

THE IMPORTANCE OF PHOTOENOLIZATION AS A ROUTE FOR RADIATIONLESS DECAY IN β -ALKYL- α,β -UNSATURATED CARBONYL COMPOUNDS

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Summary

The quantum yield for photochemical conversion of an α,β -unsaturated ester (ethyl 2-methyl-2-butenolate) to the corresponding β,γ -unsaturated isomer was determined as 0.062 ± 0.006 in methanol-*O-d* in the presence of 1,2-dimethylimidazole. The amount of deuterium incorporation into the unconverted conjugated ester relative to the amount of conversion to the deconjugated isomer was used to determine the quantum yield of photoenolization which was found to be 0.08 ± 0.01 . The quantum yield of photoenolization was compared with the quantum yields of $E \rightarrow Z$ and $Z \rightarrow E$ isomerization for ethyl 2-methyl-2-butenolate (determined in both methanol and methanol-*O-d* as 0.25 ± 0.02 and 0.16 ± 0.02 respectively), and it was concluded that the photoenolization process does not account for more than 8% of the decay of the 59% of the excited states of ethyl 2-methyl-2-butenolate which are not involved in $E-Z$ isomerization.

1. Introduction

Direct UV light irradiation of acyclic α,β -unsaturated esters and ketones results in isomerization around the carbon-carbon double bond [1, 2]. This process appears to be highly efficient for unsaturated ketones but less so for unsaturated esters. For example, the quantum yields for $E \rightarrow Z$ and $Z \rightarrow E$ isomerization for the ketone 3-methyl-3-penten-2-one (1a) are $\Phi_{E \rightarrow Z} = 0.42$ and $\Phi_{Z \rightarrow E} = 0.40$ respectively [1], while for the ester methyl 2-methyl-2-butenolate (1, X \equiv OMe) the corresponding quantum yields are reported to be 0.09 and 0.03 [2]. The sum of the quantum yields for isomerization for each compound indicate that for the ketone 82% of the excited states produced by direct irradiation decay via $E-Z$ isomerization while for the ester only 12% decay via this route. Consequently there must be some other processes leading to deactivation of the excited states of these compounds which are more efficient in the case of the ester than the ketone.

It has been suggested [1, 2] that the extent to which the excited states of unsaturated esters and ketones such as 1a and ethyl 2-methyl-2-butenolate

(1b) decay via isomerization around the carbon-carbon double bond can be related to the presumed energy separation and degree of mixing of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states, and it has been proposed in the case of the unsaturated ester that mixing of the states allows more efficient internal conversion to the ground state to occur, so decreasing the efficiency of double bond isomerization.

A possible alternative explanation for the differing efficiencies of $E-Z$ isomerization of unsaturated esters and ketones such as **1a** and **1b** lies in the well-known ability of these compounds to undergo another excited state process under direct irradiation; this is photoenolization to give a dienol [**3** - **9**]. The photoenolization reaction is a singlet excited state process [8] in which the carbonyl group accepts a hydrogen atom from the syn-oriented γ position to give a Z -dienol [**6**] and which may be regarded as a concerted antarafacial photochemical 1,5-hydrogen shift. Thus for **1a** and **1b** the singlet excited states of the Z isomers (which are distinct from the singlet excited states of the E isomers [6]) can form the dienols **2a** and **2b** shown in Fig. 1. It has been demonstrated that the photochemically produced dienols can reketonize by two competing mechanisms to give either the conjugated precursors **1a** and **1b** or the β,γ -unsaturated carbonyl compounds **4a** and **4b** [4, 6, 8]. These competing mechanisms are shown in Fig. 1: in the presence of a base catalyst the dienol can be intercepted and converted to the corresponding dienolate (**3a** and **3b** in Fig. 1) which can then reketonize by protonation at carbon to give either the conjugated or the deconjugated carbonyl compounds; in the absence of a catalyst the dienol can revert to the conjugated carbonyl compound exclusively via what is proposed [3 - 9] to be a thermal suprafacial 1,5-sigmatropic hydrogen shift (designated by rate constant k_σ in Fig. 1).

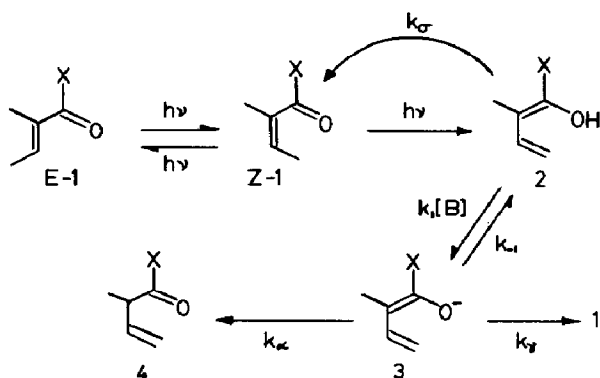


Fig. 1. Photoenolization reaction (a, $X \equiv \text{Me}$; b, $X \equiv \text{OEt}$).

The photoenolization process described above provides a mode of non-productive decay of the excited state of unsaturated esters and ketones if the 1,5-shift mechanism competes efficiently with the catalysed route for reketonization. For example, ketone **1a** has been shown to form the

deconjugated isomer 4a when irradiated in the presence of a weak organic base, while in the absence of the base the ketone appears to be inert and no deconjugated isomer is formed [8]. The quantum yield of deconjugation has not been reported for 1a but for the closely related compound 4-methyl-3-penten-2-one it is 0.03 in ether in the presence of 1,2-dimethylimidazole and zero in the absence of base [8]. The photochemical deconjugation process has also been reported to occur for the methyl ester 1 ($X \equiv \text{Me}$); in the absence of added base the deconjugated ester 4 ($X \equiv \text{Me}$) is formed with a quantum yield of 0.005 in cyclohexane [2].

As photoenolization represents an alternative pathway for decay of the excited states this suggested that the difference in *E-Z* isomerization efficiency of ketones such as 1a and esters such as 1b might be due to more efficient photoenolization in the case of the ester to give a dienol which then decays predominantly to the conjugated precursor 1b rather than to the deconjugated product 4b. In this paper an investigation is described in which the quantum yield of deconjugation of the ester 1b was measured and the quantum yield of photoenolization estimated, and hence the contribution of photoenolization to the decay of the singlet excited state was determined.

2. Results and discussion

For the mechanism of photoenolization and subsequent reketonization shown in Fig. 1, application of the steady state approximation to the kinetics of formation of the deconjugated product 4 allows the quantum yield Φ_d of deconjugation to be related to the base concentration [B] and the quantum yield Φ_e of photoenolization [4, 8]. The relation is given as

$$\Phi_d = \frac{k_\alpha \Phi_e k_1 [\text{B}]}{(k_\sigma + k_1 [\text{B}])(k_{-1} + k_\alpha + k_\gamma) - k_{-1} k_1 [\text{B}]} \quad (1)$$

where the constants are as defined in Fig. 1. Equation (1) predicts that at zero base concentration Φ_d should be zero, corresponding to all the photochemically produced dienols reverting to the conjugated carbonyl compound via the proposed 1,5-sigmatropic hydrogen shift; as the base concentration is increased the value of Φ_d should also increase and eventually reach a limiting value corresponding to the interception of all the dienols by base and their conversion to the dienolate. Under these conditions eqn. (1) reduces to

$$\Phi_d = \frac{k_\alpha}{k_\alpha + k_\gamma} \Phi_e \quad (\text{if } [\text{B}] \text{ is large}) \quad (2)$$

since when [B] is large k_σ becomes small compared with $k_1[\text{B}]$. In eqn. (2), k_α and k_γ are the rate constants for protonation of the dienolate to give the deconjugated and conjugated carbonyl compounds respectively. Thus a knowledge of the quantum yield of deconjugation at high base concentrations and of the ratio k_α/k_γ allows the determination of the quantum yield Φ_e of photoenolization from eqn. (2). Equations (1) and (2) have been

shown to hold for α,β -unsaturated ketones [8]; however, for esters eqn. (1) fails at low base concentrations and at zero base concentration the quantum yield of deconjugation is still finite in some cases [6, 7]. For example, for ester 1b in ether solution the relative quantum yield of deconjugation at high base concentration is only five times greater than that when base is not added [7]. The observation of photochemical deconjugation in the absence of added base has been shown to be due to the presence of impurities in the solvent which are capable of intercepting the dienols and converting them to the deconjugated esters via the dienolates [6]. This effect is presumably not observed with ketones because of the higher pK_a of ketone-derived dienols compared with ester-derived dienols, which are more acidic as a result of the inductive effect of the extra oxygen function.

In order to determine the limiting value of Φ_d in eqn. (2), the quantum yields for appearance of the deconjugated isomer of ester 1b (*i.e.* 4b) were measured at a variety of base concentrations (Table 1) in methanol-*O-d* containing 1,2-dimethylimidazole as the base and using light of wavelength 254 nm. Under these conditions the ester absorbed all the light; conversions were kept low in order to avoid irradiation of the base or the deconjugated products. The course of a typical reaction is shown in Fig. 2. The reaction initially involves *E-Z* isomerization of the ester until the *Z* isomer has accumulated sufficiently to absorb light. At this point photoenolization can commence and the deconjugated isomer begins to form. Until a photostationary state between the *E* and *Z* isomers has been set up the formation of the deconjugated isomer is not linear, but once the photoequilibrium has been attained the rate of formation of the deconjugated isomer becomes zero order. The quantum yields of formation of 4b were measured subsequent to this point. The observation of an induction period for the forma-

TABLE 1

Quantum yield of deconjugation of ester 1b as a function of concentration of 1,2-dimethylimidazole

Concentration of base (M)	Quantum yield of deconjugation
0	0.051
0.0015	0.061
0.0036	0.068
0.0065	0.064
0.0086	0.065
0.0090	0.075
0.0152	0.062
0.0202	0.056
0.0261	0.057
0.0275	0.055

Mean (in the absence of base), 0.062 ± 0.006 .

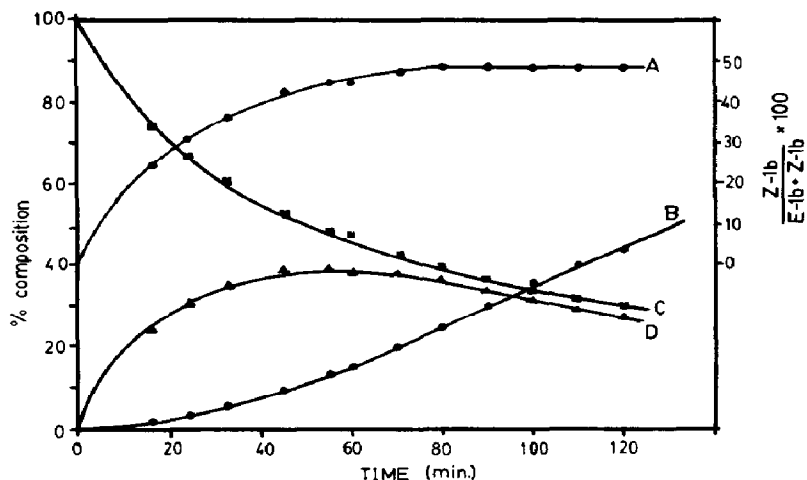


Fig. 2. Plot of percentage composition against time, as determined by gas chromatography (GC) using *n*-hexyl acetate as the internal standard, for the photochemical ($\lambda = 254$ nm) conversion of *E*-1b (0.04 M) to *Z*-1b and 4b in methanol-*O-d* in the presence of 1,2-dimethylimidazole: curve A, *E-Z* isomer composition for 1b expressed as per cent *E*-1b; curve B, deconjugated isomer 4b; curve C, *E*-1b; curve D, *Z*-1b.

tion of the deconjugated isomer confirms that it is formed from the *Z* isomer only and that the singlet excited states of the *E* and *Z* isomers are distinct [6].

The results in Table 1 indicate that for the ester 1b in methanol-*O-d* Φ_d is only slightly increased by the addition of base and that in the absence of base nearly all the dienols are intercepted by either the polar solvent acting as a Lewis base or by impurities in the solvent. This is in accord with previous results in which the quantum yield of deconjugation of an ester in the absence of a base catalyst was found to be increased on changing from ether to methanol and methanol-*O-d* solvent [6].

From Table 1 the mean value of Φ_d for 1b in the presence of added base is 0.062 ± 0.006 , and from eqn. (2) this value corresponds to Φ_e multiplied by a factor equal to the proportion of the dienolates which undergo protonation to give the deconjugated isomers, *i.e.* $k_\alpha/(k_\alpha + k_\gamma)$.

To determine the value of Φ_e from eqn. (2) it is necessary to determine the ratio k_α/k_γ . It is known that protonation of the metal salts of an ester-derived dienolate occurs predominantly at the α -carbon to give the deconjugated ester, *i.e.* $k_\alpha/(k_\alpha + k_\gamma)$ is close to unity [10]. However, the proportion of α to γ protonation would be expected to depend on the nature of the dienolate counter-ion, and in the case of the dienolate formed in the irradiation of 1b in the presence of 1,2-dimethylimidazole the counter-ion is the conjugate acid of the base and not a metal ion. Consequently it cannot necessarily be assumed that under these conditions $k_\alpha/(k_\alpha + k_\gamma)$ for 3b is close to unity. In addition, the double-bond geometry of the metal salt of an ester-derived dienolate is not known whereas, in the case of the dienolate 3b produced under base catalysis from the photochemically

formed dienol 2b, only the *Z* isomer is produced [3] and this may affect the proportion of α to γ protonation. Consequently it was necessary to measure the ratio k_α/k_γ for 3b under the irradiation conditions.

The ratio k_α/k_γ was determined by irradiation of the ester 1b in methanol-*O-d* and comparison of the amount of conversion to the deconjugated isomer with the amount of deuterium incorporation into the unconverted ester. This ratio is equal to the ratio k_α/k_γ at low conversion since k_γ is responsible for deuterium incorporation into the conjugated ester and k_α is responsible for deconjugation. The irradiations were performed in the presence of 1,2-dimethylimidazole to ensure that all the dienol was converted to the dienolate. Conversions were kept low so as to ensure that there would be insufficient deuterium incorporation into the starting carbonyl compound to give rise to a deuterium isotope effect on the value of Φ_e ; if k_γ is much smaller than k_α then even at quite high conversions little deuterium incorporation should occur and this potential complication will not interfere. As will be seen, this condition is satisfied.

The ester 1b was irradiated in methanol-*O-d* in the presence of 1,2-dimethylimidazole and the amount of conversion to the deconjugated isomer was determined by GC. The degree of incorporation of deuterium into the *E* and *Z* isomers of the conjugated ester was then determined by gas chromatography-mass spectroscopy (GC-MS) of the reaction mixture (Table 2, run A). In order to check that no deuterium was lost during the analysis procedure the *E* and *Z* isomers of the unconverted starting material were also isolated from the irradiation mixture by preparative GC and the deuterium content was measured directly by mass spectroscopy and also by GC-MS (Table 2, runs B and C). These determinations all gave the same result, confirming that no deuterium was lost during analysis. The ^1H nuclear

TABLE 2

Deuterium incorporation into the *E* and *Z* isomers of ester 1b following irradiation in methanol-*O-d* containing 1,2-dimethylimidazole

Run ^a	Conversion ^b (%)	<i>Z-1b</i>		<i>E-1b</i>	
		<i>M</i> ⁺ (%)	<i>M</i> ⁺ + 1 (%)	<i>M</i> ⁺ (%)	<i>M</i> ⁺ + 1 (%)
A	9.6	91.2 ± 0.7	8.8 ± 0.7	89.6 ± 0.9	10.4 ± 0.9
B	9.6	90.7 ± 0.2	9.3 ± 0.2	88.2 ± 0.5	11.8 ± 0.5
C	9.6	90.8 ± 0.2	9.2 ± 0.2	88.4 ± 0.3	11.6 ± 0.3
D	10	87.9 ± 0.3	12.1 ± 0.3	84.5 ± 0.5	15.5 ± 0.5
E	0	—	—	91.8 ± 0.3	8.2 ± 0.2

^aRun A, data obtained by GC-MS of the irradiation mixture; run B, data obtained by GC-MS of the *E* and *Z* isomers of 1b following separation by preparative GC; run C, data obtained by MS of the *E* and *Z* isomers of 1b following separation by preparative GC; Run D, data obtained by GC-MS of the irradiation mixture (no base present); Run E, data obtained by GC-MS of the non-irradiated ester.

^bConversion to the deconjugated isomer.

magnetic resonance (NMR) spectra of the irradiation mixture and the isolated conjugated esters following separation by preparative GC were also recorded. However, the incorporations were too small to be measured accurately by integration of the spectra. In addition, the conversions were too low to allow accurate determination of the degree of incorporation into the deconjugated isomer, but integration of the ^1H NMR spectra indicated at least 70% incorporation.

Comparison of the deuterium content of the irradiated *E* and *Z* isomers of **1b** with the deuterium content of the unirradiated ester (Table 2, run E) indicated that at 9.6% conversion to **4b** the amount of deuterium incorporated into the *Z* isomer was $(0.9 \pm 0.5)\%$ and into the *E* isomer was $(3.1 \pm 0.9)\%$; the *E*:*Z* ratio at 9.6% conversion was 58.4:41.6 so that the total deuterium incorporation into the conjugated ester was $(2.2 \pm 0.7)\%$. When the experiment was repeated without addition of 1,2-dimethylimidazole the degree of incorporation of deuterium into the conjugated ester was increased slightly (Table 2, run D) since under these conditions some of the dienol can revert to the conjugated isomer by the 1,5-hydrogen shift mechanism. In all runs it can be seen that deuterium incorporation into the *E* isomer is more efficient. This implies that the dienolate protonates to give the *E* isomer in preference to the *Z* isomer.

Since the total deuterium incorporation into **1b** at 9.6% conversion is only $(2.2 \pm 0.7)\%$ it can be concluded that the dienolate **3b** reketonizes predominantly by protonation at the α carbon atom to give the deconjugated isomer and that the ratio k_α/k_γ is 4.4 ± 1.4 . Thus for **3b** the value of $k_\alpha/(k_\alpha + k_\gamma)$ is 0.82 ± 0.05 and, from eqn. (2), Φ_e for **1b** is 0.08 ± 0.01 .

In order to allow comparison of the values of Φ_e for the ethyl ester **1b** with the quantum yields of *E*-*Z* isomerization, these were determined in both methanol and methanol-*O-d* and are shown in Table 3. No solvent isotope effect on $\Phi_{E \rightarrow Z}$ or $\Phi_{Z \rightarrow E}$ is evident but the values are somewhat larger than those previously reported for the corresponding methyl ester (1, X \equiv Me) in cyclohexane and ethanol [2]. For the methyl ester, $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$ are reported to be 0.090 ± 0.003 and 0.032 ± 0.003 respectively.

TABLE 3

Quantum yields of *E*-*Z* isomerization for ester **1b** in methanol and methanol-*O-d*

$\Phi_{Z \rightarrow E}$	Solvent	$\Phi_{E \rightarrow Z}$	Solvent
		0.274	Methanol
0.167	Methanol	0.231	Methanol
0.130	Methanol	0.225	Methanol- <i>O-d</i>
0.170	Methanol	0.279	Methanol- <i>O-d</i>
0.152	Methanol- <i>O-d</i>	0.255	Methanol- <i>O-d</i>
0.183	Methanol- <i>O-d</i>	0.250	Methanol- <i>O-d</i>

Mean $\Phi_{Z \rightarrow E}$, 0.16 ± 0.02 ; mean $\Phi_{E \rightarrow Z}$, 0.25 ± 0.02 .

3. Conclusions

For the ethyl ester **1b** the sum of the *E-Z* isomerization quantum yields ($0.25 + 0.16 = 0.41 \pm 0.04$) indicate that about 59% of the excited states decay by some other process and the quantum yield of photoenolization (0.08 ± 0.01) accounts for this only in part. Thus it can be concluded that the photoenolization process is not responsible for the lower efficiency of *E-Z* isomerization of the unsaturated ester **1b** compared with the ketone **1a** where the *E* \rightarrow *Z* and *Z* \rightarrow *E* quantum yields sum to 0.82.

A possible explanation for the lower *E-Z* isomerization efficiency of the ester was given in Section 1 of this paper; this explanation proposed that a closer proximity of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states in the ester resulted in a faster internal conversion to the ground state without *E-Z* isomerization. The absorption spectra of the ketone **1a** and the ester **1b** support this; for **1b** the $n \rightarrow \pi^*$ band is submerged beneath the $\pi \rightarrow \pi^*$ band whereas for **1a** they are well separated. Another important contributing factor which would explain why the ketone **1a** undergoes *E-Z* isomerization more efficiently than the ester could be that intersystem crossing is faster in the enone than in the ester. This would result in a shorter singlet lifetime for the ketone and more efficient triplet formation. This is consistent with the fact that for both the ketone and the ester *E-Z* isomerization from the triplet excited state is very efficient [1, 2].

4. Experimental details

4.1. General details

Analytical and preparative GC was performed using a diethylene glycol succinate (DEGS) stationary phase at 120 °C. Irradiations were carried out using a Rayonet apparatus equipped with 254 nm lamps or using a "Pen Ray" spectral calibration source (Ealing Scientific Co.). Ethyl *E*-2-methyl-2-butenate was prepared by esterification of tiglic acid (Aldrich Chemical Co.).

4.2. Determination of quantum yields of deconjugation of **1b**

Solutions of the *E* ester (0.04 M) in methanol-*O-d* (18 ml, 99% *O-d*, MSD Isotopes) containing a known quantity of *n*-hexyl acetate as an internal standard and varying quantities of 1,2-dimethylimidazole (see Table 1) were irradiated with a low pressure mercury lamp housed in a quartz well which was immersed in the solution so that all the light was absorbed by the ester. The ester solution was contained in a Pyrex tube which was suspended in a water bath held at 20 ± 0.5 °C. The formation of the *Z* ester and the deconjugated isomer were monitored by GC relative to the internal standard. The quantum yields of deconjugation were calculated from the observed rate of formation of the deconjugated isomer following attainment of a photostationary mixture of the *E* and *Z* esters (52:48) using the values of light

intensity determined for the lamp before and after the experiment by actinometry with azoxybenzene solutions as described previously [6, 11]. The absolute rates of formation of the deconjugated isomer were calculated following calibration of the internal standard against samples of pure deconjugated isomer isolated by GC from one of the irradiations which had been allowed to proceed to high conversion. The rate of formation of the deconjugated isomer was zero order until high conversion (at least 80%) although most determinations were made at less than 30% conversion. At the completion of the determination the irradiation solutions were stored in the dark and the composition monitored by GC to ensure that no dark reaction (base-catalysed re-conjugation) occurred; no dark reaction was seen, even at the highest base concentrations used, over periods equal to the total irradiation times. The quantum yields of deconjugation are summarized in Table 1.

4.3. Determination of degree of deuterium incorporation into the conjugated ester 1b

The *E* ester 1b (0.34 M) was irradiated to about 10% conversion in a Rayonet apparatus as a methanol-*O-d* solution (8 ml) which contained 1,2-dimethylimidazole (0.15 M). The exact conversion was determined by GC. A portion of the solution was then analysed by GC-MS using a DEGS column in a GC instrument attached to a Varian-MAT mass spectrometer. The ratio of ions of $m/e = 128$ (M^+) and $m/e = 129$ (monodeuterated species) for the *E* and *Z* esters was determined at various points throughout the GC peak to ensure that no deuterium isotope effect on the boiling points of the esters interfered with the analysis. Several runs were performed and an average taken. The results are given in Table 2. A second portion of the irradiation mixture was concentrated under partial vacuum and the residue was separated by preparative vapour phase chromatography to give pure samples of the *E* and *Z* esters. These were then analysed for deuterium content by ^1H NMR spectroscopy, by MS and also by GC-MS as above.

4.4. Determination of quantum yields of E-Z isomerization for ester 1b

The quantum yields of *E-Z* isomerization were measured in the same apparatus used for determination of the quantum yields of deconjugation. The *Z* isomer was prepared by irradiation of the *E* isomer and separated and purified by preparative GC. The *E* and *Z* isomers were each irradiated in both methanol and methanol-*O-d* containing *n*-hexyl acetate as an internal standard. No base was added to the solutions. Interconversion of the isomers was followed by GC. The rate of isomerization was initially zero order and curvature of the plots was observed at higher conversions due to isomerization of the isomer being formed. Consequently, quantum yield determinations were made in the linear region before the isomer being formed accumulated sufficiently to absorb light. The quantum yields determined are shown in Table 3.

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