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Photochemical Reactivity of Keto Imino Ethers. VI.[1] Type I Rearrangement and (2 + 2) Photocycloaddition to the Carbon–Nitrogen Double Bond of 2-Oxazolin-4-ones

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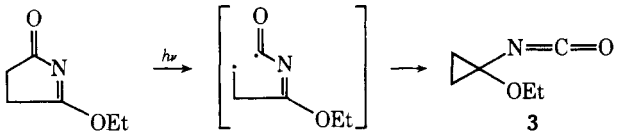
Abstract: The Norrish type I cleavage and (2 + 2) photocycloaddition reactions of five oxazolinones, 2-phenyl- (**7a**), 2-ethoxy- (**7b**), 2-*p*-methoxyphenyl- (**7c**), 2-*m*-methoxyphenyl- (**7d**), and 2-(*m*-trifluoromethylphenyl)-2-oxazolin-4-one (**7e**), are described. The Norrish type I cleavage yields oxiryl isocyanates **10a, 10b,** and **10e,** and the (2 + 2) photocycloaddition of the oxazolinones to 1,1-dimethoxyethene and furan yields the azabicyclic products **11a, 11c, 11d,** and **11e** and the azatricyclic products **14a, 14c,** and **14d,** respectively. The photoreactivity is structure dependent: **7b** only α-cleaves; **7c** and **7d** only cycloadd to olefins; and **7a** and **7e** α-cleave and cycloadd to olefins. Reactivity is discussed in terms of the configuration of the reactive excited state. Type I cleavage is thought to occur from an n,π^* state and (2 + 2) cycloaddition, from a π,π^* state.

We have recently described the Norrish type I cleavage[2] of 2-ethoxypyrrolin-5-one (**1**) and two 6-alkoxy-4,5-dihydro-2(3*H*)-pyridones (**2**).[3] Irradiation of **1,** for example, in aprotic solvent resulted in rearrangement via an initial type I cleavage to ethoxycyclopropyl isocyanate (**3**) in high isolated yield (78%) and high quantum yield (0.31). (2 + 2) photocycloaddition of olefins such as 1,1-dimethoxyethene to the carbon–nitrogen or carbon–oxygen double bonds of **1** or **2** was not competitive with type I cleavage.



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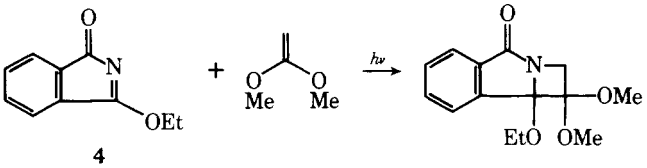
We have subsequently reported on the photoreactivity of 2-ethoxyisoindolone (**4**). The keto imino ether **4** was prepared with the idea of blocking the Norrish type I cleavage by strengthening the carbon–carbon bond α to the carbonyl with the anticipation of then observing the novel (2 + 2) photocycloaddition of olefins to the carbon–nitrogen double bond. Indeed this result was observed and irradiation of **4** in the presence of 1,1-dimethoxyethene resulted in regiospecific (2 + 2) cycloaddition.[4] In addition to strengthening the carbon–carbon single bond α to the carbonyl, the benzo substituent also changed the reactive chromophore since it is conjugated with the keto imino ether. This was evident from a dramatic change in the uv absorption spectrum of **4** compared with the uv spectra of **1** and **2**. Keto imino ethers **1** and **2** have n–π^* bands at 265 nm (ϵ 45) and 275 (60), respectively, with strong end absorption for the π–π^* bands; whereas, **4** has no resolved n–π^* band with π–π^* bands at 216 nm (ϵ 38000), 288 (1900), and 298 (2100).



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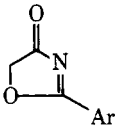
The photochemical reactivity of a series of 2-aryl-2-oxazolin-4-ones (**5**) was then examined with the idea of determining the effect of the additional conjugation of the keto imino ether chromophore with the benzo group of **4** on reactivity in (2 + 2) cycloaddition. The oxazolinones **5** are keto imino ethers which have extended conjugation with an aryl group and which are structurally capable of Norrish type I cleavage.



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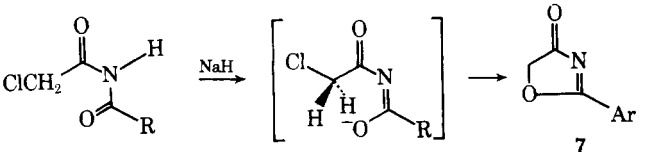
Results

Synthesis of Reactants. The 2-substituted 2-oxazolin-4-ones were synthesized using the procedure briefly described by Gordon for the preparation of 2-phenyl-2-oxazolin-4-one (**7a**).[5] The method utilizes an intramolecular O-alkylation reaction of an imide ambident anion. Treatment of *N*-(chloroacetyl)benzamide (**6a**) with slightly less than 1 equiv of sodium hydride in glyme solvent gave **7a** in 76% yield. Similarly 2-ethoxy-2-oxazolin-4-one (**7b**), 2-(*p*-methoxyphenyl)-2-oxazolin-4-one (**7c**), and 2-(*m*-methoxyphenyl)-2-oxazo-

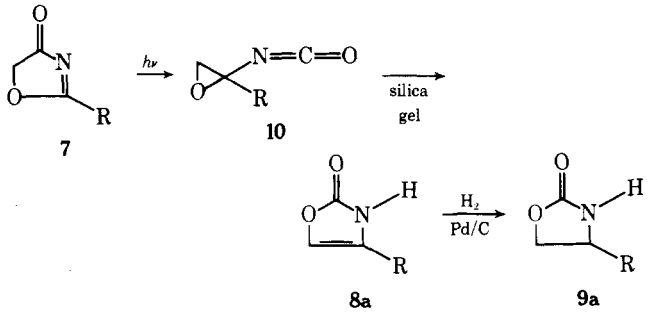


6 7

a, R = phenyl
b, R = ethoxy
c, R = *p*-methoxyphenyl
d, R = *m*-methoxyphenyl
e, R = *m*-trifluoromethylphenyl

lin-4-one (**7d**) were prepared in 68, 77, and 77% yields, respectively, from the corresponding imides **6b, 6c,** and **6d**. 2-(*m*-Trifluoromethylphenyl)-2-oxazolin-4-one (**7e**) was prepared in 48% yield by treatment of *N*-(chloroacetyl)-*m*-trifluoromethylbenzamide with slightly less than 1 equiv of potassium *tert*-butoxide in *N,N*-dimethylformamide solvent. The unknown oxazolinones were characterized by the appearance of intense carbon–oxygen and carbon–nitrogen double bond stretching bands in the regions 5.6–5.7 and 6.35–6.67 μ, respectively, in the infrared spectra and a methylene singlet in the region δ 4.6–4.8 ppm in the NMR spectra as well as the other spectral data reported in the Experimental Section.

Photochemical Reactions. Irradiation of 2-phenyl-2-oxazolin-4-one (**7a**) in glyme solvent with a 450-W mercury lamp equipped with a Corex filter followed by silica gel column chromatography resulted in the formation of 4-phenyl-4-oxazolin-2-one (**8a**) in 45% isolated yield. The rearranged oxazolinone was identified by the spectroscopic data (Experimental Section) and by catalytic hydrogenation to yield 4-phenyl-2-oxazolidone (**9a**). The physical properties of the oxazolidone **9a** were identical with those of an authentic sample.[6] When **7a** was similarly irradiated in glyme or benzene solvent followed by solvent evaporation and molecular distillation, an unstable, liquid product was isolated and identified as 2-phenyl-2-oxiryl isocyanate (**10a**). Photoproduct **10a** showed a characteristic isocyanate stretching band at 4.44 μ in the infrared spectrum. Treatment of the isocyanate with silica gel resulted in rearrangement to the previously isolated 4-phenyl-4-oxazolin-2-one (**8a**). Similarly

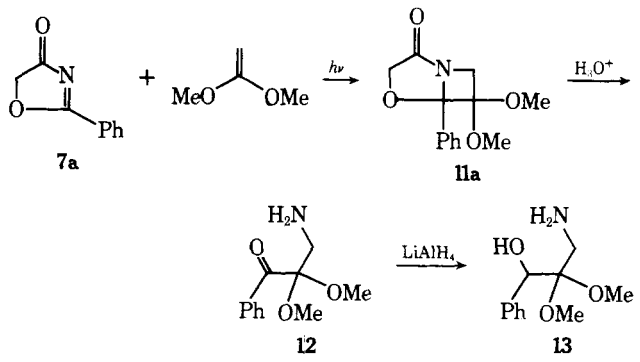


7 10 8a 9a

a, R = phenyl
b, R = ethoxy
e, R = *m*-trifluoromethylphenyl

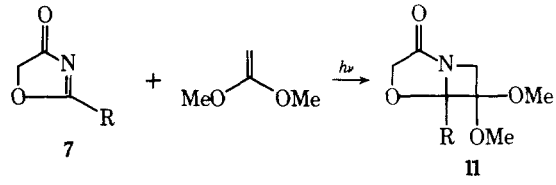
2-ethoxy-2-oxazolin-4-one (**7b**) and 2-(*m*-trifluoromethylphenyl)-2-oxazolin-4-one (**7e**) rearranged upon irradiation to the corresponding isocyanates, 2-ethoxy-2-oxiryl isocyanate (**10b**) and 2-(*m*-trifluoromethylphenyl)-2-oxiryl isocyanate (**10e**). Neither oxiryl isocyanate, **10b** nor **10e,** rearranged to oxazolinones analagous to **8a** with silica gel chromatography, although **10b** was unstable to silica gel. The methoxy-substituted oxazolinones **7c** and **7d** did not rearrange to oxiryl isocyanates when irradiated under identical conditions as indicated by analysis of the irradiation solutions with infrared spectroscopy.

Irradiation with Corex filtered ultraviolet light of 2-phenyl-2-oxazolin-4-one (**7a**) in the presence of 20 equiv of 1,1-dimethoxyethene in glyme solvent resulted in the formation of a cycloadduct, 6,6-dimethoxy-5-phenyl-4-oxa-1-azabicyclo[3.2.0]heptan-2-one (**11a**), in 65% isolated yield and no oxiryl isocyanate **10a**. The regiochemistry was suggested by the chemical shift of the azetidine methylene protons at δ 3.74 and 3.82 ppm[7] and was further substantiated by chemical degradation. Mild acid catalyzed hydrolysis yielded 3-amino-2,2-dimethoxy-1-phenylpropanone (**12;** 94%) which was reduced with lithium aluminum hydride to



7a 11a 12 13

3-amino-2,2-dimethoxy-1-phenylpropanol (**13;** 77%). The NMR spectrum of **13** indicated that the methylene protons were not strongly coupled with the methine proton consistent with the regiochemistry assigned to the cycloadduct **11a**. The amino propanol from degradation of the cycloadduct of opposite regiochemistry would have had the methylene and methine protons vicinal and strongly coupled. Irradiation of oxazolinones **7c, 7d,** and **7e** in the presence of an excess of 1,1-dimethoxyethene in glyme solvent yielded structurally analogous (2 + 2) cycloadducts **11c, 11d,** and

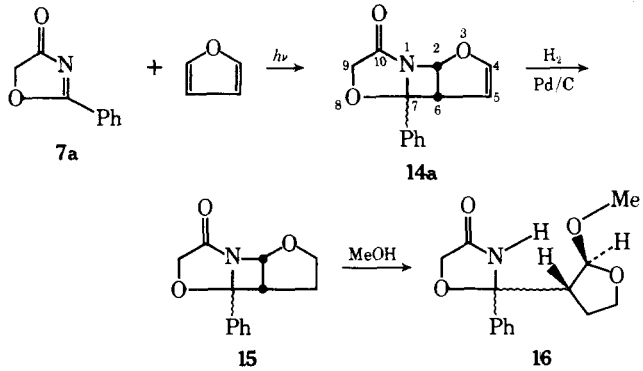


7 11

c, R = *p*-methoxyphenyl
d, R = *m*-methoxyphenyl
e, R = *m*-trifluoromethylphenyl

11e in 69, 75, and 59% yields, respectively. Only 2-ethoxy-2-oxazolin-4-one (**7b**) was unreactive with 1,1-dimethoxyethene.

When oxazolinone **7a** was irradiated in the presence of approximately 40 equiv of furan in glyme solvent, a (2 + 2) photocycloadduct **14a** was isolated in 45% yield. No oxiryl isocyanate (**10a**) was formed under these conditions. The cycloadduct was thermally unstable with respect to reversion to starting materials, and vacuum sublimation at 100° yielded only recovered **7a**. The structure, regiochemistry, and stereochemistry were established by the spectroscopic data and the spectroscopic data of the degradation products. Catalytic hydrogenation of **14a** yielded the tricyclic product **15** (82%), and reaction of **15** with methanol yielded the azetidine ring cleavage product **16** (94%). The main

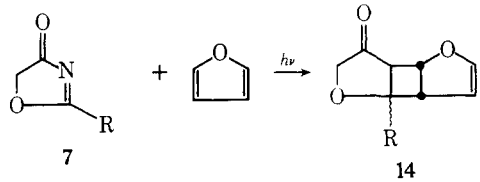


7a 14a 15 16

spectroscopic evidence for the regiochemistry of the cycloaddition is the chemical shifts of the bridge head protons of **14a** and **15**. The photon at ring position 2 adsorbs significantly further downfield than the proton at ring position 6. The proton assignments in the NMR spectra were made on

the basis of the distinct splitting patterns observed. The stereochemistry of the ring junctures of **14a** and **15** was made on the basis of ring strain and the magnitude of the vicinal coupling constant (5–6.5 Hz).[8] Structure **16** was assigned to the product of methanol addition rather than the product of cleavage of the 1,7-bond on the basis of the carbonyl stretching band at δ 5.84 μ in the infrared spectrum characteristic of a δ-lactam. The trans stereochemistry of the methine protons of **16** is consistent with a vicinal coupling constant of 2 Hz and with backside attack by methanol at carbon 2 of **15** with inversion of configuration.

Irradiation of oxazolinones **7c** and **7d** in the presence of a large excess of furan in glyme solvent yielded structurally analogous (2 + 2) cycloadducts **14c** and **14d** in 24 and 43% yields, respectively. The structural assignments were made on the basis of the similarity of the spectra with the spectra of **14a**. The photoreactivity of **7e** with furan was not examined, and **7b** did not form a photocycloadduct when irradiated in the presence of furan.



7 14

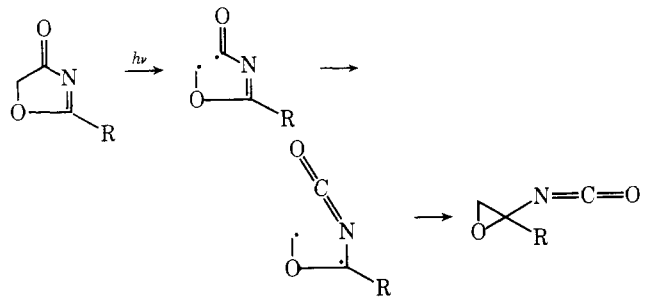
c, R = *p*-methoxyphenyl

d, R = *m*-methoxyphenyl

The oxazolinones (**7a, 7b, 7c, 7d,** and **7e**) did not give (2 + 2) photocycloadducts with other olefins tried including methyl vinyl ether, cyclohexene, *cis*-2-butene, *trans*-2-butene, and styrene. These olefins, however, were quenchers of the rearrangement of **7a, 7b,** and **7e,** and *cis*-2-butene was isomerized to *trans*-2-butene when irradiated in the presence of **7a**.

Discussion

Like the rearrangements of 2-ethoxypyrrolin-5-one (**1**) and 6-alkoxy-4,5-dihydro-2(3*H*)-pyridone (**2**), the photorearrangements of **7a, 7b,** and **7e** most likely occur by the Norrish type I mechanism. Initial homolytic cleavage α to the carbonyl would give a 1,5-diradical which with subsequent rearrangement to a 1,3-diradical and ring closure would yield the observed oxiryl isocyanates **10a, 10b,** and **10c,** respectively.



The Norrish type I reaction is a common photochemical reaction of saturated ketones. Cleavage of medium ring alkanones gives enals and/or ketenes via intermediate biradicals.[9] For cyclic α,β-unsaturated ketones, photocyclodimerization is generally so competitive that α-cleavage is not observed.[10] 2-Cyclopentenones substituted in the 5 position, however, have been shown to preferentially α-cleave in dilute solution giving cyclopropyl ketenes among other products.[11]

All of the 2-aryloxazolinones undergo (2 + 2) photocycloaddition of olefins to the carbon–nitrogen double bond. The regiochemistry parallels the regiochemistry observed in the cycloadditions to 3-ethoxyisoindolone (**4**). However, strangely the oxazolinones **7a, 7c, 7d,** and **7e** are only reactive with strongly electron rich olefins.

Table I. Uv Data

Compd	Solvent	Uv λ_{max}, nm	ϵ
1	Absolute ethanol	265	45
1	Cyclohexane	273	55
2	Cyclohexane	275	60
4	Cyclohexane	216	38000
		288	1900
		298	2100
7a	95% ethanol	263	20800
7a	Glyme	260	20700
7b	Methylcyclohexane	208	13400
		258	55
7c	95% ethanol	223	14000
		300	32000
7d	95% ethanol	220	18730
		268	18800
		318	3700
7e	Glyme	256	16000
		320 (shoulder)	100

The photochemical reactivity of the oxazolines was investigated as a possible probe for the structural requirements necessary for (2 + 2) photocycloaddition to the carbon–nitrogen double bond. A correlation between structure and reactivity is probably best seen in terms of a parallel relationship between structure and uv absorption (emission was not observed for the oxazolinones). The molecules bearing keto imino ether functional groups which α-cleave but do not cycloadd to olefins are **1, 2,** and **7b**. They all have n–π^* bands as the longest wavelength transitions in their uv spectra (see Table I). The molecules studied which cycloadd to olefins but do not α-cleave are **4, 7c,** and **7d**. These show no resolved n–π^* transitions. Of the two molecules, **7a** and **7e**, which undergo both modes of photochemical reactivity, **7e** has what appears to be a slightly resolved n–π^* band as a shoulder on the intense π–π^* transition.

In comparing the uv spectra of **7a, 7c, 7d,** and **7e**, we are examining the effect of electron-donating and electron-withdrawing substituents. The electron-donating methoxy substituent lowers the energy of the π–π^* transition relative to the n–π^* transition, and the electron-withdrawing trifluoromethyl substituent appears to lower the energy of the n–π^* transition relative to the π–π^* transition. A similar effect of substituents on the relative energies of n,π^* and π,π^* states of aromatic ketones has been observed and correlated with reactivity in photoreduction and Norrish type II cleavage reactions.[12-15]

A conclusion which might be drawn from the correlation of keto imino ether reactivity with uv absorption is that n,π^* character is required of the reactive excited state for Norrish type I cleavage and π,π^* character is required of the reactive excited state for (2 + 2) photocycloaddition. Since the multiplicity of the reactive excited states of **7a–e** has not yet been determined, the validity of a correlation with uv absorption may be questionable. However, the established reactive excited states of **1, 2,** and **4** are consistent with the correlation. The pyrrolinone **1** and dihydropyridone **2** α-cleave via the n,π^* singlet state. 3-Ethoxyisoindolone (**4**) cycloadds to olefins from a triplet state[4] probably of the π,π^* configuration.[16]

It is interesting to note that the correlation of reactivity with state configuration also suggests that the lowest energy triplet states of **1** and **2** (probably also **7b**) are of n,π^* configuration. Keto imino ethers **1** and **2** intersystem cross with efficiencies of 0.2 and 0.1, respectively.[3] The triplet lifetimes of **1** and **2** are the same order of magnitude as the triplet lifetime of **4** ($\tau = 3 \times 10^{-8}$ sec for **1** and $\tau = 1 \times$

10^{-8} sec for **4** in the presence of 0.125 *M* tetramethylethylene),[3,4] and yet **1** and **2** do not cycloadd even to electron rich olefins such as 1,1-dimethoxyethene.

Reactivity of carbocyclic systems as a function of excited state configuration parallels the reactivity of keto imino ethers. Five- and six-membered cycloalkanones undergo Norrish type I cleavage from the n,π^* singlet state as well as from a triplet state (probably also of n,π^* configuration).[9] Wagner and Bucheck have proposed that (2 + 2) photocycloaddition of olefins to excited 2-cyclopentenones and 2-cyclohexenones occurs from the π,π^* triplet state.[17]

The low reactivity of **7a, 7c, 7d,** and **7e** with olefins (other than strongly electron rich olefins) in (2 + 2) photocycloadditions compared with reactivity of **4** may result from vibronic coupling of n,π^* and π,π^* states. Whenever n,π^* and π,π^* states are close in energy, they can mix vibronically.[18] Mixing n,π^* character with the π,π^* state may then lower reactivity of the π,π^* state in photocycloaddition.

In conclusion we have shown that the additional conjugation of an aryl or benzo group with the keto imino ether chromophore is important for reactivity in (2 + 2) photocycloaddition to the carbon–nitrogen double bond in competition with Norrish type I cleavage. The additional conjugation appears to lower the energy of the π,π^* state, the reactive state in (2 + 2) cycloaddition.

Experimental Section

Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded with Perkin-Elmer Models 337 and 710A spectrophotometers. NMR spectra were recorded with Varian Associates A-60-A and HA 100 and JEOLCO PS 100 spectrometers, and chemical shifts are reported in parts per million on the δ scale from internal tetramethylsilane. Uv spectra were obtained with a Cary Model 17 spectrophotometer and mass spectra with a Varian Mat CH-5 mass spectrometer at 70 eV. Aerograph Models 1700 and 200 were used for analytical and preparative gas liquid chromatography. All immersion well irradiations were conducted with a 450-W Hanovia medium-pressure mercury arc lamp. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

Chemicals. 1,2-Dimethoxyethane (glyme) was purchased from Ansul Co. and was dried by distillation from lithium aluminum hydride through a 100-cm Todd column packed with glass helices. Benzene (reagent grade) was dried by distillation from phosphorus pentoxide through the same column. *N,N*-Dimethylformamide was dried with 4A molecular sieves. Styrene was distilled prior to use, and 1,1-dimethoxyethene was prepared by the method reported by Corey and co-workers, bp 85–86°, 630 mm (lit.[19] bp 88–91°). *m*-Trifluoromethylbenzamide was prepared according to the method described by Buu-Hoi and co-workers [mp 124–125° (lit.[20] mp 123°)].

***N*-(Chloroacetyl)benzamide (6a).** *N*-(Chloroacetyl)benzamide was prepared according to the procedure described by Polya and Spotsword.[21] The product was obtained in 76% yield with mp 159–159.5° (lit. mp 157°) and gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 4.77 (2 H, s), 7.75 (5 H, m), and 9.0 ppm (1 H, broad); ir ($CHCl_3$) 2.96, 5.78, and 5.87 μ; mass spectrum *m/e* 197 (M^+, 7), 162 (22), 105 (base), 77 (87), and 51 (38).

Ethyl *N*-(Chloroacetyl)carbamate (6b). The method for preparing *N*-(chloroacetyl)benzamide was used with 17.8 g (0.20 mol) of ethyl carbamate and 22.6 g (0.20 mol) of chloroacetyl chloride. The reaction mixture was heated at 110° for 1 hr. The solid was recrystallized from chloroform, yielding 27.6 g (84%) of a white solid with mp 128.5–129°. The following spectral data were obtained: NMR ($CDCl_3$, 60 MHz) δ 1.34 (3 H, t, J = 7 Hz), 4.31 (2 H, q, J = 7 Hz), 4.54 (2 H, s), and 8.1 ppm (1 H, broad); ir ($CHCl_3$) 2.95, 5.57, 5.68, 5.79, and 6.72 μ; mass spectrum *m/e* 165 (M^+, 7), 137 (45), 77 (49), 49 (34), 44 (71), 29 (base), and 27 (31).

Anal. Calcd for $C_5H_8O_3NCl$: C, 36.41; H, 4.85; N, 8.50. Found: C, 36.26; H, 4.87; N, 8.45.

***N*-(Chloroacetyl)-*p*-methoxybenzamide (6c).** The procedure for preparing *N*-(chloroacetyl)benzamide was used with 21 g (0.14 mol) of *p*-methoxybenzamide and 45 g (0.40 mol) of chloroacetyl chloride. The reaction mixture was heated at 110° for 30 min, and the solid was recrystallized from benzene, yielding 21 g (77%) of a white crystalline solid with mp 174–175°. The product was identified as *N*-(chloroacetyl)-*p*-methoxybenzamide (**6c**) from the following spectral data: NMR (acetone-d_6, 60 MHz) δ 3.93 (3 H, s), 4.83 (2 H, s), 7.0–7.3, and 8.0–8.3 ppm (AA′BB′); ir ($CHCl_3$) 2.97, 5.80, 5.90, and 6.24 μ; mass spectrum *m/e* 227 (M^+, 12), 135 (base), 92 (13), and 77 (16).

Anal. Calcd for $C_{10}H_{10}O_3NCl$: C, 52.76; H, 4.41; N, 6.17. Found: C, 52.95; H, 4.49; N, 6.16.

***N*-(Chloroacetyl)-*m*-methoxybenzamide (6d).** The method for preparing *N*-(chloroacetyl)benzamide was used with 10 g (0.066 mol) of *m*-methoxybenzamide and 20 g (0.18 mol) of chloroacetyl chloride. The reaction mixture was heated at 110° for 1 hr. The solid was recrystallized from chloroform, yielding 11 g (73%) of a white solid with mp 131–132° with the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 3.92 (3 H, s), 4.80 (2 H, s), 7.1–7.6 ppm (4 H, m); ir ($CDCl_3$) 2.96, 5.78, 5.85, and 6.79 μ; mass spectrum *m/e* 227 (M^+, 24), 135 (base), 107 (25), and 77 (21).

Anal. Calcd for $C_{10}H_{10}O_3NCl$: C, 52.76; H, 4.41; N, 6.17. Found: C, 52.84; H, 4.51; N, 6.18.

***N*-(Chloroacetyl)-*m*-trifluoromethylbenzamide (6e).** The procedure for preparing *N*-(chloroacetyl)benzamide was used with 44 g (0.23 mol) of *m*-trifluoromethylbenzamide[20] and 30 g (0.26 mol) of chloroacetyl chloride. The reaction mixture was heated at 110° for 1 hr. After cooling, the resulting solid was recrystallized from ether, yielding 32 g (52%) of white crystals with mp 128–129°. The imide **6e** gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 4.81 (2 H, s), 7.5–8.3 (4 H, m), and 9.86 ppm (1 H, broad); ir ($CHCl_3$) 2.96, 5.78, 5.85, 5.91, and 7.51 μ; mass spectrum *m/e* 265 (M^+, 4), 230 (31), 173 (base), 145 (55), and 95 (16).

Anal. Calcd for $C_{10}H_7O_2NClF_3$: C, 45.21; H, 2.64; N, 5.28. Found: C, 45.39; H, 2.65; N, 5.30.

2-Phenyl-2-oxazolin-4-one (7a).[5] A 1000-ml, oven-dried round-bottomed flask was equipped with a magnetic stirrer, heating mantle, condenser, and drying tube. To the flask was added 800 ml of glyme, which was then cooled to freezer temperature. Then 2.10 g (0.050 mol) of 57% sodium hydride in mineral oil was mashed and added to the flask. Stirring was started, and 9.90 g (0.050 mol) of *N*-(chloroacetyl)benzamide was added. After 0.5 hr of stirring, the hydrogen evolution ceased, and the mixture was slightly yellow and slightly cloudy. Stirring was stopped, and any small bits of sodium hydride were mashed with a stirring rod. Stirring was then resumed and heating started. After 0.5 hr of heating, reflux started, and the mixture was cloudy and pale red-orange. The heat was removed after 4.5 hr, and the mixture was allowed to cool and settle. After filtration through Celite, the solvent was removed by rotary evaporation. The resulting orange crystalline solid was sublimed at 140° (0.01 mm) and recrystallized from about 70 ml of chloroform to give 6.40 g (80%) of a white crystalline solid with mp 158–159° (lit.[22] mp 154–156°). The oxazoline **7a** gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 4.75 (2 H, s) and 7.9 ppm (5 H, m); ir ($CHCl_3$) 5.69, 5.76, 6.24, 6.30, and 6.45 μ; mass spectrum *m/e* 161 (M^+, 88), 160 (30), 103 (base), 91 (27), and 76 (26); uv λ_{max} (ethanol) 263 nm (ϵ 20800); uv λ_{max} (glyme) 260 nm (ϵ 20700).

2-Ethoxy-2-oxazolin-4-one (7b). The procedure used for preparing 2-phenyl-2-oxazolin-4-one (**7a**) was used with 400 ml of dry glyme, 1.60 g (0.038 mol) of 57% sodium hydride in mineral oil, and 6.60 g (0.040 mol) of ethyl *N*-(chloroacetyl)carbamate. The product was recrystallized from ether without sublimation, yielding 3.33 g (68%) of a white solid with mp 64–65°. This compound (**7b**) gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 1.47 (3 H, t, J = 7 Hz), 4.66 (2 H, q, J = 7 Hz), and 4.78 ppm (2 H, s); ir ($CHCl_3$) 5.64 and 6.35 μ; mass spectrum *m/e* 129 (M^+, 27), 102 (38), 101 (21), 35 (24), 70 (base), 44 (33) and 31 (65); uv λ_{max} (methylcyclohexane) 208 nm (ϵ 13400) and 258 (55).

Anal. Calcd for $C_5H_7O_3N$: C, 46.51; H, 5.47; N, 10.85. Found: C, 46.35; H, 5.55; N, 10.80.

2-(*p*-Methoxyphenyl)-2-oxazolin-4-one (7c). The method used for preparing 2-phenyl-2-oxazolin-4-one (**7a**) was employed with 800 ml of dry glyme, 1.60 g (0.038 mol) of 57% sodium hydride in

mineral oil, and 9.20 g (0.040 mol) of *N*-(chloroacetyl)-*p*-methoxybenzamide. The product was recrystallized from glyme, yielding 5.60 g (77%) of a white solid with mp 143–144°. The product was identified as 2-(*p*-methoxyphenyl)-2-oxazolin-4-one (**7c**) from the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 3.93 (3 H, s), 4.71 (2 H, s), 6.85–7.15 and 8.00–8.30 ppm (AA'BB'); ir ($CHCl_3$) 5.66, 5.75, 6.22, 6.31, 6.43, and 6.67 μ; mass spectrum *m/e* 191 (M^+, 75), 190 (34), 133 (base), 103 (22), and 90 (39); uv λ_{max} (ethanol) 223 nm (ϵ 14000) and 300 (32000).

Anal. Calcd for $C_{10}H_9O_3N$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.88; H, 4.81; N, 7.29.

2-(*m*-Methoxyphenyl)-2-oxazolin-4-one (7d). The method for preparing 2-phenyl-2-oxazolin-4-one (**7a**) was used with 400 ml of dry glyme, 0.80 g (0.019 mol) of 57% sodium hydride in mineral oil, and 4.60 g (0.020 mol) of *N*-(chloroacetyl)-*m*-methoxybenzamide. The solid was sublimed at 110° (0.01 mm) and recrystallized from benzene, yielding 2.68 g (77%) of a white solid with mp 121–122°. The product (**7d**) gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 3.87 (3 H, s), 4.75 (2 H, s), and 7.1–7.9 ppm (4 H, m); ir ($CHCl_3$) 5.66, 5.74, and 6.43 μ; mass spectrum *m/e* 191 (M^+, base), 160 (21), 133 (93), 103 (38), and 90 (32); uv λ_{max} (ethanol) 220 nm (ϵ 18730), 268 (18800), and 318 (3700).

Anal. Calcd for $C_{10}H_9O_3N$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.79; H, 4.84; N, 7.28.

2-(*m*-Trifluoromethylphenyl)-2-oxazolin-4-one (7e). About 800 ml of dry *N,N*-dimethylformamide was added to a 1000-ml round-bottomed flask equipped with addition funnel, drying tube, magnetic stirrer, and oil bath. This was heated to 60°, and 2.0 g (0.0075 mol) of *N*-(chloroacetyl)-*m*-trifluoromethylbenzamide was added. Then 0.80 g (0.0072 mol) of potassium *tert*-butoxide was dissolved in 100 ml of dry DMF and added dropwise over 3 hr with stirring. The mixture was stirred for an additional 0.5 hr and then allowed to cool. The solvent was rotary evaporated (10^{-2} mm) using a water bath kept at 50°. The residue was recrystallized from ether yielding 0.80 g (48%) of a yellow solid, which after further recrystallization and sublimation [50° (10^{-5} mm)] gave a white solid with mp 93–93.5°. The product was identified as 2-(*m*-trifluoromethylphenyl)-2-oxazolin-4-one (**7e**) and gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 4.84 (2 H, s) and 7.5–8.6 ppm (4 H, m); ir ($CHCl_3$) 5.64, 6.17, 6.23, and 6.38 μ; mass spectrum *m/e* 229 (M^+, 47), 171 (base), 160 (21), 152 (24), and 121 (34); uv λ_{max} (glyme) 256 nm (ϵ 16000) and a shoulder at 320 (100).

Anal. Calcd for $C_{10}H_6O_2NF_3$: C, 52.40; H, 2.62; N, 6.12. Found: C, 52.28; H, 2.72; N, 6.14.

2-Phenyl-2-oxiryl Isocyanate (10a) from Irradiation of 2-Phenyl-2-oxazolin-4-one (7a). To 120 ml of benzene (distilled from phosphorus pentoxide) was added 0.50 g (0.0031 mol) of 2-phenyl-2-oxazolin-4-one. This solution was placed in an immersion well with quartz water jacket and Corex filter and irradiated for 8 hr, yielding a slightly yellow solution. Starting material destruction and product formation were monitored by ir spectroscopy. The solvent was removed by rotary evaporation in cold water (0.10 mm). TLC (eluting with 30% acetonitrile in benzene on silica gel) of the residue showed no starting material and only one product. The residue was molecularly distilled at 100° (10^{-2} mm). A few drops of a colorless liquid with a strong, sharp odor was recovered and was identified as 2-phenyl-2-oxiryl isocyanate (**10a**) from the following spectral data: NMR ($CDCl_3$, 60 MHz), δ 4.49 (2 H, s) and 7.37 ppm (5 H, s); ir (neat) 4.44 μ; mass spectrum *m/e* 161 (M^+, 1) 133 (88), 105 (41), 104 (46), 91 (base), 77 (51), and 51 (51). The product was not sufficiently stable for elemental analysis.

Isomerization of 2-Phenyl-2-oxiryl Isocyanate (10a) to 4-Phenyl-4-oxazolin-2-one (8a) on Silica Gel. An irradiation was carried out as described for the preparation of 2-phenyl-2-oxiryl isocyanate (**10a**). After the benzene was evaporated, the residue was gravity chromatographed on a 2 × 15 cm silica gel column (cooled by a cold water jacket) eluting with 15% acetonitrile in benzene. When material stopped eluting from the column, as indicated by TLC, all fractions were combined, and the solvent was removed by rotary evaporation leaving a white solid. The solid was recrystallized from about 5 ml of benzene, yielding 0.23 g (45%) of a white crystalline material with mp 157–157.5°. The product was identified as 4-phenyl-4-oxazolin-2-one (**8a**) and gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 7.10 (1 H, d, J = 1.5 Hz), 7.42 (5 H, s), and 5.0 (1 H, broad) (when D_2O was added, the peak at δ 5.0 disappeared, and the doublet at δ 7.10 ppm collapsed to a singlet); ir ($CHCl_3$) 2.93 (weak) and 5.72 μ; mass spectrum *m/e* 161 (M^+, 44), 105 (19), 104 (base), 77 (36), and 51 (19).

Anal. Calcd for $C_9H_7O_2N$: C, 67.07; H, 4.38; N, 8.69. Found: C, 67.03; H, 4.49; N, 8.67.

Catalytic Hydrogenation of 4-Phenyl-4-oxazolin-2-one (8a). A 0.165-g (0.0010 mol) sample of 4-phenyl-4-oxazolin-2-one (**8a**) in 12 ml of glacial acetic acid was reduced under 1 atm of hydrogen in the presence of 0.100 g of 5% palladium on charcoal. The reaction was stopped after the uptake of 0.00095 mol of hydrogen (approximately 30 min). The mixture was then filtered through Celite, and the solvent was removed by rotary evaporation. The resulting solid was recrystallized from chloroform, yielding 0.045 g (27%) of a white crystalline solid with mp 138–139° (lit.[6] mp 138–139.5°). The product was identified as 4-phenyl-2-oxazolidone (**9a**) by comparison of its spectra with the spectra of a sample prepared by an independent synthesis.[6]

6,6-Dimethoxy-5-phenyl-4-oxa-1-azabicyclo[3.2.0]heptan-2-one (11a) from Irradiation of 2-Phenyl-2-oxazolin-4-one (7a) in the Presence of 1,1-Dimethoxyethene. In 125 ml of dry glyme was dissolved 0.50 g (0.0031 mol) of 2-phenyl-2-oxazolin-4-one and 5.5 g (6 ml, 0.063 mol) of 1,1-dimethoxyethene. This solution was placed in an immersion well with quartz water jacket and Corex filter and irradiated with a 450-W mercury lamp. After 2 hr of irradiation, TLC on silica gel with 30% acetonitrile in benzene as eluent indicated that the reaction was complete. The glyme was removed by rotary evaporation until about 2 ml was left. Pentane was added until the solution was cloudy, and the mixture was placed in the freezer. A total yield of 0.42 g (55%) of a white solid with mp 50–51° was obtained. When the product was isolated by GLC with a 10 ft × 0.375 in. column of 5% SE-30 on 60–80 mesh Chromosorb W at 200°, 0.505 g (65%) of product was obtained. The photoproduct was identified as **11a** and gave the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 2.95 (3 H, s), 3.40 (3 H, s), 3.74 (1 H, d, J = 10.2 Hz), 3.82 (1 H, d, J = 10.2 Hz), 4.28 (2 H, s), and 7.3–7.7 ppm (5 H, m); ir ($CHCl_3$) 5.76 μ; mass spectrum *m/e* 249 (M^+, 1), 179 (25), 105 (38), 88 (80), 77 (37), 58 (96), 45 (25), and 43 (base).

Anal. Calcd for $C_{13}H_{15}O_4N$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.74; H, 6.18; N, 5.69.

Hydrolysis of 6,6-Dimethoxy-5-phenyl-4-oxa-1-azabicyclo-[3.2.0]heptan-2-one (11a). To a 50-ml round-bottomed flask was added 25 ml of 3 *N* hydrochloric acid and 0.75 g (0.0030 mol) of 6,6-dimethoxy-5-phenyl-4-oxa-1-azabicyclo[3.2.0]heptan-2-one. After the solution had been stirred at ambient temperature for 4 hr, there was no longer any suspended oxazabicycloheptanone **11a**. The solution was placed in a separatory funnel and washed with chloroform. Sodium bicarbonate was added until the aqueous solution was saturated and the mixture was then extracted with two 25-ml portions of chloroform. The latter chloroform fractions were combined and dried with sodium sulfate. Rotary evaporation of the solvent left 0.61 g (94%) of a yellow liquid which the NMR spectrum indicated was very nearly pure. Molecular distillation at 110° (10^{-2} mm) yielded a colorless liquid which was identified as 3-amino-2,2-dimethoxy-1-phenylpropanone (**12**) from the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 1.09 (2 H, s), 3.21 (2 H, s), 3.40 (6 H, s), 7.25–7.65 (3 H, m), and 8.10–8.35 ppm (2 H, m) (when a drop of D_2O was added, the singlet at δ 1.09 disappeared); ir (neat) 2.97, 3.01, and 5.91 μ; mass spectrum *m/e* 180 (38), 105 (base), 104 (50), 77 (37), and 72 (32). The product was not sufficiently stable for elemental analysis.

3-Amino-2,2-dimethoxy-1-phenylpropanol (13). About 10 ml of ether (distilled from sodium) was placed in a 25-ml round-bottomed flask equipped with condenser and drying tube. Lithium aluminum hydride (0.093 g, 2.4 mmol) and 3-amino-2,2-dimethoxy-1-phenylpropanone (**12**) (0.120 g, 0.58 mmol) were added, and the reaction mixture was stirred at room temperature for 2 hr. Water was added very slowly until the mixture turned white. After filtration through Celite, the ether solvent was rotary evaporated, leaving a colorless oil. The product crystallized from ether, yielding 0.095 g (77%) of a white solid with mp 87–87.5°. The product was identified as 3-amino-2,2-dimethoxy-1-phenylpropanol (**13**) and gave the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 2.4–3.1 (5 H, m), 3.20 (3 H, s), 3.47 (3 H, s), 4.92 (1 H, d, J = 1.5 Hz), and 7.2–7.7 ppm (5 H, m) (when D_2O was added, a broad

peak at δ 2.95 disappeared and a simplified ABX pattern appeared with $\delta_A = 2.53$, $\delta_B = 2.92$, $\delta_X = 4.92$ ppm; $J_{AB} = 13$, $J_{AX} = 0$, and $J_{BX} = 1.5$ Hz); ir ($CHCl_3$) 2.96 and 3.10 μ; mass spectrum *m/e* 181 (37), 104 (100), 88 (43), 75 (47), 74 (34), 72 (89), and 30 (48).

Anal. Calcd for $C_{11}H_{17}O_3N$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.61; H, 8.16; N, 6.58.

7-Phenyl-1-aza-3,8-dioxa-4-tricyclo[5.3.0.0^{2,6}]decen-10-one (14a) from Irradiation of 2-Phenyl-2-oxazolin-4-one (7a) in the Presence of Furan. In 115 ml of dry glyme were dissolved 0.50 g (0.0031 mol) of 2-phenyl-2-oxazolin-4-one (**7a**) and 9.4 g (10 ml, 0.14 mol) of furan. This solution was irradiated with a 450-W mercury lamp in an immersion well with quartz water jacket and Corex filter for 2 hr, at which time TLC on silica gel with 30% acetonitrile in benzene as eluent indicated the reaction was complete. The glyme was rotary evaporated in a bath of cold water. The resulting residue was dissolved in about 50 ml of ether and filtered. The solution was evaporated to about 3 ml by heating on a steam bath and blowing nitrogen onto the surface to exclude moisture during evaporation. The solution was cooled in the freezer, yielding 0.32 g (45%) of a white crystalline solid which melted at 144–147° with decomposition. The product was identified as **14a** and gave the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 4.26 (1 H, d, J = 14.5 Hz), 4.46 (1 H, d, J = 14.5 Hz), 4.58 (1 H, d of d of d, J = 6.4, 3.1, 1.4 Hz), 4.92 (1 H, t, J = 3.1 Hz), 6.48 (1 H, d of d, J = 6.5, 0.5 Hz), 6.80 (1 H, d of d of d, J = 3.1, 1.4, 0.5 Hz), and 7.76–8.40 ppm (5 H, m); ir ($CHCl_3$) 5.70 and 6.22 μ; mass spectrum *m/e* 229 (M^+, 3), 161 (30), 103 (60), 68 (base), and 39 (32).

Anal. Calcd for $C_{13}H_{11}O_3N$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.11; H, 4.84; N, 6.12.

Catalytic Hydrogenation of 7-Phenyl-1-aza-3,8-dioxa-4-tricyclo[5.3.0.0^{2,6}]decen-10-one (14a). A 0.40-g (0.0018 mol) sample of **14a** in 15 ml of ethyl acetate was reduced under 1 atm of hydrogen in the presence of 0.050 g of 10% palladium on charcoal. The reaction was stopped after the uptake of 0.0018 mol of hydrogen (approximately 15 min). After filtration through Celite, the solvent was removed by rotary evaporation. The product was recrystallized from ether–pentane yielding 0.33 g (82%) of white crystals with mp 90–91° and was identified as 7-phenyl-1-aza-3,8-dioxatricyclo[5.3.0.0^{2,6}]decan-10-one (**15**) from the following spectroscopic data: NMR ($CDCl_3$, 60 MHz) δ 1.3–2.1 (2 H, m), 3.5–4.3 (3 H, m), 4.01 (1 H, d, J = 14 Hz), 4.16 (1 H, d, J = 14 Hz), 5.88 (1 H, d, J = 5.0 Hz), and 7.4–7.6 ppm (5 H, m); ir ($CHCl_3$) 5.74 μ; mass spectrum *m/e* 231 (M^+, 0.1), 161 (base), 160 (33), 104 (33), 103 (49), 70 (65), 42 (31), and 28 (71). The product was not sufficiently stable for elemental analysis.

Reaction of 7-Phenyl-1-aza-3,8-dioxatricyclo[5.3.0.0^{2,6}]decan-10-one (15) with Methanol. In a 25-ml flask was dissolved 0.20 g (0.87 mmol) of 7-phenyl-1-aza-3,8-dioxatricyclo[5.3.0.0^{2,6}]decan-10-one (**15**) in 10 ml of spectroquality methanol and allowed to stand for 15 min. The solvent was then rotary evaporated and the residue recrystallized in 5% methanol–ether, yielding 0.19 g (94%) of white crystals with mp 164–164.5°. This compound gave the following spectral data, which were consistent with the structure 2-phenyl-2-(2′-methoxy-3′-tetrahydrofuranyl)-4-oxazolidone (**16**): NMR ($CDCl_3$, 60 MHz) δ 1.6–2.0 (2 H, m), 2.90 (1 H, t of d, J = 2, 9 Hz), 3.22 (3 H, s), 3.6–4.1 (2 H, m), 4.22 (1 H, d, J = 14 Hz), 4.42 (1 H, d, J = 14 Hz), 4.96 (1 H, d, J = 2 Hz), and 7.2–7.5 ppm (5 H, m); ir ($CHCl_3$), 2.92 (weak) and 5.84 μ; mass spectrum *m/e* 163 (34), 162 (base), 126 (64), and 104 (60).

Anal. Calcd for $C_{14}H_{17}O_4N$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.72; H, 6.54; N, 5.28.

Attempts to Add Cyclohexene, Styrene, and *cis*-2-Butene to 2-Phenyl-2-oxazolin-4-one (7a). A solution containing 0.50 g (0.0031 mol) of 2-phenyl-2-oxazolin-4-one and 10 g (0.18 mol) of purified cyclohexene in dry benzene was placed in an immersion well with quartz water jacket and Corex filter. After 8 hr of irradiation with a 450-W mercury lamp, TLC on silica gel eluting with 30% acetonitrile in benzene showed no oxazolinone and only a faint streak. Infrared analysis of the solution showed no distinct carbonyl stretching bands and a weak isocyanate stretching band. Irradiation of 0.50 g of **7a** and 10 g (0.096 mol) of styrene under similar conditions gave the same results after 12 hr of irradiation. The irradiation procedure was repeated with 0.50 g of **7a** and 1.7 g (0.030 mol) of *cis*-2-butene in dry glyme. After 1 hr of irradiation, there was 35% less 2-butene by glc, and 20% of the oxazolinone by infrared analysis had been destroyed. GLC with a 25 ft × 0.25 in. column of 25% β,β-oxydipropionitrile on 80–100 mesh Chromosorb P at 25° showed that 16% of the remaining 2-butene was *trans*-2-butene. The infrared spectrum in glyme solvent showed a very small amount of isocyanate and a broad small carbonyl at 5.80 μ. When this procedure was repeated in dry benzene with 10 g (0.18 mol) of *cis*-2-butene and 10 hr of irradiation, 75% of the oxazolinone was destroyed but only 10% of the butene was destroyed. No new carbonyl stretching bands appeared, but a weak isocyanate stretching band did appear. GLC analysis showed that 19% of the remaining butene was *trans*-2-butene.

2-Ethoxy-2-oxiryl Isocyanate (10b) from Irradiation of 2-Ethoxy-2-oxazolin-4-one (7b). To 120 ml of benzene, dried by distillation from phosphorus pentoxide, was added 0.50 g (0.0039 mol) of 2-ethoxy-2-oxazolin-4-one (**7b**). This solution was irradiated with a 450-W mercury lamp in an immersion well with quartz water jacket and Vycor filter for 10 hr. The solvent was rotary evaporated in cold water (0.10 mm), and the residue was molecularly distilled in an oil bath at 100° (0.01 mm). A few drops of colorless liquid, which began to turn yellow immediately, were obtained. The photoproduct was identified as 2-ethoxy-2-oxiryl isocyanate (**10b**) from the following spectral data: NMR ($CDCl_3$, 100 MHz), δ 1.46 (3 H, t, J = 7.2 Hz), 4.60 (2 H, q, J = 7.2 Hz), and 4.73 ppm (2 H, s); ir ($CDCl_3$) 4.47 μ; mass spectrum *m/e* 129 (M^+, 19), 102 (52), 70 (75), 44 (44), 31 (52), 29 (base), and 27 (63). The isocyanate was not sufficiently stable for elemental analysis. When the above reaction was repeated and the residue after evaporation was chromatographed on silica gel with 30% acetonitrile in benzene as eluent, no product could be recovered. In two subsequent experiments, attempts to trap the isocyanate with methanol or diethylamine were unsuccessful. In both cases, infrared analysis of the solutions showed that the isocyanate had quickly reacted with the trapping agent, but no new carbonyl compounds were formed. Only tars were obtained from the reaction mixture.

Irradiation of 2-Ethoxy-2-oxazolin-4-one (7b) in the Presence of Furan. In 120 ml of dry glyme was dissolved 0.50 g (0.0039 mol) of 2-ethoxy-2-oxazolin-4-one and 9.4 g (0.14 mol) of furan. This solution was irradiated with a 450-W mercury lamp in a quartz immersion well with Vycor filter for 10 hr. The infrared spectrum of the solution showed a small amount of isocyanate and no distinct carbonyl stretching bands.

6,6-Dimethoxy-5-(*p*-methoxyphenyl)-4-oxa-1-azabicyclo[3.2.0]heptan-2-one (11c) from Irradiation of 2-(*p*-Methoxyphenyl)-2-oxazolin-4-one (7c) in the Presence of 1,1-Dimethoxyethene. In 120 ml of dry glyme was dissolved 0.50 g (0.0026 mol) of 2-(*p*-methoxyphenyl)-2-oxazolin-4-one (**7c**) and 5.5 g (6.0 ml, 0.062 mol) of 1,1-dimethoxyethene. This solution was irradiated with a 450-W mercury lamp in a Pyrex immersion well for 4 hr, at which time the ir spectrum of the solution indicated complete reaction. The solution was rotary evaporated and the residue recrystallized from ether, yielding 0.50 g (69%) of a white solid with mp 117–118°. The photoproduct was identified as **11c** and gave the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 3.02 (3 H, s), 3.41 (3 H, s), 3.80 (3 H, s), 3.80 (1 H, d, J = 9.9 Hz), 3.88 (1 H, d, J = 9.9 Hz), 4.32 (2 H, s), and 6.8–7.5 ppm (4 H, m); ir ($CHCl_3$) 5.74 μ; mass spectrum *m/e* 279 (M^+, 0.25), 88 (base), 58 (32), and 43 (42).

Anal. Calcd for $C_{14}H_{17}O_5N$: C, 60.20; H, 6.14; N, 5.02. Found: C, 60.23; H, 6.18; N, 4.99.

7-(*p*-Methoxyphenyl)-1-aza-3,8-dioxa-4-tricyclo[5.4.0.0^{2,6}]decen-10-one (14c) from Irradiation of 2-(*p*-Methoxyphenyl)-2-oxazolin-4-one (7c) in the Presence of Furan. In 115 ml of dry glyme were dissolved 0.50 g (0.0026 mol) of 2-(*p*-methoxyphenyl)-2-oxazolin-4-one (**7c**) and 9.4 g (10 ml, 0.14 mol) of furan. This solution was irradiated with a 450-W mercury lamp in a Pyrex immersion well for 4 hr. The solvent was removed by rotary evaporation and the residue recrystallized from ether, yielding 0.16 g (24%) of a white solid with mp 84–85°. This compound was assigned structure **14c** and gave the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 3.82 (3 H, s), 3.97 (1 H, d, J = 13.9 Hz), 4.13 (1 H, d, J = 13.9 Hz), 4.24 (1 H, d of d of d, J = 6.0, 3.0, 1.3 Hz), 4.61 (1 H, t, J = 3.0 Hz), 6.04 (1 H, d of d, J = 6.0, 0.5 Hz), 6.39 (1 H, d of d of d, J = 3.0, 1.3, 0.5 Hz), and 6.9–7.6 ppm (4 H, m); ir ($CHCl_3$) 5.70 and 6.20 μ; mass spectrum *m/e* 191 (base), 190 (53), 133 (89), 68 (40), and 39 (25).

Anal. Calcd for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05; N, 5.40. Found:

C, 64.98; H, 5.09; N, 5.31.

Attempts to Add Methyl Vinyl Ether, Styrene, and Cyclohexene to 2-(*p*-Methoxyphenyl)-2-oxazolin-4-one (7c). In 115 ml of dry benzene was dissolved 10 g (0.17 mol) of methyl vinyl ether and 0.50 g (0.0026 mol) of 2-(*p*-methoxyphenyl)-2-oxazolin-4-one (**7c**). This solution was irradiated with a 450-W mercury lamp in a Pyrex immersion well for 7 hr. At this time no change could be detected by ir spectroscopy of the solution. This procedure was repeated with 10 g (0.096 mol) of styrene, and there was no reaction after 12 hr of irradiation. With 10 g (0.12 mol) of cyclohexene, there was no reaction of **7c** after 6 hr of irradiation.

6,6-Dimethoxy-5-(*m*-methoxyphenyl)-4-oxa-1-azabicyclo-[3.2.0]heptan-2-one (11d) from Irradiation of 2-(*m*-Methoxyphenyl)-2-oxazolin-4-one (7d) in the Presence of 1,1-Dimethoxyethene. In 120 ml of dry glyme was dissolved 0.40 g (0.0021 mol) of 2-(*m*-methoxyphenyl)-2-oxazolin-4-one (**7d**) and 5.5 g (6 ml, 0.063 mol) of 1,1-dimethoxyethene. This solution was irradiated with a 450-W mercury lamp in a Pyrex immersion well for 5 hr, at which time the ir spectrum of the solution indicated no oxazolinone. The solvent was rotary evaporated, and the residue was molecularly distilled at 120° (2×10^{-3} mm) yielding 0.44 g (75%) of a viscous, yellow oil. Analytical samples were obtained by collection from GLC at 240° with a 10 ft × 0.375 in. column of 5% Apiezon L on 60–80 mesh Diatoport S. The retention time was 9 min with a helium flow rate of 64 ml/min. This compound (**11d**) gave the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 3.04 (3 H, s), 3.45 (3 H, s), 3.81 (3 H, s), 3.82 (1 H, d, J = 9.6 Hz), 3.88 (1 H, d, J = 9.6 Hz), 4.21 (2 H, s), and 6.8–7.3 ppm (4 H, m); ir ($CHCl_3$) 5.76 μ; mass spectrum *m/e* 88 (98), 86 (62), 84 (base), 83 (31), 58 (31), 49 (32), 47 (50), and 43 (56). The cycloadduct could not be isolated in a sufficiently pure state for an accurate elemental analysis.

7-(*m*-Methoxyphenyl)-1-aza-3,8-dioxa-4-tricyclo[5.3.0.$0^{2,6}$]dec-en-10-one (14d) from Irradiation of 2-(*m*-Methoxyphenyl)-2-oxazolin-4-one (7d) in the Presence of Furan. A solution of 0.50 g (0.0026 mol) of 2-(*m*-methoxyphenyl)-2-oxazolin-4-one (**7d**) and 9.4 g (10 ml, 0.14 mol) of furan in 115 ml of dry glyme was irradiated with a 450-W mercury lamp in a Pyrex immersion well for 10 hr. The solvent was rotary evaporated and the residue recrystallized from ether, yielding 0.29 g (43%) of a white solid with mp 97–99°. The product was assigned structure **14d** and gave the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 3.81 (3 H, s), 3.98 (1 H, d, J = 12.6 Hz), 4.14 (1 H, d, J = 12.6 Hz), 4.25 (1 H, d of d of d, J = 6.0, 3.0, 1.4 Hz), 4.63 (1 H, t, J = 3.0 Hz), 6.05 (1 H, d of d, J = 6.0, 0.4 Hz), 6.38 (1 H, d of d of d, J = 3.0, 1.4, 0.4 Hz), and 6.8–7.4 ppm (4 H, m); ir ($CHCl_3$) 5.70 and 6.23 μ; mass spectrum *m/e* 191 (base), 133 (79), 68 (67), 45 (36), 39 (55), 28 (57), and 18 (59).

Anal. Calcd for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.75; H, 5.11; N, 5.43.

Attempts to Add Cyclohexene, Styrene, Butadiene, and Methyl Vinyl Ether to 2-(*m*-Methoxyphenyl)-2-oxazolin-4-one (7d). In 115 ml of dry benzene were dissolved 10 g (0.12 mol) of cyclohexene and 0.5 g (0.0026 mol) of 2-(*m*-methoxyphenyl)-2-oxazolin-4-one (**7d**). After irradiation with a 450-W mercury lamp in a Pyrex immersion well for 5 hr, the solution was examined by ir spectroscopy. There was no apparent reaction. This procedure was repeated three times with 10 g (0.096 mol) of styrene, 10 g (0.185 mol) of butadiene, and 10 g (0.17 mol) of methyl vinyl ether, respectively. In all cases, irradiation for 5 hr gave no reaction.

2-(*m*-Trifluoromethylphenyl)-2-oxiryl Isocyanate (10e) from Irradiation of 2-(*m*-Trifluoromethylphenyl)-2-oxazolin-4-one (7c). A solution of 0.50 g (0.0022 mol) of 2-(*m*-trifluoromethylphenyl)-2-oxazolin-4-one (**7e**) in 120 ml of dry benzene was irradiated with a 450-W mercury lamp in a quartz immersion well with a Corex filter. After 4 hr of irradiation, the ir spectrum of the solution indicated complete destruction of the oxazolinone **7e**. The solvent was rotary evaporated in a cold water bath (0.1 mm), and the residue was molecularly distilled in an oil bath at 100° (0.01 mm). A few drops of a colorless liquid was obtained which was assigned structure **10e** from the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 4.38 (2 H, s) and 7.2–7.5 ppm (4 H, m); ir (neat) 4.42 μ; mass spectrum *m/e* 201 (base), 172 (31), 159 (42), 145 (33), 132 (63), and 28 (34). The isocyanate was not sufficiently stable for elemental analysis. When this reaction was repeated and the residue chromatographed on a 2 × 15 cm silica gel column eluting with 10% acetonitrile in benzene, 0.25 g (50%) of the isocyanate **10e** was recovered. No other products would elute from the column.

6,6-Dimethoxy-5-(*m*-trifluoromethylphenyl)-4-oxa-1-azabicyclo[3.2.0]heptan-2-one (11e) from Irradiation of 2-(*m*-Trifluoromethylphenyl)-2-oxazolin-4-one (7e) in the Presence of 1,1-Dimethoxyethene. In 120 ml of dry glyme was dissolved 0.50 g (0.0022 mol) of 2-(*m*-trifluoromethylphenyl)-2-oxazolin-4-one (**7e**) and 5.5 g (6 ml, 0.062 mol) of 1,1-dimethoxyethene. The solution was irradiated with a 450-W mercury lamp in a Pyrex immersion well for 5 hr, at which time the ir spectrum indicated that complete destruction of oxazolinone had occurred. The solvent was rotary evaporated, and the residue was molecularly distilled at 120° (2×10^{-3} mm) yielding 0.39 g (59%) of a viscous yellow oil. The product was further purified by preparative GLC at 180° with a 10 ft × 0.375 in. column of 5% Apiezon L on 60–80 mesh Diatoport S. The retention time was 13 min with a helium flow of 60 ml/min. The photoproduct was assigned structure **11e** from the following spectral data: NMR ($CDCl_3$, 100 MHz) δ 3.04 (3 H, s), 3.46 (3 H, s), 3.85 (1 H, d, J = 9.9 Hz), 3.93 (1 H, d, J = 9.9 Hz), 4.36 (2 H, s), 7.4–7.8 (4 H, m); ir ($CHCl_3$) 5.73 μ; mass spectrum *m/e* 317 (M^+, 0.6), 88 (base), 58 (46), and 43 (71). The cycloadduct could not be isolated in a sufficiently pure state for an accurate elemental analysis.

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