamate, there is nonetheless signif-

TABLE 2. Photostationary state (PSS), absorption coefficient and photoisomerization quantum yield ratios for methyl α-arylcinnamates and other olefins. Data refer to 308 nm excitation wavelength and air saturation except where noted

Olefin	$(E/Z)_{PSS}$	ϵ_Z/ϵ_E	ϕ_{ZE}/ϕ_{EZ}	Solvent
1a	2.8 ± 0.3	1.6 ± 0.3	1.8 ± 0.3	CH_3OH
	2.8 ± 0.3	1.6 ± 0.3	1.8 ± 0.3	Hexane
	2.7 ± 0.3	1.6 ± 0.3	1.7 ± 0.3	Hexane[a]
1b	0.38 ± 0.03	1.2 ± 0.3	0.31 ± 0.06	CH_3OH
1c	3.8 ± 0.6	1.7 ± 0.6	2.3 ± 0.5	CH_3OH
1d	2.6 ± 0.3	1.4 ± 0.4	1.9 ± 0.3	CH_3OH
Methylcinnamate[b]	1.2	1.3	0.97	C_6H_6
p-Cl-methylcinnamate[b]	0.8	0.93	0.86	C_6H_6
p-CH_3-methylcinnamate[b]	0.75	1.3	0.58	C_6H_6
Ethylcinnamate[b]	1.3	1.4	0.93	C_6H_6

[a] Degassed. [b] At 313 nm [18].

icant interaction of the phenyl ring with the enone system. If the α-methyl group is replaced by phenyl to give (*Z*)-**1**, an additional red shift of about 30 nm occurs, indicating that this latter phenyl group must also interact with the π system.

*4.2. Photoisomerization of **1a***

Scheme 2 shows the various reaction pathways open to **1a** on UV photolysis in a hydrogen donor solvent such as methanol [26–28, 39]. Product **3** can form in the presence or absence of oxygen in this case, but in hexane **3** does not form even in the absence of oxygen. Our results for **1a** correspond completely to this reaction scheme.

Since laser and lamp photolysis yield identical products and the photoisomerization reaction is independent of the laser pulse energy, it can be concluded that sequential two-photon processes do not occur in the former case. This is reasonable if the photoisomerization mechanism of **1a** is similar to that of stilbene [1–4], *i.e.* **1a** probably isomerizes from a short-lived *E* or *Z* singlet excited state ($\tau_f < 1$ ns for *trans*-stilbene in organic solvents at room temperature [2, 4]). The short lifetime makes sequential two-photon absorption unlikely even at relatively high laser pulse energies [40].

Our data show that the introduction of irreversible decay channels for **2** (*i.e.* **2**→**3**, **2**→**4**) causes no change in the PSS. Rather, such channels only serve to deplete the overall concentrations of (*E*)- and (*Z*)-**1a**.

The most interesting result here is that the *E* content of the **1a** PSS is about three times larger than typically observed for alkyl cinnamates irradiated at a similar wavelength (Table 2).

Further insight can be gained by examining the PSS data (Table 2) in terms of the following equation [2]

$$\left(\frac{[E]}{[Z]}\right)_{PSS} = \left(\frac{\epsilon_Z}{\epsilon_E}\right) \times \left(\frac{\phi_{ZE}}{\phi_{EZ}}\right) \tag{1}$$

The PSS composition is determined by the relative degree of excitation of the two isomers and by the ratio of the overall quantum yields of the isomerization processes. In this context it is evident (Table 2) that the major reason for the enhanced *E* content of the PSS of **1a** compared with the alkyl cinnamates is that ϕ_{ZE}/ϕ_{EZ} is twofold larger in the former system. Preferential excitation of the *Z* isomer may also play a limited role.

This increase in the quantum yield ratio may be due to an increase in ϕ_{ZE} or a decrease in ϕ_{EZ} (or both) relative to the alkyl cinnamates. We consider the former possibility first.

The overall quantum yields of photoisomerization are determined by: (i) the fraction of the excited surface twisted intermediate p* decaying to the ground state of either isomer [1–4] and (ii) the existence of processes other than isomerization which may be open to the ester excited states.

One way in which ϕ_{ZE} may become larger relative to the alkyl cinnamates is for the geometry of the twisted intermediate p* to shift closer to that of the ground state *E* isomer (compared with the alkyl cinnamate situation), thus increasing the probability that *E* rather than *Z* forms when p* decays. In the stilbene system the angle of twist about the olefinic bond in p* is essentially 90° allowing maximum stabilization. From this, we would expect approximately 50% probability of p* decaying to *trans*-stilbene. Recent work on stilbene has shown that this probability is 0.50 [30]. It is hard to imagine why the situation would change in the case of arylcinnamates, since the α-carbon carries two groups which seem to have similar degrees of interaction with the β-phenyl (as indicated by the small differences between E and Z λ_{max} values, Table 1). While we cannot completely rule out an enhancement of $p^* \rightarrow E$, it is difficult to see why one isomer or the other would be favoured on relaxation of p* in the systems examined here.

Now let us consider the possibility that ϕ_{EZ} for **1a** is lower than for typical alkyl cinnamates. If we assume that fluorescence from excited (*E*)-**1a** is minimal (ϕ_f is negligible for (*E*)-methyl cinnamate [18] and very small for *cis*-stilbene [2]), then a decrease in ϕ_{EZ} could arise because of an increase in either the quantum yield of non-radiative decay processes or of a photochemical reaction other than isomerization. Non-radiative processes are not usually sensitive to chloro substitution in stilbene derivatives at room temperature [41, 42]. However, alternative decay routes are open to (*E*)-**1a** which are not available to the (*E*)-alkyl cinnamates, namely the ring closure reaction shown in Scheme 2.

Therefore we conclude that the large *E*/*Z* PSS ratio of **1a** results from a decrease in ϕ_{EZ} because of the existence of the ring closure decay channel in this system. The result is a relative reduction in the fraction of excited (*E*)-**1a** decaying via the isomerization route and therefore to a reduction in the concentration of the *Z* isomer in the PSS relative to alkyl cinnamates.

A comparison of our data with photoisomerization results for α-substituted stilbenes would perhaps seem appropriate. However, few data are available [29, 43] and they provide an inconsistent picture. For example, the ratio ϕ_{tc}/ϕ_{ct} for α,α′-difluorostilbene has been reported as 0.8, whereas that for α,α′-dichlorostilbene is 2.9 [43]. The value for α-methylstilbene is 0.8 [43]. These points, together with the fact that the ester groups of compounds **1** are clearly involved in resonance with the stilbene moieties (*vide supra* and Table 1), make a comparison of our data with α- or, α,α′-substituted stilbenes untenable.

4.3. *Effect of p-chloro substitution*

Table 2 also presents the PSS values for three *p*-chloro derivatives of **1a**. The most interesting observation is that *p*-chloro substitution of the β ring (**1b**) leads to a dramatic decrease in the *E* content of the PSS relative to the parent ester **1a**. The reduction is so marked that *Z* rather than *E* dominates the PSS mixture in the **1b** system. By contrast, placing *p*-chloro on the α ring (**1c**) or *p*-chloro on both rings (**1d**) has very little influence. The values of ϕ_{ZE}/ϕ_{EZ} for **1a**, **1c** and **1d** are the same within experimental error. These three compounds can be said to behave normally in the sense that ring substituents have negligible influence on the quantum yield of ring closure [44, 45].

Returning to **1b**, a decrease in the PSS *E* content has been reported previously for *p*-chloro- and *p*-methyl-substituted alkyl cinnamates [14, 18], also resulting in an *E*/*Z* ratio of less than unity (Table 2). The unusual thing here is the magnitude of the effect. Clearly this inversion of the *E* to *Z* ratio cannot be due to a steric effect because of the para position of the chloro substituents.

In terms of eqn. (1) such a reduction in the *E*/*Z* ratio could be due to an increase in ϕ_{EZ} or a decrease in ϕ_{ZE} relative to **1a**. One way for this to happen is for the geometry of the twisted intermediate p* to shift closer to that of the ground state *Z* isomer, thus increasing the probability that *Z* rather than *E* forms when p* decays. Using similar arguments to those outlined above we conclude that such a shift in geometry is unlikely.

Another possible explanation for the trends observed in the PSS values is that chloro substitution causes a change in the photoisomerization mechanism which, in turn, alters the values of ϕ_{ZE} and ϕ_{EZ}. A switch from isomerization on the singlet surface to isomerization on the triplet surface is the most likely candidate for such a change in mechanism. Such behaviour is known for 4-chlorostilbene [2, 42], but only at low temperatures. Room temperature isomerization of 4-chlorostilbene occurs via the singlet manifold [42]. We therefore rule out enhanced intersystem crossing leading to triplet state isomerization in our systems.

A final possibility is that *p*-chloro substitution of the β ring inhibits the ring closure process resulting in an increase in ϕ_{EZ} and thus a decrease in the *E* content of the PSS relative to **1a**. While this does not correlate with the lack of influence of ring substituents on stilbene ring closures [44, 45], it would explain our observations. Why β-ring *p*-chloro-substituted **1** should be unique in this respect is not clear. However, there is no doubt that the ester π system of **1** interacts with the stilbene π system and probably also with the chloro substituents. Perhaps this plays a role. Unfortunately, there is very little information available on the photoisomerization of stilbene-type molecules containing a π electron system as an α substituent. The present results suggest that such systems may behave somewhat differently from stilbenes themselves and warrant further investigation.

We conclude that the provision of a decay route other than isomerization for the *E* excited state of methyl α-arylcinnamates results in a *Z*-depleted

PSS (relative to alkyl cinnamates). We also note that p-chloro substitution on the β ring causes a dramatic reduction in the E content of the PSS for esters **1**. We suspect that the p-chloro group reduces the quantum yield of the (E)-**1** → **2** process, resulting in an increased ϕ_{EZ}, although further work is required to establish this point.

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