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Photoisomerization and photocyclization reactivity of a cinnamaldehyde oxime analog

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Abstract

The photochemistry of the *E,E*- and *E,Z*-isomers of benzalcyclohexanone oxime has been investigated. Direct irradiation of the *E,E*-isomer gives primarily isomerization about the C=N bond; sensitized irradiation of the *E,E*-isomer gives primarily isomerization about the C=C bond. The *E,Z*-isomer gives primarily isomerization about the C=C bond under both direct and sensitized conditions. The relative energies of the twisted intermediates and steric effects are used to rationalize these results. In the presence of acid, direct irradiation of either isomer gives isomerization about both double bonds. Electrocyclization to produce tetrahydroacridine is also enhanced under acidic conditions.

Keywords: α,β-unsaturated oxime; Photoisomerization; Photocyclization

1. Introduction

Photochemical reactions of arylated dienes have long been of interest to organic photochemists. Suitably constructed molecules can give products of photoisomerization and photo-electrocyclization reactions. Photoisomerization of the olefinic groups can occur from both singlet and triplet states and the reactions are generally formulated as proceeding through twisted intermediates [1]. Electrocyclization to produce polycyclic compounds is usually a singlet state process and is typically followed by a ground state elimination or an oxidation reaction to generate an aromatic product [2].

Azadienes have until recently received much less attention [3]. Interest in the photochemistry of these compounds has increased in recent years, partly because of the relationship to the photochemistry of visual pigments. α,β-Unsaturated oxime derivatives constitute one class of aza analogues that are readily available but have received very little attention. Excited state reactivity patterns which have been reported for these compounds in the literature are mixed. Pratt and Abdul-Majid investigated the photoisomerization of the methyl ether of benzalacetone oxime and found high selectivity for C=N bond photoisomerization under both direct and sensitized conditions [4]. Okami et al. have investigated the direct and sensitized photochemistry of cinnamaldehyde oxime methyl ether [5]. Under both conditions isomerization occurs most efficiently at C=N if the C=C bond has *E*-stereochemistry. Conversely, isomerization occurs preferentially at C=C if that bond has *Z*-stereochemistry. They also reported synchronous C=C and C=N photoisomerization [5,6]. Photocyclization to produce quinoline derivatives was not observed by either group, although it has been reported by others [7,8].

We recently reported the photocyclization of benzalcyclohexanone oxime, a conformationally constrained cinnamaldehyde oxime analog, as a route to quinoline derivatives [9]. We now wish to report the results of a study which compares the relative efficiencies of isomerization and cyclization reactions and examines the photochemistry under acidic conditions and under triplet sensitization conditions.

2. Experimental details

2.1. Materials

The two stereoisomers of benzalcyclohexanone were prepared by literature procedures. Aldol condensation between cyclohexanone and benzaldehyde produced the *E*-isomer [10]; photoisomerization converted the *E*- to the *Z*-isomer [11].

The oximes (*E,E*-**1** and *E,Z*-**1**) were prepared by a standard method [12].

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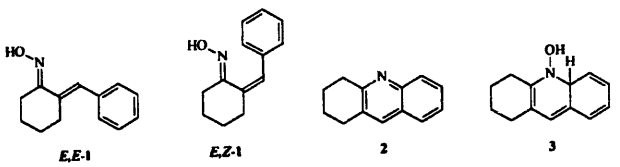

2.1.1. E,E-1

M.p., 123–125 °C (Lit. [13], 126.5 °C). IR (Nujol): 690, 755, 890, 960, and 3170 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.5–1.8 (m, 4H), 2.5–2.7 (m, 4H), 6.8–6.9 (m, 1H), 7.1–7.5 (m, 5H) and 9.61 (bs, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 23.4, 25.0 (two overlapping peaks?), 29.0, 127.1, 127.4, 128.1, 129.7, 135.0, 136.9 and 160.3; UV (MeOH) λ(max) 272 nm (log ϵ=4.15), (cyclohexane) λ(max) 274 nm (log ϵ=4.16), (MeOH/H^+) λ(max) 300 nm (log ϵ=4.14).

2.1.2. E,Z-1

M.p., 105–106 °C. IR (Nujol): 680, 730, 895, 950 and 3250 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.6–1.8 (m, 4H), 2.3–2.5 (m, 2H), 2.5–2.7 (m, 2H), 6.3–6.4 (m, 1H), 7.1–7.3 (m, 5H) and 8.45 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.5, 26.1, 27.2, 37.9, 126.5, 127.2, 128.0, 128.5, 136.2, 136.6 and 157.5; UV: (MeOH) λ(max) 264 nm (log ϵ=4.00), (cyclohexane) λ(max) 262 nm (log ϵ=3.99), (MeOH/H^+) λ(max) 294 nm (log ϵ=3.75).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.56; H, 7.68; N, 6.88.

All solvents were purified by distillation; sensitizers were purified by recrystallization. NMR spectra were recorded using a Chemagnetics A-200 spectrometer. Infrared spectra were recorded on a Perkin–Elmer 1320 spectrophotometer. UV spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

2.2. Photochemical reactions

Photochemical reactions were conducted in quartz tubes using a Rayonet RPR-100 reactor fitted with 254, 300 or 350 nm lamps. All solutions were purged with nitrogen for 20 min prior to irradiation. In sensitization experiments, the concentration of sensitizer was sufficient to absorb at least 99% of the incident light. The following sensitizers (triplet energies in kcal mol^{-1}) were used: 9,10-dibromoanthracene (E_T=40), anthracene (E_T=42), benzanthrone (E_T=46), pyrene (E_T=49), benzil (E_T=53), acetonaphthone (E_T=56), Michler's ketone (E_T=61) and benzophenone (E_T=69).

Quantum yields were measured using potassium ferrioxalate actinometry [14]. Substrate concentrations were approximately 0.02 M and conversions were held under 10–15%. Product concentrations were measured by ^1H NMR analysis.

3. Results and discussion

3.1. Absorption spectra

Ultraviolet absorption spectra of both *E,E*-**1** and *E,Z*-**1** showed intense $\pi \rightarrow \pi^*$ absorptions with absorption maxima in methanol at 272 nm (log ϵ=4.15) and 264 nm (log ϵ=4.00) respectively. The spectra were essentially identical in cyclohexane. In acidic methanol, the protonated oximes gave absorption maxima at 300 nm (log ϵ=4.14) and 295 nm (log ϵ=3.75) respectively. When spectra of *E,E*-**1** and *E,Z*-**1** were recorded at varying acid concentrations, isobestic points were noted at 284 nm and 287 nm respectively, indicating an equilibrium between the oxime and a protonated species.

3.2. Direct irradiations

3.2.1. Direct irradiation of E,E-1

Photolysis of *E,E*-**1** in methanol at 300 nm gave two primary photoproducts in a ratio of 11:1 as evidenced by the appearance of two vinylic proton NMR signals. The signal for the major product appeared at 7.00 ppm, indicative of a proton still under the ring current effects of the C=N bond thus consistent with a product resulting from isomerization about the C=N bond (*Z,E*-**1**). The signal for the minor product appeared at 6.36 ppm, indicative of a proton no longer under the ring current effects of the C=N bond, thus consistent with a product resulting from isomerization about the C=C bond (*E,Z*-**1**). Continued irradiation yielded two secondary photoproducts. One was *Z,Z*-1 (vinyl proton signal at 6.37 ppm) produced by the photoisomerization of either primary photoproduct. The other was 1,2,3,4-tetrahydroacridine (**2**) produced by electrocyclization followed by dehydration of a putative N-hydroxyhexahydroacridine intermediate (**3**). This product was identified by ^1H NMR signals for the C-8 and C-9 protons at 7.95 ppm (d, J=7.9 Hz) and 7.82 ppm (s) respectively. Photolysis in cyclohexane gave the same initial photoproducts in a ratio of 7.5:1. Continued irradiation gave the secondary isomerization product, but no tetrahydroacridine was observed. Prolonged irradiation in cyclohexane gave a photostationary mixture which contained 33% *Z,E*-, 33% *E,Z*-, 24% *E,E*- and 11% *Z,Z*-isomer.

Photolysis at 254 nm gave similar results although a wavelength effect on the product ratios was noted. In methanol a 2.8:1 ratio favoring C=N isomerization was observed; in cyclohexane the ratio was 3.1:1. We have not yet explored the nature of the wavelength effect.

Quantum yields were measured using ferrioxalate actinometry and are presented in Table 1.

3.2.2. Direct irradiation of E,Z-1

Photolysis of *E,Z*-**1** in methanol at 300 nm gave three primary photoproducts. The *E,E*- and *Z,Z*-isomers were produced in a ratio of approximately 12:1; tetrahydroacridine

Table 1
Quantum yields

Reactant	λ (nm)	Product	Solvent	Quantum yield
E,E-Oxime	254	*Z,E*-Oxime	MeOH	0.13 (±.01)
		E,Z-Oxime	MeOH	0.046 (±.002)
		Z,E-Oxime	CHEX	0.093 (±.009)
		E,Z-Oxime	CHEX	0.030 (±.001)
E,E-Oxime	300	*Z,E*-Oxime	MeOH	0.28 (±.01)
		E,Z-Oxime	MeOH	0.026 (±.001)
		Z,E-Oxime	CHEX	0.21 (±.04)
		E,Z-Oxime	CHEX	0.028 (±.002)
E,Z-Oxime	254	*E,E*-Oxime	MeOH	0.077 (±.007)
		Z,Z-Oxime	MeOH	0.014 (±.001)
		Acridine	MeOH	0.052 (±.001)
		E,E-Oxime	CHEX	0.049 (±.002)
		Z,Z-Oxime	CHEX	0.016 (±.001)
		Acridine	CHEX	0
E,Z-Oxime	300	*E,E*-Oxime	MeOH	0.073 (±.004)
		Z,Z-Oxime	MeOH	≈0.006
		Acridine	MeOH	0.063 (±.001)
		E,E-Oxime	CHEX	0.040 (±.003)
		Z,Z-Oxime	CHEX	≈0.005
		Acridine	CHEX	0

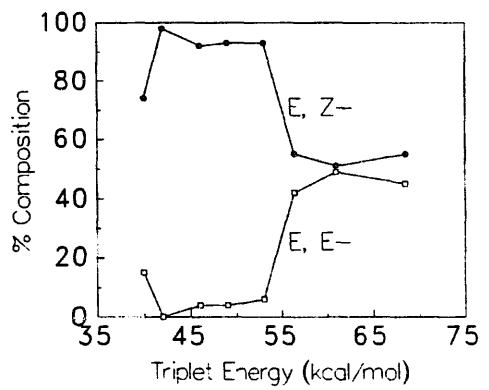

Fig. 1. Photosationary state composition versus sensitizer triplet energy.

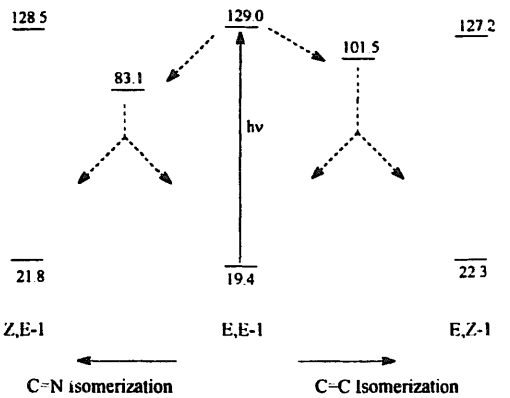

Fig. 2. AM1 energies (kcal mol^{-1}) of the ground and singlet excited states of three isomers of **1** and the energies of the twisted intermediates leading to C=N and C=C isomerization.

was also produced. Prolonged irradiation gave the *Z,E*-isomer as a secondary product. In cyclohexane the *E,E*- and *Z,Z*-isomers were produced in an approximately 8:1 ratio. Again, in cyclohexane no tetrahydroacridine was observed. Prolonged irradiation gave a photostationary mixture identical to that obtained in the irradiation of the *E,E*-isomer.

Quantum yields were measured using ferrioxalate actinometry and are presented in Table 1.

3.3. Sensitized irradiations

The triplet state behavior of both *E,E*- and *E,Z*-oxime isomers was studied by carrying out sensitization experiments. Irradiations were performed at 350 nm in benzene using a variety of sensitizers with different triplet energies. Triplet state isomerization reactivity was localized almost exclusively at the C=C bond giving photostationary mixtures of *E,E*- and *E,Z*-isomers. Only minor amounts (<5%) of isomers resulting from isomerization about the C=N bonds were observed. Triplet energies, estimated from a plot of photostationary state composition vs. sensitizer triplet energy (Fig. 1), are 55 kcal mol^{-1} for the *E,E*-isomer and 40 kcal mol^{-1} for the *E,Z*-isomer.

3.4. Irradiation in acidic methanol

When *E,E*-**1** was irradiated in acidic methanol (2 wt.% sulfuric acid), isomerization of the C=C bond (formation of *E,Z*-**1**) was enhanced and isomerization of the C=N bond (formation of *Z,E*-**1**) was suppressed. In the latter case, a control experiment showed that the *Z,E*-isomer will isomerize thermally to the *E,E*-isomer under the acidic reaction conditions. Prolonged irradiation resulted in the production of tetrahydroacridine as the major product. Measurement of quantum yields was difficult under these conditions, but we estimate that at 300 nm the *E,E*- to *E,Z*- quantum yield is approximately 0.16 and the *E,E*- to *Z,E*- quantum yield is approximately 0.1.

The effect of acid on the photochemistry of the *E,Z*-oxime was similar to that described above for *E,E*-**1**. Isomerization of the C=C bond was enhanced, as was acridine formation. Again, production of the *Z,E*-isomer was suppressed.

3.5. Discussion

Direct irradiation of the *E,E*-isomer gives isomerization primarily at the C=N bond, a result which is similar to those which have been described for other α,β-unsaturated oxime derivatives. Because sensitization experiments give almost exclusive isomerization about the C=C bond it is apparent that the behavior of this oxime under direct irradiation arises from the singlet state. One explanation for this selectivity is greater stability of the twisted intermediate which leads to C=N isomerization. AM1 [15] calculations support this suggestion (Fig. 2). The twisted intermediate leading to C=N isomerization is calculated to be 18 kcal mol^{-1} more stable than the twisted intermediate leading to C=C isomerization. The lack of a significant solvent effect in these isomerizations is consistent with a diradical rather than zwitterionic structure for the twisted intermediate.

In the direct irradiation of the *E,Z*-isomer reactivity shifts to the C=C bond. It is interesting to note that the changes in product ratio arise from a dramatic drop in the quantum yields for C=N isomerization, but that the quantum yields for C=C isomerization are of the same order of magnitude as those measured for the *E,E*-isomer. Steric congestion may inhibit the formation of the *Z,Z*-isomer forcing that twisted intermediate to decay back to the reactant ground state. The presence of an electrocyclization pathway when the benzylidene double bond is *Z*- may also lead to a reduced efficiency for C=N isomerization.

Sensitized irradiation in both isomers gives C=C isomerization with very high selectivity. This is unusual behavior for α,β-unsaturated oxime derivatives and no ready explanation presents itself.

Formation of the electrocyclization product (tetrahydroacridine) from the *E,Z*-isomer is highly sensitive to reaction conditions. It is completely suppressed in cyclohexane and is enhanced in acidic methanol. It is likely that the initial cyclized intermediate (**3**) is formed in all cases and that the apparent difference in reactivity is due to changes in the rate of dehydration of **3**.

In no cases did we see evidence for synchronous isomerization about both C=N and C=C bonds.

The effect of acid on the oxime photochemistry appears to be a combination of several factors. Acid protonates the oxime giving an oximinium cation which exhibits different photochemical behavior, including the enhancement of isomerization about the C=C bond (vide supra). Acid also influences the chemistry by two thermal reactions. First is the acid catalyzed thermal isomerization of the *Z,E*-isomer back to the *E,E*- form. Second is the likely enhancement of the production of tetrahydroacridine by the acid catalyzed dehydration of intermediate **3**. All of these factors promote the ultimate formation of the electrocyclized product and provide a mechanistic rationale for our earlier observation that optimum yields for tetrahydroacridine formation are obtained in acidic methanol [9].

Acknowledgements

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