0.85–2.20 (m, 2 H), 3.00 (t, J = 7.2 Hz, 2 H), 3.61 (t, J = 6.6 Hz, 2 H), 6.78 (s, 1 H), 7.18–7.78 (m, 7 H), 8.15–8.20 (m, 1 H).

(3*E*)-4-Methoxy-3-methyl-2-[(trimethylsilyl)oxy]-1,3-butadiene (8). (a) (3*E*)-4-Methoxy-3-methyl-3-buten-2-one. A modification of the literature procedure[8b] was used. Methyl ethyl ketone (8.5 mL, 94.9 mmol) was added dropwise over 30 min to a refluxing mixture of NaH (60% w/w dispersion in oil, 3.50 g, 91.3 mmol) and methyl formate (4.2 mL) in THF (500 mL). After 1 h, Me_2SO_4 (12.667 g, 100.4 mmol) was injected, and refluxing was continued for 30 min. Water (15 mL) was then added, and heating was continued for a further 30 min. The mixture was cooled and diluted with ether (500 mL). The organic phase was washed with aqueous ammonia (2 M, 300 mL), water (300 mL), and brine (300 mL) and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (5 × 15 cm) with 1:3 EtOAc–hexane gave (3*E*)-4-methoxy-3-methyl-3-buten-2-one (3.5 g, 34%) as a homogeneous (^{1}H NMR) oil: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.65 (s, 3 H), 2.25 (s, 3 H), 3.85 (s, 3 H), 7.25 (s, 1 H).

(b) (3*E*)-3-Methyl-4-methoxy-2-[(trimethylsilyl)oxy]-1,3-butadiene (8). A different procedure from that reported[8] in the literature was followed. The above butenone (2.21 g, 19.36 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of LDA [21.39 mmol, from *n*-butyllithium (1.55 M, 13.8 mL, 21.39 mmol) and *i*-Pr_2NH (2.17 g, 21.40 mmol)] in THF (30 mL). After 30 min, Me_3SiCl (75% v/v in Et_3N, 5 mL) was added dropwise. After a further 10 min, the cooling bath was removed. After about 1 h, the mixture was quenched with ether (50 mL), filtered through Florisil, evaporated, and distilled to give diene 8[8] (2.50 g, 70%): bp 65–70 °C (14 mmHg); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.22 (s, 9 H), 1.68 (s, 3 H), 3.65 (s, 3 H), 4.14 (s, 1 H), 4.25 (s, 1 H) 6.50 (s, 1 H).

(±)-2-(3-Furyl)-2,3-dihydro-5-methyl-1-[3-(phenylseleno)propyl]-4-pyridinone (9). The crude imine 7 (79 mg, 0.271 mmol) in THF (1 mL) was added to a stirred solution of diene 8 (250 mg, 1.340 mmol) and anhydrous $ZnCl_2$ (60 mg, 0.440 mmol) in THF (2 mL) at room temperature. After 40 h, the resulting mixture was diluted with EtOAc (10 mL), washed with water (2 × 5 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) with 1:1 EtOAc–hexane gave 9 (73 mg, 72%) as an oil containing 8% of an isomer (^{1}H NMR, 400 MHz): FT-IR ($CHCl_3$ cast) 1602, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.68 (s, 3 H), 1.89 (quintet, J = 7.0 Hz, 2 H), 2.58 (AB q, J = 16.5, 7.5 Hz, 1 H), 2.72 (AB q, J = 16.5, 6.5 Hz, 1 H), 2.77–2.93 (m, 2 H), 3.19 (t, J = 7.0 Hz, 2 H), 4.42 (dd, J = 7.5, 6.5 Hz, 1 H), 6.34, (s, 1 H), 6.85 (s, 1 H), 7.25–7.30 (m, 4 H), 7.37 (s, 1 H), 7.45–7.51 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 12.57, 24.26, 29.00, 42.69, 52.30, 52.96, 105.49, 109.03, 123.01, 127.24, 129.15, 132.95, 140.09, 143.71, 151.50, 190.03; exact mass m/z calcd for $C_{19}H_{21}NO_3Se$ 375.0738, found 375.0738.

(±)-5-(3-Furyl)hexahydro-8-methyl-7(1*H*)-indolizinone (5). The general procedure for radical cyclization[6] was followed by using the above selenide 9 (93 mg, 0.248 mmol) in benzene (20 mL), Ph_3SnH (105 μL, 144 mg, 0.411 mmol) in benzene (10 mL), and AIBN (8 mg, 0.048 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) with 3:2 EtOAc–hexane gave 5 (45 mg, 83%) as a homogeneous (^{1}H NMR, 400 MHz) oil: FT-IR ($CHCl_3$ cast) 1709 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (d, J = 6.3 Hz, 3 H), 1.54–1.64 (m, 1 H), 1.65–1.75 (m, 1 H), 1.88–2.03 (m, 2 H), 2.34–2.39 (m, 2 H), 2.46 (q, J = 8.3 Hz, 1 H), 2.57 (dd, J = 6.5, 2.8 Hz, 2 H), 2.91–3.02 (m, 2 H), 4.45 (dd, J = 6.5, 2.3 Hz, 1 H), 6.70 (s, 1 H), 7.22 (s, 1 H), 7.38 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 10.52, 21.96, 30.68, 45.35, 49.50, 50.50, 52.01, 61.83, 111.08, 121.53, 140.66, 142.59, 211.33; exact mass m/z calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1258. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.15; H, 7.72; N, 6.53.

(5α,7α,8α,8aα)-(±)-5-(3-Furyl)octahydro-8-methyl-7-indolizinol (10). $NaBH_4$ (ca. 50 mg, 1.32 mmol) was added to a cooled (0 °C) solution of ketone 5 (200 mg, 0.904 mmol) in EtOH (2 mL). After 10 min the mixture was filtered through a pad of silica gel. Evaporation of the solvent followed by crystallization of the crude product from 1:19 EtOAc–hexane gave 10 (175 mg, 86%): FT-IR ($CHCl_3$ cast) 3500 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (d, J = 7.0 Hz, 3 H), 1.35–1.51 (m, 1 H), 1.51–2.10 (m, 7 H), 2.18–2.28 (m, 1 H), 2.49 (br q, J ~ 8.3 Hz, 1 H), 2.70 (br q, J ~ 8.2 Hz, 1 H), 2.80 (td, J = 6.0, 3.6 Hz, 1 H), 3.90–3.96 (m, 1 H), 4.06 (dd, J = 5.9, 3.6 Hz, 1 H), 6.49 (s, 1 H), 7.36 (s, 1 H), 7.50 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.33, 20.96, 29.35, 37.82, 40.56, 50.24, 50.60, 57.27, 69.35, 111.96, 124.90, 140.70, 142.38; exact mass m/z calcd for $C_{13}H_{19}NO_2$ 221.1416, found 221.1411.

(5α,7β,8α,8aα)-(±)-5-(3-Furyl)octahydro-8-methyl-7-(phenylseleno)indolizine (11). A modification of a general literature procedure[10] was used. A solution of PhSeCN (66 mg, 0.360 mmol) in THF (1.5 mL) was added over 15 min to a refluxing solution of 10 (40 mg, 0.181 mmol) and Bu_3P (73 mg, 0.360 mmol) in THF (2 mL), and refluxing was continued for a further 1.5 h. The solvent was then evaporated, and flash chromatography of the residue over silica gel (1 × 15 cm) with 2:5 EtOAc–hexane gave 11 (41 mg, 63%) as a homogeneous (^{1}H NMR, 400 MHz) oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18 (d, J = 7.0 Hz, 3 H), 1.35–1.55 (m, 3 H), 1.70–1.810 (m, 1 H), 1.89–1.98 (m, 1 H), 2.17–2.33 (m, 3 H), 2.36 (q, J = 8.3 Hz, 1 H), 2.78 (td, J = 6.0, 3.6 Hz, 1 H), 3.12 (td, J = 8.2, 5.0 Hz, 1 H), 4.12 (dd, J = 8.3, 3.6 Hz, 1 H), 6.27 (s, 1 H), 7.20–7.30 (m, 4 H), 7.36 (s, 1 H), 7.50–7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 18.10, 20.96, 30.14, 39.33, 42.62, 46.05, 49.89, 52.83, 62.20, 111.94, 122.59, 127.63, 128.96, 129.20, 135.57, 140.05, 142.33; exact mass m/z calcd for $C_{19}H_{23}NOSe$ 361.0944, found 361.0953.

(5α,8α,8aα)-(±)-5-(3-Furyl)octahydro-8-methylindolizine (2). A solution of selenide 11 (32 mg, 0.089 mmol), Ph_3SnH (134 μL, 47 mg, 0.133 mmol), and AIBN (4 mg, 0.024 mmol) in benzene (10 mL) was refluxed for 2 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 15 cm) with 1:1 EtOAc–hexane gave 2 (18 mg, 99%) as a homogeneous (^{1}H NMR, 400 MHz) oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (d, J = 6.4 Hz, 3 H), 1.22–1.42 (m, 3 H), 1.48–1.69 (m, 1 H), 1.62–1.93 (m, 4 H), 2.00–2.10 (m, 2 H), 2.29 (q, J = 8.7 Hz, 1 H), 2.82 (td, J = 8.7, 2.8 Hz, 1 H), 4.16 (m, 1 H), 6.34 (s, 1 H), 7.35–7.37 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.07, 20.36, 29.44, 29.55, 30.67, 37.40, 50.03, 51.85, 62.09, 112.42, 123.00, 140.13, 141.99; exact mass m/z calcd for $C_{13}H_{19}NO$ 205.1466, found 205.1461.

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Supplementary Material Available: Crystal structure data for 9 and ^{1}H NMR spectra of 2, 6, 9, and 11 (13 pages). Ordering information is given an any current masthead page.

Photocyclization in an Alcohol Solution Containing Dissolved Base. A New Development in Enamide Photochemistry

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Introduction

To organic chemists, the photocyclization of 1,3,5-hexatrienic systems undoubtedly represents one of the most synthetically useful photochemical processes. Indeed, the photoinduced electrocyclic ring closure of 6π electron conjugated hydrocarbon systems has been extensively exploited. For example, it has been known for over 40 years that stilbene and related compounds undergo pho-

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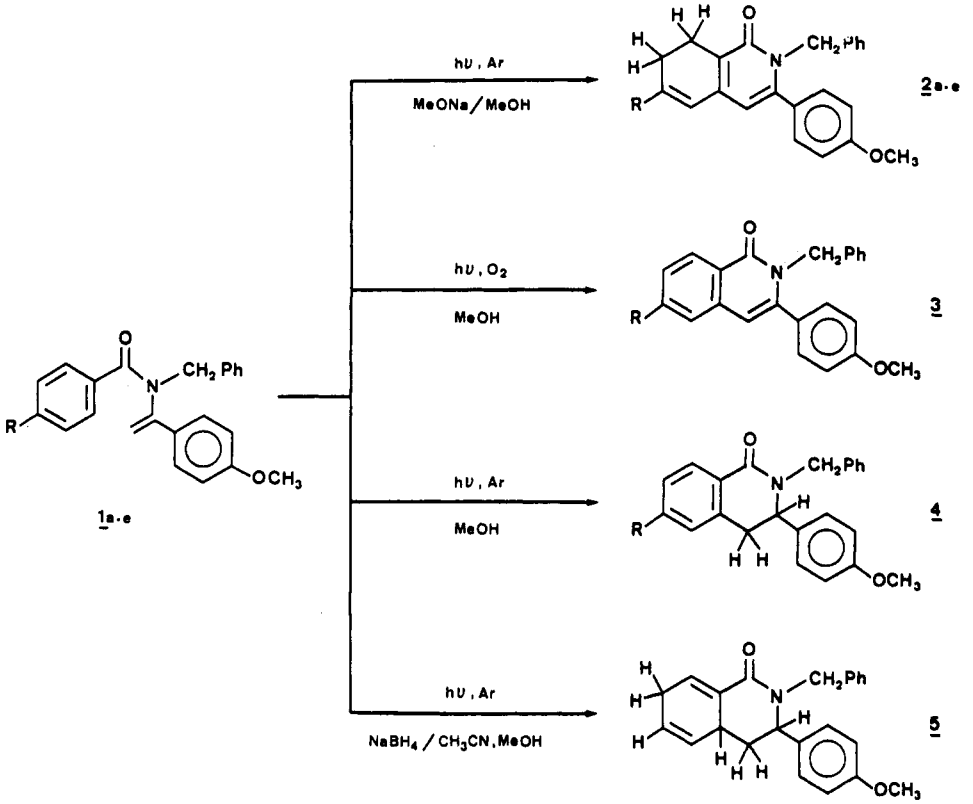
Table I. Properties of *N*-Aroyl-*N*-benzyl-4-methoxy-α-methylenebenzylamines 1

compd. no.	R	yield (%)	mp[a] (°C)	formula[b,c]	MS *m/z* (rel int)[d]	^{1}H NMR[e]
1a	H	82	107–108	$C_{23}H_{21}NO_2$	343 (M^+, 4), 252 (67), 105 (69), 91 (100)	δ 3.8 (s, 3 H, OCH_3), 4.5 (s, 1 H, olefinic H), 4.8 (s, 2 H, N-CH_2), 5.1 (s, 1 H, olefinic H), 6.8–7.5 (m, 14 H, Ar)
1b	CH_3	78	72–73	$C_{24}H_{23}NO_2$	357 (M^+, 2), 266 (33), 119 (42), 91 (100)	δ 2.3 (s, 3 H, CH_3), 3.8 (s, 3 H, OCH_3), 4.5 (s, 1 H, olefinic H), 4.8 (s, 2 H, N-CH_2), 5.1 (s, 1 H, olefinic H), 6.8–7.6 (m, 13 H, Ar)
1c	OCH_3	74	93–94	$C_{24}H_{23}NO_3$	373 (M^+, 3), 282 (68), 135 (100), 91 (84)	δ 3.7 (s, 3 H, OCH_3), 3.8 (s, 3 H, OCH_3), 4.5 (s, 1 H, olefinic H), 4.8 (s, 2 H, N-CH_2), 5.1 (s, 1 H, olefinic H), 6.6–7.6 (m, 13 H, Ar)
1d	Cl	89	85–86	$C_{23}H_{20}ClNO_2$	377 (M^+, 2), 286 (44), 139 (37), 91 (100)	δ 3.8 (s, 3 H, OCH_3), 4.5 (s, 1 H, olefinic H), 4.8 (s, 2 H, N-CH_2), 5.2 (s, 1 H, olefinic H), 6.8–7.6 (m, 13 H, Ar)
1e	CF_3	79	83–84	$C_{24}H_{20}F_3NO_2$	411 (M^+, 4), 320 (41), 173 (36), 91 (100)	δ 3.8 (s, 3 H, OCH_3), 4.5 (s, 1 H, olefinic H), 4.8 (s, 2 H, N-CH_2), 5.2 (s, 1 H, olefinic H), 6.8–7.6 (m, 13 H, Ar)

[a] Uncorrected; recrystallized from EtOH. [b] Results of microanalyses were within ±0.25 of theory. [c] All compounds show UV absorption band at λ_{max} = 263 and 360 nm; IR (KBr) ν 1650, 1670 (CONH). [d] M^+, $(M - C_6H_5CH_2)^+$, $(M - RC_6H_4CO)^+$, $(C_6H_5CH_2)^+$. [e] 80 MHz ($CDCl_3$ solution).

Scheme I



tochemical cyclodehydrogenation to form phenanthrenes.[1] The photocyclization of 1,3,5-hexatrienic systems that incorporate heteroatoms is also well known. The photocyclization of aromatic enamides, which provides a general route to a wide variety of six-membered lactams,[2] can be regarded as the best example of such a process. In recent years, investigations have focused primarily on photocyclizations in solutions that contain reagents (an additional solute or the solvent itself) that are capable of inducing unexpected modes of photocyclization and consequently giving rise to previously unattainable photoproducts. Thus, we demonstrated that the photolysis of various 1,2-diarylethylenes dissolved in deaerated primary amines[3,4] or in alcohols that also contained dissolved base was accompanied by unselective prototropic rearrangements of the initially formed photoproducts, which led, ultimately, to the formation of a variety of dihydrophenanthrene-like compounds. Concurrently, Ninomiya and co-workers[2c] described new reductive photocyclization conditions which involved irradiating solutions of aromatic enamides in ether/methanol[5] or acetonitrile/methanol[6] that also contained a hydride reagent. They recently demonstrated the usefulness of this procedure in a synthesis of Ipecac and Heteroyohimbine alkaloids.[7]

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Table II. Data for the Different Photoproducts 2, 3, 4, and 5

compd no.	R	yield (%)	mp (°C)[a] (recryst solvent)	formula[b]	MS m/z (rel int)	^{1}H NMR (J in Hz)[c]	^{13}C NMR[d] (δ) C-5	C-6	C-7	C-8
2a	H	72	138–139 (hexane/toluene)	$C_{23}H_{21}NO_2$	343 (M^+, 64), 342 (100), 91 (86)	δ 2.31 (tdd, J = 9.3, 4.1, 2.1, 2 H, CH_2), 2.73 (t, J = 9.3, 2 H, CH_2), 3.71 (s, 3 H, OCH_3), 5.10 (br s, 2 H, N-CH_2), 5.82 (s, 1 H, H-4), 6.11 (dt, J = 9.8, 2.1, 1 H, H-5), 6.20 (dt, J = 9.8, 4.1, 1 H, H-6), 6.72–7.13 (m, 9 H, Ar)	125.3	134.9	22.7	16.9
2b	CH_3	63	196–197 (hexane/toluene)	$C_{24}H_{23}NO_2$	357 (M^+, 78), 356 (88), 91 (100)	δ 1.84 (dt, J = 1.5, 1.3, 3 H, CH_3), 2.23 (tdq, J = 9.1, 1.5, 1.3, 2 H, CH_2), 2.76 (t, J = 9.1, 2 H, CH_2), 3.70 (s, 3 H, OCH_3), 5.09 (br s, 2 H, N-CH_2), 5.77 (s, 1 H, H-4), 5.86 (tq, J = 1.5, 1.5, 1 H, H-5), 6.70–7.11 (m, 9 H, Ar)	120.4	145.6	28.5	20.6
2c	OCH_3	64	228–229 (hexane/toluene)	$C_{24}H_{23}NO_3$	373 (M^+, 29), 372 (52), 91 (33)	δ 2.39 (td, J = 9.1, 0.8, 2 H, CH_2), 2.86 (t, J = 9.1, 2 H, CH_2), 3.64 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 5.09 (br s, 2 H, N-CH_2), 5.17 (t, J = 0.8, 1 H, H-5), 5.80 (s, 1 H, H-4), 6.73–7.13 (m, 9 H, Ar)	93.9	165.8	27.1	21.6
2d	Cl	74	193–194 (hexane/toluene)	$C_{23}H_{20}ClNO_2$	377 (M^+, 41), 376 (45), 91 (100)	δ 2.64 (td, J = 9.1, 1.5, 2 H, CH_2), 2.92 (t, J = 9.1, 2 H, CH_2), 3.74 (s, 3 H, OCH_3), 5.10 (br s, 2 H, N-CH_2), 5.78 (s, 1 H, H-4), 6.24 (t, J = 0.8, 1 H, H-5), 6.74–7.15 (m, 9 H, Ar)	122.7	141.0	31.3	22.0
2e	CF_3	61	179–180 (hexane/toluene)	$C_{24}H_{20}F_3NO_2$	411 (M^+, 23), 410 (18), 91 (100)	δ 2.53 (td, J = 9.1, 1.8, 2 H, CH_2), 2.94 (t, J = 9.1, 2 H, CH_2), 3.82 (s, 3 H, OCH_3), 5.19 (br s, 2 H, N-CH_2), 6.00 (s, 1 H, H-4), 6.70 (tq, J = 1.8, 1.8, H-5), 6.83–7.26 (m, 9 H, Ar)	126.5	131.9	20.3	20.0
3b[e]	CH_3	82	196–197 (EtOH)	$C_{24}H_{21}NO_2$	355 (M^+, 82), 354 (86), 91 (100)	δ 2.5 (s, 3 H, CH_3), 3.8 (s, 3 H, OCH_3), 5.2 (br s, 2 H, N-CH_2), 6.35 (s, 1 H, H-4), 6.75–7.8 (m, 11 H, Ar), 8.35 (m, 1 H, H peri)				
4b[e]	CH_3	79	102–103 (hexane/toluene)	$C_{24}H_{23}NO_2$	357 (M^+, 33), 252 (100)	δ 2.3 (s, 3 H, CH_3), 3.0 and 3.55 (ddd, J = 16, 7, 2, together 2 H, CH_2), 3.7 and 5.85 (dd, J = 15, together 2 H, N-CH_2), 3.75 (s, 3 H, OCH_3), 4.7 (m, 1 H, H-3), 6.7–7.6 (m, 11 H, Ar), 8.1 (m, 1 H, H peri)				
5	H	47	134–135 (hexane/Et_2O)	$C_{23}H_{23}NO_2$	345 (M^+, 21), 343 (78), 91 (100)	δ 1.74 (ddd, J = 13.3, 13.1, 11.5, 1 H, H-4), 2.18 (ddd, J = 13.3, 5.1, 3.2, 1 H, H-4), 2.91 (m, 2 H, H-7), 3.02 (m, 1 H, H-4a), 3.46 and 5.51 (dd, J = 14.7, together 2 H, N-CH_2), 3.81 (s, 3 H, OCH_3), 4.36 (dd, J = 11.5, 5.1, 1 H, H-3), 5.55 (dd, J = 10.0, 4.1, 1 H, H-5), 5.73 (br d, J = 10, 1 H, H-6), 6.85–7.25 (m, 10 H, Ar + H-8)				

[a] Uncorrected. [b] Results of microanalyses were within ±0.30 of theory. [c] 400 MHz ($CDCl_3$ solution) for 2a–e and 5a; 80 MHz ($CDCl_3$ solution) for 3b and 4b. [d] 100 MHz ($CDCl_3$ solution). [e] Compounds 3a and 4a are described in ref 8b.

Because of our interest in the photoreactivity of enamides[8] and in evaluating enamide photocyclization as a synthetic tool, we undertook a detailed study of the photocyclization of aromatic enamides dissolved in alcohol that also contained dissolved base.

Results and Discussion

The investigation involved the aromatic acyclic enamides 1a–e (Table I). The presence of an aromatic substituent at the 1-position of the vinyl group is required for photocyclization to occur.[8b] The photolysis of alkyl-substituted enamides gives exclusively enamino ketones, the products of a photo-Fries rearrangement.[9]

Irradiation of the aromatic enamides 1a–e (5×10^{-3} M solutions in deaerated 5×10^{-2} M methanolic $NaOCH_3$) for 2 h afforded high yields of the previously unknown 7,8-dihydroisoquinolin-1(2*H*)-ones 2a–e (Scheme I, Table II). The structures of 2a–e were inferred from the ^{1}H NMR spectra. All the spectra show two two-proton multiplets due to the vicinal allylic methylene protons. The assigned structures were confirmed by 100-MHz ^{13}C NMR spectroscopy and by comparison of DEPT spectra recorded with different pulse angles (θ). These unambiguously established the presence in 2b, for example, of two methyl (δ 23.5, 55.2), three methylene (δ 20.6, 28.5, 48.7), 11 methine (δ 107.6, 113.3 (×2), 120.4, 126.6 (×3), 128.1 (×2), 129.9 (×2)), and eight quaternary carbon atoms (δ 118.0, 128.0, 137.8, 142.1, 145.6, 146.9, 159.7, 162.4).

Compounds 2a–e did not arise by the photoreduction of the isoquinolin-1(2*H*)-ones 3 or by the thermal or photochemical base-induced prototropic rearrangement of the 3,4-dihydroisoquinolin-1(2*H*)-ones 4. Indeed, no trace of 2a,b could be detected after irradiation of 3a,b and 4a,b (the photoproducts obtained by photolysis of 1a,b in methanol under oxidative and nonoxidative conditions, respectively) in basic methanolic solution (Scheme I).[8b] The nature of compounds 2 is also dramatically different from that of the fused isoquinolones 5 that were obtained by irradiation under the reductive conditions described by Ninomiya.[6] A typical result of irradiation under reductive

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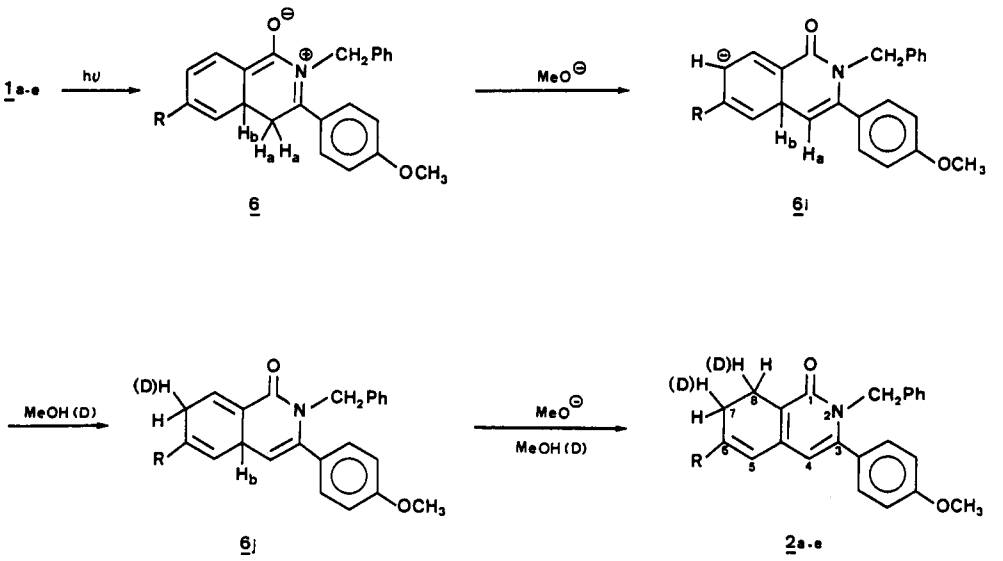
Scheme II



conditions is the formation of 3,4,4a,7-tetrahydro-3-(4-methoxyphenyl)-2-benzylisoquinolin-1(2*H*)-one (**5**) from enamide **1a** (Scheme I). From the results of experiments performed with methanolic solutions that contained no added base, it was clear that the presence of a base is necessary for the photoproducts **2a–e** to be formed and also that an ionic process is undoubtedly responsible for their formation. A mechanism that explains the photoconversion of **1a–e** to **2a–e** is shown in Scheme II. It is by now well known that the photoinduced electrocyclic ring closure of the parent 6π electron conjugated systems gives a 4,4a-dihydrocyclic intermediate, **6**.[10] Abstraction of a proton (Ha) from C-4 of **6** would be favored because the developing anion would be stabilized by formation of a species (**6i**) that contains an uncharged nitrogen atom. Carbanions like **6i** are quite similar in structure to the cyclohexadiene intermediates involved in the Birch reduction and also to the transient species postulated by Ninomiya to account for the reductive photocyclization of compounds like **1a–e**.[5] A some point, protonation of **6i** would lead to **6j**. Compounds **2a–e** would then be formed via a second deprotonation/protonation sequence.

To test the validity of this hypothesis, the photocyclization was performed in CH_3OD and the extent and location of deuterium incorporation into the product was determined. Because the C–H bonds of methanol are more likely to undergo homolytic cleavage than is the O–H bond (the bond energies are 92 and 102 kcal/mol, respectively),[11] if a radical process occurred in CH_3OD as the solvent, incorporation of deuterium into the photoproduct should not be observed. Thus, a 5×10^{-3} M solution of **1c** (also 0.05 M in $NaOCH_3$) in CH_3OD was irradiated. The products of the reaction were isolated by TLC and were characterized by ^1H NMR spectroscopy. That deuterium had been incorporated at the two methylene positions of the product was made immediately evident by the presence in the NMR spectrum of a less extensively split signal due to the methylene protons at C-7 and C-8. If it is assumed that no deuterium was incorporated into the methoxy group, then integration indicated that (50 ± 5)% of the deuterium was incorporated at C-7, (40 ± 5)% at C-8, and (10 ± 5)% at C-5 (the last is probably the result of deuterium incorporation into the developing carbanion **6i**). It should also be noted that **2c** dissolved in $NaOCH_3/CH_3OD$ did not show any incorporation of deuterium after standing for several hours at room temperature or after irradiation under the conditions described above.

These results unambiguously establish the ionic nature of the reaction and support the proposed mechanism. In summary, it can then be stated that, under basic conditions, the initially formed valence photoisomers of the parent enamides **1a–e** tautomerize to the 7,8-dihydroisoquinolin-1(2*H*)-ones **2a–e**. Thus, together with the oxidative, nonoxidative, and reductive photocyclizations already reported, this new photocyclization under basic conditions reveals a new aspect of the cyclization chemistry of enamides. The reaction described here represents a novel method for elaborating an isocarbostyril skeleton that possesses previously inaccessible hydrogenated sites. The presence of two allylic positions in the products should allow the introduction of diverse functional groups and consequently permit access to new dihydroisoquinolines, compounds which possess a wide spectrum of biological activity.[12,13]

Experimental Section

Starting Materials. Compounds **1a–e** were prepared by the reaction of the appropriate arenecarbonyl chloride with the imine obtained by the condensation of 4-methoxyacetophenone and benzylamine.[8b]

Irradiation. All the irradiations were performed through quartz in a Rayonet RPR-208 photoreactor fitted with eight RuI (λ = 253.7 nm) lamps. Methanolic solutions of the reactants were deareated by flushing them with Ar for 30 min. Deaeration and stirring of the solution were maintained during irradiation (2 h). Ar was freed of O_2 by passing it through a BTS catalyst. The gas was dried by passing it through P_2O_5, activated SiO_2, and KOH.

The solvent was evaporated from the reaction mixture in vacuo. The residual photoproduct was dissolved in CH_2Cl_2, and the solution was washed several times with water. The CH_2Cl_2 solution was dried ($MgSO_4$) and then concentrated in vacuo. The photoproducts **2a–e** were isolated by TLC on silica gel 60 HF-254 (EtOAc/hexane, 2:3).

Compounds **3a,b**[8b] **4a,b**,[8b] and **5**[5] were synthesized photochemically.

(10) Ninomiya, I.; Naito, T. *Heterocycles* **1981**, *15*, 1433.
(11) (a) Buckley, E.; Whittle, E. *Trans. Faraday Soc.* **1962**, *58*, 536. (b) Shaw, R.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1960**, 3210.
(12) Dyke, S. F. In *Rodd's Chemistry of Carbon Compounds*; Coffey, S., Ed.; Elsevier: New York, 1978; Vol. 4, Chapter 1.
(13) For example, see: *Annual Reports in Medicinal Chemistry*; Academic Press: New York, 1965–1981; Vols 1–16.