Synthesis, Photooxidation and Z ⇌ E Photoisomerization of Benzalpyrrolinones

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In contrast to oxodipyrromethenes and bilirubin, benzalpyrrolinones (H, *p*-OCH_3, *p*-Cl, *p*-$N(CH_3)_2$ and *o*-CH_3) and α-pyridalpyrrolinones appear not to undergo dye-sensitized photooxygenation. They do, however, undergo an unsensitized E ⇌ Z photoisomerization reminiscent of stilbene photoisomerization, and the photostationary state varies with substituent. Intramolecular H-bonding is implicated in the α-pyridalpyrrolinone isomerization. In each case, the Z isomers are the thermodynamically more stable ones, but the corresponding E isomers have been isolated and characterized following photoirradiation.

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The photochemistry of simple pyrrole compounds (1) especially their photooxidation, is of special interest in connection with bilirubin (**1**) photochemistry (2) as it relates to the phototherapy method for neonatal jaundice (3,4). One of the important photo-reactions of **1** in solution appears to involve (self-sensitized) formation of singlet oxygen [$^1O_2$] (5) which attacks the ene-amide carbon-carbon double bonds (at *a* and *c*) (5,6) and leads to imide (7) and pyrrole aldehyde products (8). This reactive site of **1** has been of interest to us, and we have explored reactions of $^1O_2$ there with **1** and extensively with model compounds (9). Of the latter, certain oxodipyrromethenes, *e.g.* **2**, were found to react with $^1O_2$ to produce imides and pyrrole aldehydes (diethylmaleimide and kryptopyrrole aldehyde from **2**) – presumably *vic* a dioxetane intermediate (9). However, the factors governing the reactions were not clear, and, indeed, were even complicated by other competing reactions involving (presumably) 1,4-addition of $^1O_2$ to the pyrrole ring of **2** (7) and of **1** (10). In order to focus more clearly on just the ene-amide reaction with $^1O_2$, model systems involving but one derivatized pyrrole ring were constructed and examined.

The essential ene-amide unit may be found in the monopyrrolic compounds **3** and **4**. These substances could be prepared from available materials: **3** from acid-catalyzed dehydration of the kryptopyrrole photo-product, 3,5-dimethyl-4-ethyl-5-hydroxy-3-pyrrolin-2-one (11); **4** from condensation of acetone with 3-pyrrolin-2-one (12). In contrast to **1** and **2**, expectedly, neither **3** nor **4** underwent self-sensitized photooxidation (500 W Quartz Iodine lamp), and both materials were recovered unchanged. Surprisingly, however, neither **3** nor **4** underwent a Rose Bengal-sensitized photooxidation or photooxygenation and were also recovered unchanged. It thus became clear that the ene-amide grouping alone was not necessarily responsible for the photo-oxygenative cleavages observed in the more highly conjugated systems (6,7,8). While these results obviously do not as such reveal the necessary criteria for *successful* reactions with $^1O_2$, they do provide important limiting information and also demonstrate that the imide products found in dye-sensitized photooxygenations of α-alkylated monopyrroles (1,11,13) do not arise from ene-amide intermediates (14). Other work (15) indicates that an ene-amide may undergo dye-sensitized photooxygenation, and while an unstable dioxetane may be isolated, the major products are α-hydroxy or α-alkoxy-ketones and not cleavage products. The reasons for the failure of **3** and **4** to react with $^1O_2$ are not clear; however, the fact that the more highly conjugated systems **1** and **2** do undergo the enamine-like reactive cleavage with $^1O_2$ suggests that extended conjugation renders the ene-amide more vulnerable to attack (16). To investigate this concept, we prepared a variety of more conjugated ene-amides with only one pyrrole-like ring: benzalpyrrolinones **5-9** and pyridalpyrrolinones **10** shown in Table I.

The crystalline pyrrolinone derivatives (**5-10**, all Z of Table I) were each prepared by base-catalyzed condensation of the appropriate aromatic aldehyde with 3,4-diethyl-3-pyrrolin-2-one (17). Benzalpyrrolinone (**5**-Z) failed to undergo a photooxidation reaction, either self-sensitized or Rose Bengal sensitized. With the thought that electron donors (resonance) would make the ene-amide carbon-carbon double bond more electron rich, hence more susceptible of attack by $^1O_2$ (18), **6** and **7** were treated

Table I

Spectroscopic Properties of Monocyclic Ene-Amides and Benzalpyrrolinones

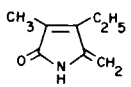
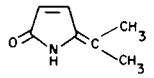
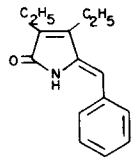
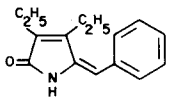
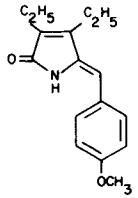
Compound	^{1}H - Nmr (Deuteriochloroform *vs* TMS, in ppm)	MS m/e (Relative Intensity)	Uv (λ, ϵ max, methanol)	Ir (Chloroform, cm^{-1})
 **3** Oil	1.14 (t, 3H, J = 7 Hz, CH_3) 1.89 (s, 3H, CH_3) 2.44 (q, 2H, J = 7 Hz, -CH_2-) 4.80 (d, 1H, J = 5 Hz, =CH) 4.86 (d, 1H, J = 5 Hz, =CH) 8.12 (br. s, 1H, NH)	137 (100%) [M] 122 (68%) 108 (46%) 94 (55%)	262 nm (8,800) 212 nm (4,900)	
 **4** M.p. 186-190° white crystals	2.00 (s, 3H, CH_3) 2.03 (s, 3H, CH_3) 6.12 (d, 1H, J = 6 Hz, =CH) 7.25 (d, H, J = 6 Hz, =CH)	123 (100%) [M] 108 (50%) 94 (30%)	298 nm (17,800)	3460 (NH) 3200 (NH-bonded) 1675 (C=O)
 **5-Z** M.p. 133-135° white needles	1.16 (t, 3H, J = 7.5 Hz, CH_3) 1.23 (t, 3H, J = 7.5 Hz, CH_3) 2.44 (q, 2H, J = 7.5 Hz, CH_2) 2.56 (q, 2H, J = 7.5 Hz, CH_2) 6.12 (s, 1H, =CH) 7.40 (m, 5H, arom. H) 7.88 (br. s, 1H, NH)	227 (100%) [M] 212 (76%) 198 (32%) 183 (24%) 167 (17%) 154 (12%) 141 (12%)	324 nm (27,000) *323 nm (27,200) *in chloroform	3500 (NH) 1690 (C=O) 1650 (C=C)
 **5-E** M.p. 138-140° white plates	0.7 (t, 3H, J = 8 Hz, CH_3) 1.10 (t, 3H, J = 8 Hz, CH_3) 2.20 (2q, 4H, J = 8 Hz, CH_2) 6.49 (s, 1H, =CH) 7.27 (m, 5H, arom. H)	227 (100%) [M] 212 (65%) 198 (25%) 183 (17%) 168 (13%) 153 (18%) 138 (14%) 128 (10%) 91 (21%)	287 nm (5,600)	3450 (NH) 1690 (C=O) 1640 (C=C)
 **6-Z** M.p. 144-146° white plates	1.17 (t, 3H, J = 7.5 Hz, CH_3) 1.20 (t, 3H, J = 7.5 Hz, CH_3) 2.47 (2q, 4H, J = 7.5 Hz, CH_2) 3.82 (s, 3H, OCH_3) 6.03 (s, 1H, =CH) 6.95 (d, 2H, J = 4.5 Hz, arom. H) 7.35 (d, 2H, J = 4.5 Hz, arom. H) 7.66 (br. s, 1H, NH)	257 (100%) [M] 242 (32%) 228 (14%) 141 (11%) 121 (14%)	339 nm (27,800)	3460 (NH) 1690 (C=O) 1610 (C=C) 1610 (C=C)

Table I (continued)

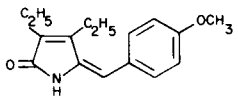
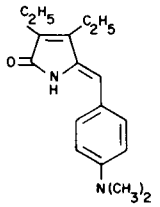
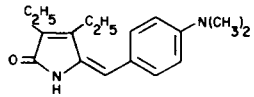
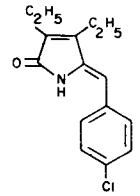
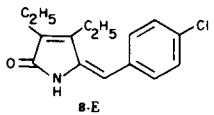
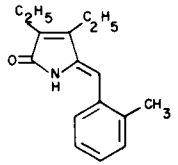
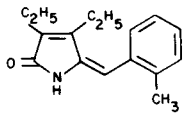
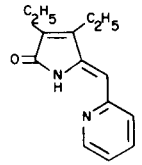
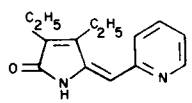
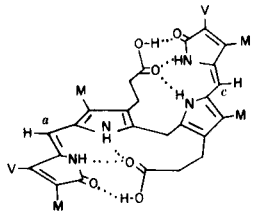
Compound	^{1}H - Nmr (Deuteriochloroform *vs* TMS, in ppm)	MS m/e (Relative Intensity)	Uv (λ, ε max, methanol)	Ir (Chloroform, cm^{-1})
 6-E M.p. 147-150° white plates	0.73 (t, 3H, J = 7.5 Hz, CH_3) 1.20 (t, 3H, J = 7.5 Hz, CH_3) 2.28 (2q, 4H, J = 7.5 Hz, CH_2) 3.80 (s, 3H, OCH_3) 6.44 (s, 1H, =CH) 6.85 (d, 2H, J = 9.0 Hz, arom. H) 7.23 (d, 2H, J = 9.0 Hz, arom. H) 7.60 (br. s, H, NH)	257 (100%) [M^+] 242 (28%) 228 (13%) 121 (11%)	331 nm (7,600)	3450 (NH) 1680 (C=O) 1608 (C=C)
 7-Z M.p. 167-170° yellow needles	1.13 (t, 3H, J = 7.5 Hz, CH_3) 1.21 (t, 3H, J = 7.5 Hz, CH_3) 2.50 (2q, 4H, J = 7.5 Hz, CH_2) 3.05 (s, 6H, NCH_3) 6.11 (s, 1H, =CH) 6.71 (d, 2H, J = 9 Hz, arom. H) 7.31 (d, 2H, J = 9 Hz, arom. H) 7.64 (br. s, 1H, NH)	271 (31%) [M+1] 270 (100%) [M] 255 (50%) 238 (20%) 226 (22%) 211 (17%) 196 (21%) 168 (27%) 159 (66%) 134 (44%) 118 (44%) 91 (39%)	390 nm (23,900)	3450 (NH) 1670 (C=O)
 7-E	0.77 (t, 3H, J = 8 Hz, CH_3) 1.16 (t, 3H, J = 8 Hz, CH_3) 2.40 (m, 4H) 3.05 (s, 6H, NCH_3) 6.45 (s, 1H, =CH) 7.6 (m, aromatic)	not isolated		
 8-Z M.p 165-167° white needles	1.15 (t, 3H, J = 7.5 Hz, CH_3) 1.22 (t, 3H, J = 7.5 Hz, CH_3) 2.45 (2q, 4H, J = 7.5 Hz, CH_2) 6.07 (s, 1H, =CH) 7.40 (m, 4H, arom. H) 8.23 (br. s, 1H, NH)	263 (46%) [^{37}M] 262 (38%) 261 (100%) [^{35}M] 246 (55%) 232 (30%) 211 (29%)	332 nm (18,300)	3450 (NH) 1690 (C=O) 1650 (C=C)
 8-E M.p. 159-160° white needles	0.73 (t, 3H, J = 7.5 Hz, CH_3) 1.21 (t, 3H, J = 7.5 Hz, CH_3) 2.20 (2q, 4H, J = 7.5 Hz, CH_2) 6.42 (s, 1H, =CH) 7.29 (s, 4H, arom. H) 7.76 (br. s, 1H, NH)	263 (35%) [^{37}M] 261 (100%) [^{35}M] 246 (44%) 232 (26%) 227 (26%) 226 (26%) 211 (22%) 197 (20%) 89 (20%)	301 nm (15,300)	3450 (NH) 1685 (C=O) 1600 (C=C)

Table I (continued)

Compound	^{1}H - Nmr (Deuteriochloroform *vs* TMS, in ppm)	MS m/e (Relative Intensity)	Uv (λ, ϵ max, methanol)	Ir (Chloroform, cm^{-1})
 **9-Z** M.p. 146-148° white prisms	1.15 (t, 3H, J = 7.5 Hz, CH_3) 1.25 (t, 3H, J = 7.5 Hz, CH_3) 2.35 (s, 3H, $=CCH_3$) 2.50 (2q, 4H, J = 7.5 Hz, CH_2) 6.16 (s, 1H, =CH) 7.23 (m, 4H, arom. H)	241 (100%) [M^+] 226 (54%) 212 (68%) 184 (22%)	322 nm (15,000)	3450 (NH) 1690 (C=O)
 **9-E** M.p. 153-154° white needles	0.67 (t, 3H, J = 7.5 Hz, CH_3) 1.10 (t, 3H, J = 7.5 Hz, CH_3) 2.17 (2q, 4H, J = 7.5 Hz, CH_2) 2.27 (s, 3H, $=C-CH_3$) 6.33 (s, 1H, =CH) 7.13 (d, 4H, arom. H) 7.76 (br. s, 1H, NH)	241 (100%) [M^+] 226 (50%) 212 (59%)	283 nm (18,800)	3500 (NH) 1700 (C=O) 1660 (C=C)
 **10-Z** M.p. 63-64° white prisms	1.13 (t, 3H, J = 8 Hz, CH_3) 1.20 (t, 3H, J = 8 Hz, CH_3) 2.45 (2q, 4H, J = 8 Hz, CH_2) 5.87 (s, 1H, =CH) 7.00 (m, 1H, pyr 5-H) 7.20 (m, 1H, pyr 3-H) 7.60 (m, 1H, pyr 4-H) 8.50 (d, 1H, J = 5 Hz, pyr 6-H)	228 (100%) [M^+] 213 (70%) 199 (40%) 185 (43%) 171 (43%)	342 nm (26,300)	3350 (NH) 1690 (C=O) 1649 (C=C)
 **10-E** M.p. 95-97° white prisms	0.73 (t, 3H, J = 8 Hz, CH_3) 1.07 (t, 3H, J = 8 Hz, CH_3) 2.40 (2q, 4H, J = 8 Hz, CH_3) 6.30 (s, 1H, =CH) 7.40 (m, 4H, arom.)	228 (93%) [M] 213 (100%) 199 (43%) 185 (40%) 171 (20%)	300 nm (15,200)	3481 (NH) 3700 (NH) 1700 (C=C) 1645 (C=C)

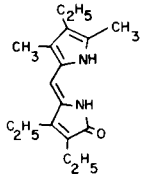


1

Bilirubin IXα

M = CH_3

V = $CH{-}CH_2$



2

similarly but also resisted photooxidation. In fact all of our derivatives **5-10** failed to undergo photooxidation or attack by $^1O_2$. Obviously, extended conjugation alone is not sufficient to explain the differing reactivities of **1** and **2** and **3-10**. The success or failure of the $^1O_2$ reaction with ene-amides, may, as Foote suggests for enamines (19), be linked to the ease of a prior one-electron oxidation step of the system.

Although we could not observe a photooxidation reaction of **5-10**, we discovered that a facile *cis-trans* or E-Z photoisomerization took place with **5-9** during attempted Rose Bengal sensitized photooxidation with broad visible light irradiation. More conveniently, the photoisomerization could be studied in the absence of Rose Bengal and oxygen using a high pressure Hg lamp. Moreover, the less thermodynamically stable E isomers of **5, 6, 8,** and **9** could be isolated, characterized (Table I) and their photochemical isomerizations or thermal reversions back to Z studied. The E isomer of **7** was too labile to isolate. The Z ⇌ E photochemical isomerization is similar in form to the stilbene isomerization (20) and has been reported recently by Falk *et al.*, (21) for other benzalpyrrolinones. α-Pyridalpyrrolinone **10**-Z presented the interesting possibility for intramolecular N-H···N bonding, and indeed **10**-Z would not undergo photoisomerization to **10**-E in deuteriochloroform, acetone-d_6 or THF. However, in the more strongly H-bonding solvents deuteriomethanol, DMSO-d_6 and protic or aprotic solvents with added trifluoroacetic acid, photoisomerization could be observed, and **10**-E could be isolated, characterized and studied.

The isomerizations from Z → E or E → Z were followed by nmr, or by uv at very low concentrations, $10^{-4}M$ in methanol (Table II). The methene hydrogen at the bridging carbon has a very different chemical shift in the Z and E isomers with the latter always at lower field, *e.g.* **5**-Z (6.12 δ) and **5**-E (6.49 δ). Therefore, we could study the rates and determine photostationary states by observing and integrating those two signals. The nmr data are also consistent with the structural assignments designated: the methyl group of the pyrrolinone C-4 ethyl is strongly shielded by the aromatic ring in the E configuration. Those methyl hydrogens of the E isomers sit over the face of the aromatic ring but are much farther away in the Z-isomers. The observation that the more sterically crowded (E) isomer is also the less thermodynamically stable toward thermal isomerization is also consistent with the configurational assignments. All of the E isomers studied thermally revert to the Z form upon heating at their melting points (21).

Table II

Photostationary States in the Z ⇌ E Benzalpyrrolinone Direct Irradiation

Solvent Concentration	Data	Phenyl Substituent				
		H (**5**)	*p*-OCH_3 (**6**)	*p*-$N(CH_3)_2$ (**7**)	*p*-Cl (**8**)	*o*-CH_3 (**9**)
Tetrahydrofuran	%E	39	33	42	41	46
7.7×10^{-2} *M* (Z)	%Z	61	67	58	59	54
	(a) k(min^{-1}) x 10^2	10.0	12.0	3.8	11.0	13.5
Tetrahydrofuran	%E	38	32		41	48
7.7×10^{-2} *M* (E)	%Z	62	68		59	52
	(a) k(min^{-1}) x 10^2	15.0	13.0		16.0	16.0
Acetone	%E	47	43	44	55	51
4.6×10^{-2} *M* (Z)	%Z	53	57	56	45	59
	(a) k(min^{-1}) x 10^2	3.4	8.2	11.0	6.0	9.1
Methanol-O-d(Z)	concentration (*M*) x 10^{-2}	7.7	2.6	1.2	1.4	2.9
	%E	47	44	41	49	59
	%Z	53	56	59	51	41
	(a) k(min^{-1}) x 10^2	4.8	12.5	6.0	8.5	16.0
Methanol	%E	51	48	44	58	67
4.2×10^{-4} *M* (Z)	%Z	49	52	56	42	33

(a) k Values are the initial first order rate constants for the photoisomerization Z → E.

Table III

Photostationary States in the Z ⇌ E α-Pyridalpyrrolinone (**10**) Direct Irradiation

Solvent (Concentration **10**-Z)	% E	Data % Z	k(min^{-1})
Deuteriochloroform	0	100	
THF	0	100	
DMSO-d_6	10	90	
Deuterioethanol/5.4 x 10^{-4} *M* trifluoroacetic acid (7.3 x 10^{-2} *M*)	13	87	
Deuterioethanol/10^{-1} *M* trifluoroacetic acid (7.3 x 10^{-2} *M*)	17	83	
Deuteriomethanol (8.0 x 10^{-2} *M* **10**-Z)	18	82	2.2 x 10^{-2}
Deuteriomethanol (8.0 x 10^{-2} *M* **10**-E)	20	80	9.4 x 10^{-2}
Trifluoroacetic acid (7.0 x 10^{-2} *M* **10**-Z)	29	71	5.8 x 10^{-2}

The photoisomerization studies are summarized in Tables II and III. It may be noted (Table II) that the photostationary states of **5-9** are not very different and are close to 50:50, especially in solvents with higher dielectric constants (acetone and methanol). Furthermore, there is only a small effect of substrate conformation on the photoequilibrium in methanol. The data of Table III illustrate the importance of intramolecular H-bonding in the photoisomerization of α-pyridalpyrrolinone **10**-Z. In the absence of a solvent which can effectively disrupt internal H-bonds, **10**-Z does not isomerize to **10**-E (in deuteriochloroform and THF); whereas, especially with added trifluoroacetic acid, that H-bonding is weakened or broken competitively, and **10**-Z behaves in a way similar to benzal pyrrolinones **5-9**.

In summary, the resistance of **3-10** toward photooxidation or reaction with $^1O_2$ suggests that simple $^1O_2$ addition to bilirubin at the ene-amide bonds may not actually be implicated as such in bilirubin photodegradation, although the products are consistent with that mechanism. Furthermore, the observations that Z ⇌ E isomerization of the ene-amide carbon-carbon double bonds of **5-10** can occur may provide an understanding for the recognized excretion of unconjugated bilirubin in the bile of jaundiced infants or Gunn rats undergoing light treatment (22). For a change in configuration in bilirubin from Z → E at its ene-amide carbon-carbon double bonds would necessarily expose its polar parts and render it more water soluble (hence more excretable into the bile) than form **1**. Although the type of H-bonding exhibited in bilirubin (**1**) is not quite like that of **10**-Z, the photoisomerization data on the latter nonetheless suggest that **1** may not undergo a facile Z → E isomerization at the end rings unless the intramolecular H-bonds can be broken by solvent influence. Therefore the local environment of **1** may be crucial to a successful Z → E photochemical isomerization followed by excretion.

EXPERIMENTAL

General

All melting points were determined on a Thomas-Hoover Unimelt capillary apparatus and are uncorrected, as are the boiling points. All solvents used were reagent grade unless otherwise specified. Infrared spectra (ir) were run in chloroform or carbon tetrachloride on a Beckman IR-8 spectrophotometer. Nmr spectra were measured in deuteriochloroform or deuteriomethanol on a Perkin-Elmer R-24B or Jeol 4H-100 spectrometer. Chemical shifts are reported in parts per million (δ) downfield from TMS as an internal standard with multiplicities: s = singlet, d = doublet, br = broad and m = multiplet. Mass spectra were determined on a JEOL JMS-07 instrument at 12 ev or 70 ev. Uv spectra were recorded on a Cary 14 spectrophotometer. All liquid chromatography utilized silica gel 0.05-0.2 mm (M. Woelm, Eschwege) for column chromatography and silica gel F (M. Woelm, Eschwege) for analytical and preparative thin layer chromatography (tlc). Preparative photochemistry was carried out in a water-cooled pyrex immersion well apparatus (with circulating oxygen for photooxygenation experiments) using a Sylvania 500 Q/CL 500-W tungsten-halogen lamp. Kinetic photoisomerization studies were carried out in quartz nmr tubes using a Hanovia 100 w, 1.2 amp high pressure mercury lamp, model SH. The methanol and acetone used in this work were Baker Analyzed anhydrous reagents, the tetrahydrofuran was Matheson distilled freshly from lithium aluminum hydride, and the deuteriated nmr solvents were obtained from E. Merck.

Benzalpyrrolinones - General Procedure.

In a typical experiment 1.66 g. (0.0119 mmole) of 3,4-diethyl-3-pyrrolin-2-one (**17**) and one mole equivalent of aromatic aldehyde were dissolved in 21 ml. of methanol and heated to reflux while 40 ml. of 4 *M* aqueous sodium hydroxide were added dropwise during 20 minutes. After complete addition of the sodium hydroxide, some solid typically came out of solution. The reaction was heated for 1 hour and quenched by the addition of ice. The solid was removed by filtration and recrystallized from pyridine water. The following benzalpyrrolinones were prepared. Their spectroscopic properties are shown in Table I.

Z-3,4-Diethyl-5-(phenylmethylidene)-3-pyrrolin-2-one (**5**).

This compound was obtained in a yield of 79%, white needles, m.p. 133-135°, (E isomer, 138-140°).

Anal. Calcd. for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.22; H, 7.61; N, 6.55.

Z-3,4-Diethyl-5-(*p*-methoxyphenylmethylidene)-3-pyrrolin-2-one (**6**).

This compound was obtained in a yield of 69%, white plates, m.p. 144-146°, (E-isomer 147-150°).

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.75; H, 7.59; N, 5.32.

Z-3,4-Diethyl-5-(*p*-dimethylaminophenylmethylidene)-3-pyrrolin-2-one (**7**).

This compound was obtained in a yield of 79%, thick, yellow

needles, m.p. 167-170°).

Anal. Calcd. for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36. Found: C, 75.76; H, 8.25; N, 10.55.

Z-3,4-Diethyl-5-(*p*-chlorophenylmethylidene)-3-pyrrolin-2-one (**8**).

This compound was obtained in a yield of 68%, white needles, m.p. 165-167°, (E-isomer 159-160° needles).

Anal. Calcd. for $C_{15}H_{16}ClNO$: C, 68.83; H, 6.16; N, 5.35. Found: C, 68.66; H, 6.13; N, 5.26.

Z-3,4-Diethyl-5-(*p*-tolylmethylidene)-3-pyrrolin-2-one (**9**).

This compound was obtained in a yield of 85%, white plates, m.p. 146-148°, (E-isomer 153-154° white needles).

Anal. Calcd. for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.81; H, 7.84; N, 5.88.

Z(syn)-3,4-Diethyl-5-(2-pyridylmethylidene)-3-pyrrolin-2-one (**10**).

This compound was obtained in a yield of 51%, cream colored prisms, m.p. 63-64°, (E-isomer 95-97° white plates).

Anal. Calcd. for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.66; H, 7.23; N, 12.54.

Attempted Photooxygenation of Benzalpyrrolinones - General Procedure.

To a large (500 ml.) pyrex immersion well photolysis unit with provisions for circulating oxygen was added 250 ml. of an approximately 3.5 x 10^{-3} *M* methanolic solution of Z-benzalpyrrolinone (**5**, **6**, **7**, **8** or **9** or **10**) containing 5 mg. of Rose Bengal. With oxygen circulation, the solution was irradiated with a 500 W Tungsten-halogen lamp at 100 V for 4.25 hours during which no oxygen uptake was observed and the starting material (Z + E mixture) could be recovered quantitatively following evaporation of solvent and crystallization or column chromatography. The percent E isomer found (by nmr) under these reaction conditions were: **5**, 39%; **6**, 21%; **7**, 0.2%; **8**, 8%; **9**, 5% and **10**, 0%.

Photochemical Isomerization of Benzalpyrrolinones in an Nmr Tube.

Direct photochemical isomerization of the Z-benzalpyrrolinones (**5**, **6**, **7**, **8**, **9** or **10**) to their photostationary state Z + E mixture was accomplished in quartz nmr tubes and followed by nmr until the photostationary state was achieved. In a typical reaction, enough benzalpyrrolinone was dissolved in 0.6 ml. of solvent (tetrahydrofuran, methanol, methanol-O-d, acetone or d_6-acetone) to achieve a concentration of *ca.* 0.1 *M*. Solutions were irradiated with a 100 W high pressure Hg lamp cooled in a quartz water jacket with the sample solution held at a distance of 1.0 cm from the lamp. The disappearance of the Z isomer and the formation of the E isomer was followed by nmr, integrating the =CH signals near 6.0 δ (Z) and 6.5 δ (E). The results are summarized in Table II.

Preparation of E-Benzalpyrrolinones - General.

To a small water-jacketed quartz immersion well photolysis unit was added 120 ml. of a 5 m*M* methanolic solution of benzalpyrrolinone. The solution was irradiated for 2 hours 10 minutes with a Hanovia 100 W Hg lamp. The solution was evaporated at reduced pressure, and the residue was separated by preparative tlc to yield the E-isomer and recovered Z-isomer. The results are tabulated as follow:

Starting Z-isomer	Isolated Yield, E-isomer	M.p. E-isomer	Hours Irradiated
5	52%	138-140°	2.2
6	30%	147-150°	2.5
8	40%	159-160° white needles	2
9	44%	153-154° white needles	1.2
10	16%	95-97° white needles	3.5 with added trifluoroacetic acid

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