Table II. Signal Intensities as Function of T^a

Solvent	h, mm	T, °K	Log hT
	Slope = $-2.402 \pm 0.125 \times 10^3$		
Chloroform	50.6	320.5	4.209
	80.4	325.1	4.416
	102.6	331.5	4.531
	117.4	336.7	4.597
	162.6	342.6	4.746
	215.9	348.2	4.874
	229.0	352.0	4.906
	Slope = $-2.347 \pm 0.131 \times 10^3$		
Benzene	31.0	334.0	4.015
	33.5	339.0	4.055
	50.0	346.0	4.238
	66.0	355.0	4.370
	110.0	365.0	4.604
	Slope = $-1.153 \pm 0.037 \times 10^3$		
Ethanol	25.0	322.0	3.906
	32.0	334.0	4.029
	41.5	346.0	4.157
	46.3	355.0	4.216
	59.5	365.0	4.337

[a] The symbol h represents the average heights of from three to five scans of one of the major peaks in the EPR spectrum, and T is the absolute temperature of the measurement.

ples was simplified by using a specially designed apparatus consisting of a 190 × 5 mm quartz tube sealed to an 80 × 9 mm quartz tube to which a 20 × 9 mm quartz side arm was attached near the former junction. Reductive dimer mixture, 0.150 g, was placed in the side arm, and 0.8 ml of solvent was placed into the 5-mm tube. The system was freeze-thaw degassed to 10^{-4} mm residual pressure and the 9-mm tube sealed off. The dimer was then mixed into the solvent and the solution frozen into the 5-mm tube and sealed off at a length of 140 mm. The EPR spectral data as shown in Table I were then obtained at 80-90°.

Determination of the Enthalpy of Dissociation for the Reductive Dimers 2 and 3. Samples were prepared as described above for each solvent. The samples were each placed in the cavity of the EPR spectrometer and the signal height of one of the peaks measured at several different temperatures between 40 and 95°. (Table II). Several scans were made at each temperature, the average being used for the calculation. The temperature of the cavity was measured with a copper-constantan thermocouple. During the experiment and upon termination, initial and midpoint measurements were repeated to check for any dimer destruction by disproportionation. The enthalpies of dissociation, ΔH, were calculated by the method of Vincow and co-workers.[4]

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Photochemical Reactivity of Keto Imino Ethers. V.[1] (2 + 2) Photocycloaddition to the Carbon-Nitrogen Double Bond of 3-Ethoxyisoindolone

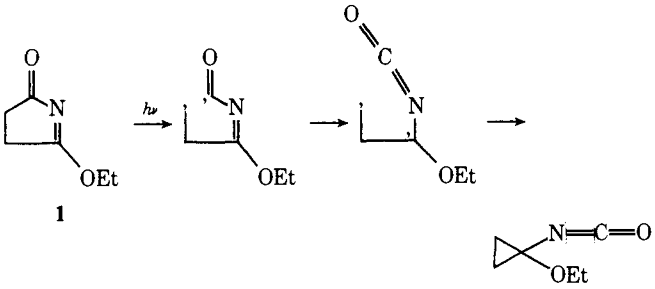
Kent A. Howard and Tad H. Koch*

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received October 19, 1974*

Abstract: The photochemical reactivity of 3-ethoxyisoindolone (**2**) with 1,1-dimethoxyethene, cyclohexene, furan, isobutylene, *cis*-2-butene, *trans*-2-butene, tetramethylethylene, and fumaronitrile is described. The modes of photochemical reactivity observed include the novel regiospecific (2 + 2) cycloaddition to the carbon-nitrogen double bond of **2** to give products **3**, **5**, **7**, **9**, **11**, **12**, and **18**, a photochemical ene type reaction to give products **8**, **15**, **16**, and **19**, and a unique cycloaddition of tetramethylethylene at the 1,2-positions of **2** to give the azepinone **20**. The photochemical ene reaction is partially stereospecific but the (2 + 2) cycloaddition reaction is not. The (2 + 2) cycloadducts undergo hydrolytic ring opening to give benzoazepinediones in high yield. The photoreactions of 3-ethoxyisoindolone with olefins occur in high quantum yield from a triplet state, and the singlet state is quenched by the olefins. The mechanism is discussed in terms of a triplet exciplex leading to the ene products and to a long-lived biradical intermediate.

While (2 + 2) photocycloadditions of olefins to carbon-carbon[2] and carbon-oxygen double bonds[3] are well-documented reactions often employed in synthetic schemes,[4] similar cycloadditions to carbon-nitrogen multiple bonds are rare. Benzaldehyde N-cyclohexylimine was reported to undergo (2 + 2) photodimerization;[5] however, the product was later shown to be N,N'-dicyclohexyl-1,2-diamino-1,2-diphenylethene.[6] A 1,2-diazetidine[7] and an azetine[8] have been proposed as unstable intermediates in the photoreactions of N-p-diaminobenzylidenaniline and benzonitrile, respectively. Tsuge and co-workers have described the cycloaddition of 2,5-diphenyl-1,3,4-oxadiazole to indene and furan to form (2 + 2) cycloadducts,[9] and Swenton and Hyatt have recently shown that 1,3-dimethyl-6-azauracil photocycloadds to a variety of olefins regioselectively in high yield with acetone sensitization.[10]

We began our search for this elusive mode of photoreactivity by studying nitrogen heterocycles which structurally resembled cyclic α,β-unsaturated ketones. This approach was selected because cyclic α,β-unsaturated ketones undergo facile (2 + 2) photocycloaddition reactions.[11] With cyclic molecules, energy wasting syn-anti isomerization was also eliminated.[12] The first system examined was 2-ethoxypyrrolin-5-one (**1**). (2 + 2) photocycloaddition to the carbon-nitrogen or carbon-oxygen double bonds of **1**, however, was not competitive with Norrish type I cleavage. Ultraviolet irradiation of **1** gave ethoxycyclopropyl isocyanate in high isolated yield and high quantum yield.[13] 3-Ethoxyisoindolone (**2**), the subject of this report, was then selected for investigation because Norrish type I cleavage would be unfavorable, resulting in formation of a high-energy phenyl radical and (2 + 2) photocycloaddition might be competitive.



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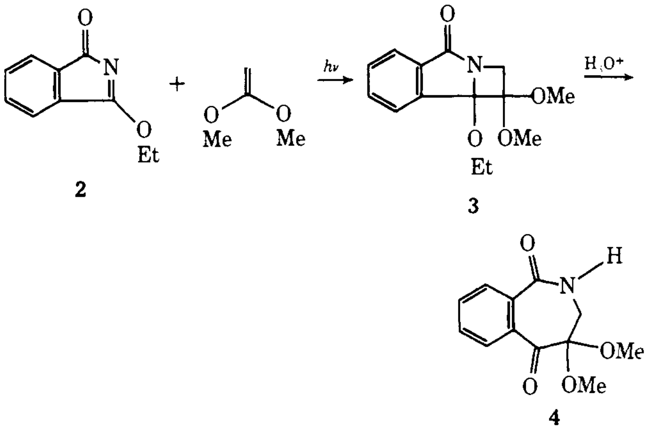
Results

Synthesis of Reactant. 3-Ethoxyiosindolone (**2**) was prepared by the O-alkylation of the silver salt of phthalimide with ethyl iodide. The occurrence of alkylation on oxygen was established by the appearance of an intense carbon-nitrogen double bond stretching band at 6.46 μ in the infrared. In the NMR spectrum, the methylene protons of **2** absorbed at δ 4.77 ppm also consistent with O-alkylation. 3-Ethoxyisoindolone in cyclohexane solvent showed maxima in the ultraviolet spectrum at 216 nm (ϵ 38000), 288 (1900), and 298 (2100). There was no resolved n-π^* band.

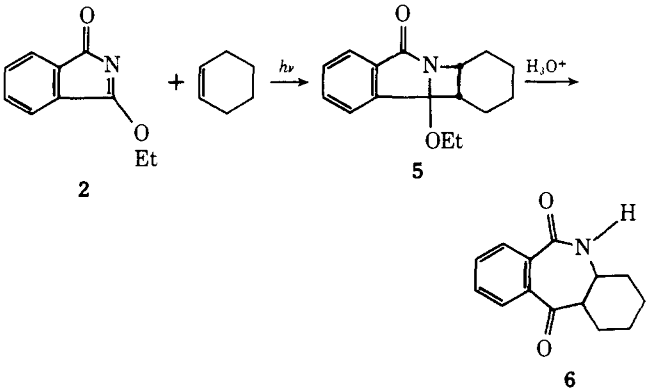
Photochemical Reactions. As predicted, irradiation of **2** with a 450-W mercury lamp through a Corex filter in acetonitrile solvent did not result in formation of products expected from Norrish type I cleavage. 3-Ethoxyisoindolone was slowly destroyed by the irradiation, and high molecular weight products seemed to be formed by an as yet unexplained mechanism.

When **2** was irradiated with a 450-W mercury lamp with a Pyrex filter in *tert*-butyl alcohol, benzene, or methylene chloride solvent in the presence of 4 equiv of 1,1-dimethoxyethene, a (2 + 2) photocycloadduct (**3**) was formed in 50% isolated yield. No reaction was observed when **2** and 1,1-dimethoxyethene were allowed to stand in the dark for an equivalent period of time. The structure of **3** was established by the spectroscopic data (Experimental Section). Characteristically this photocycloadduct and others to be described show a carbonyl stretch (5.84–5.90 μ) and no carbon-nitrogen double bond stretch in the infrared, and the ethoxy protons appear as an ABX$_3$ pattern in the NMR spectrum. The regiochemistry of the cycloaddition was suggested by the chemical shifts of the azetidine methylene protons (δ 3.86 and 4.04 ppm)[14] and was further established by the NMR spectrum of the product of mild hydrolysis of **3**. Treatment of **3** with 3 *N* hydrochloric acid at ambient temperature resulted in ring opening to give the azepinedione **4** in 76% yield. In the NMR spectrum of **4** (Me_2SO-d_6), the methylene protons appeared as a doublet (J = 6.5 Hz) resulting from coupling with the amide proton. Exchange with deuterium oxide resulted in collapse of the doublet to a singlet. The methylene protons of an analogous azepinedione from hydrolysis of a photocycloadduct of the opposite regiochemistry would have appeared as a singlet.



2 **3** **4**

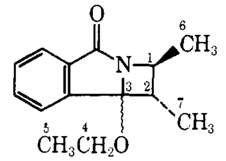
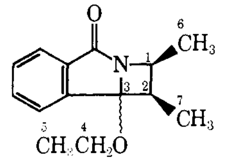
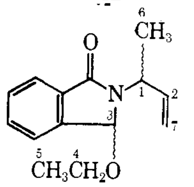
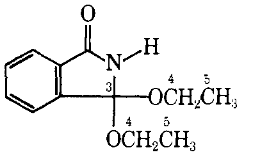
Irradiation of 3-ethoxyisoindolone with 4 equiv of cyclohexene in methylene chloride solvent under similar conditions gave a 51% yield of the (2 + 2) cycloadduct **5**. The cis-anti-cis stereochemistry was assigned on the basis of the NMR spectrum (Experimental Section). The methine proton on the carbon adjacent to nitrogen appeared as a quartet (J = 8.5 Hz) with approximately equal coupling to the remaining methine and adjacent methylene protons. Only a cis-ring juncture has the appropriate dihedral angles to produce this coupling pattern. Since none of the cyclohexane protons were strongly shielded by the benzene ring, as would be expected of a cycloadduct of the cis-syn-cis configuration, the anti configuration was assigned. Hydrolysis of **5** with 3 *N* hydrochloric acid as described gave a benzoazepinedione assigned structure **6**.



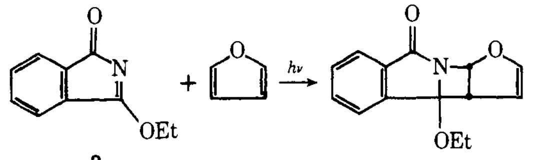
2 **5** **6**

Irradiation of **2** with 3 equiv of furan in methylene chloride solvent yielded cycloadduct **7** in 54% isolated yield. The assignment of regiochemistry was based upon the chemical shifts and splitting patterns of the methine and olefinic protons in the NMR. One methine proton appeared as a doublet at δ 5.63 ppm, and the other methine proton appeared as a doublet of doublets of doublets at δ 4.06 ppm. The chemical shifts of the methine protons of the other regioisomer would be much closer. The photocycloadduct **7** was sensitive to thermal decomposition to starting materials. Sublimation or GLC of **7** resulted in isolation of 3-ethoxyisoindolone.

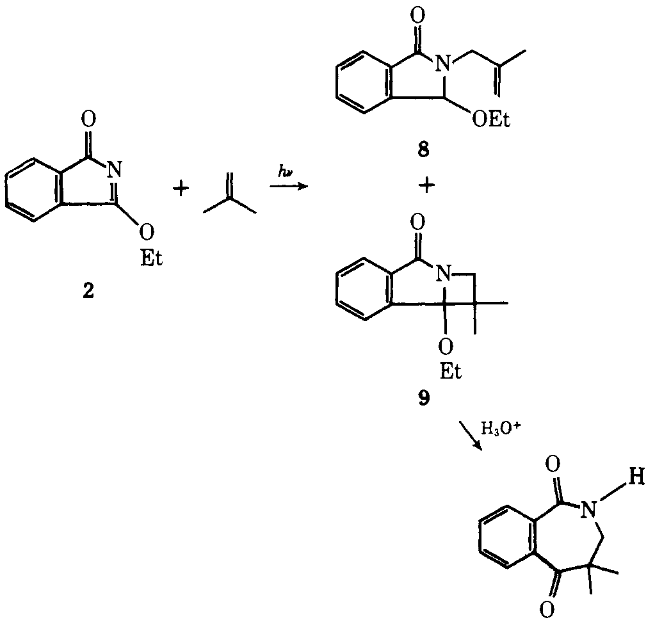
Table I. ^{13}C NMR Spectral Data

Compd	Chemical shifts[a] for carbon number 1	2	3	4	5	6	7
 11	65.23	46.01	99.98	58.44	15.34	23.33	15.58
 12	59.50	41.89	98.87	57.90	15.05	17.47	7.81
 15 + 16	50.48 50.19	138.23 139.20	85.67 85.23	56.84 56.98	15.00 15.00	18.30 17.72	116.15 115.18
			109.01	59.80	15.29		

[a] ^{13}C NMR spectra were obtained by Fourier transform NMR in benzene-d_6, and chemical shifts are reported in ppm from internal Me$_4$Si. Chemical shifts were assigned by noting splitting patterns in off-resonance decoupled spectra and from the chemical shifts of the carbons of the ethoxy group of 3,3-diethoxy-2,3-dihydroisoindolone.



2 7



8 9 2 10

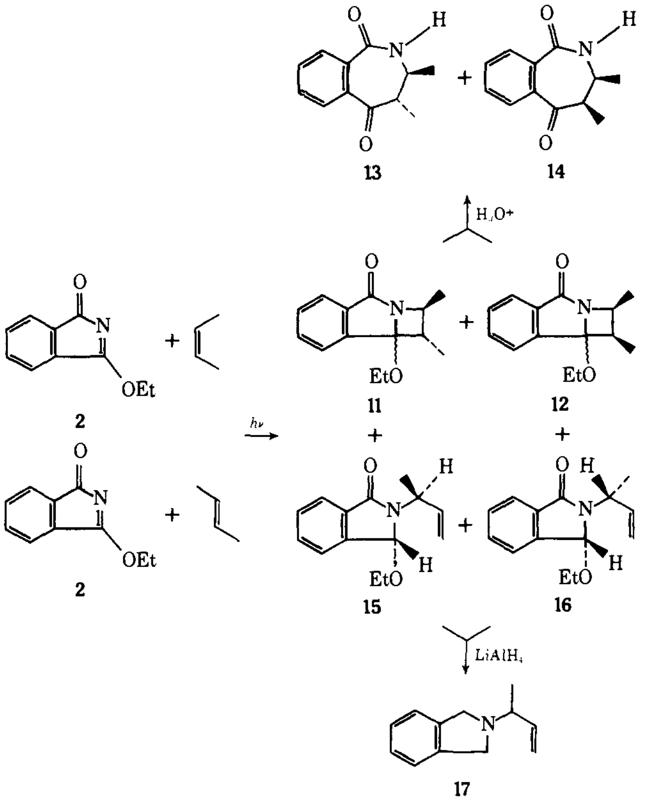
Two products (**8** and **9**) were formed in 63 and 23% uncorrected, gas chromatographic yields, respectively, when 3-ethoxyisoindolone was irradiated with isobutylene. The reaction was carried out in a Pyrex immersion well in methylene chloride solvent at −12°. The major product (**8**) was identified as the product of a photochemical ene type reaction from the spectroscopic data (Experimental Section). Two olefinic protons absorbed at δ 4.83 and 5.00 ppm in the NMR spectrum. The cycloadduct structure (**9**) was assigned to the minor photoproduct from the spectroscopic data and the spectroscopic data of the benzoazepinedione (**10**) from hydrolysis of **9**, using the logic described for the structural assignment of **3**.

Irradiation of 3-ethoxyisoindolone (**2**) with 9 equiv of *cis*-2-butene at −15° in a Pyrex immersion well resulted in four products. Two were formed in 18 and 8% yields and two as a mixture totaling 36% yield. The two products formed in 18 and 8% yields were identified spectroscopically as the (2 + 2) photocycloadducts **11** and **12**, respectively. The assignment of stereochemistry of the methyl groups of **11** and **12** is based upon the methine–methine proton coupling constants of 3.3 and 8.3 Hz, respectively. Similar coupling constants have been observed for cis and trans hydrogens in 1-alkyl-2-phenyl-3-aroylazetidines.[15] Additional evidence for the stereochemical assignment appears in the ^{13}C NMR spectra (Table I). The absorptions of carbons numbered 1, 2, 6, and 7 of the cis isomer (**12**) consistently appear upfield from the absorptions of the same carbons of the trans isomer (**11**) by 4 to 7 ppm. This is consistent with the steric shift predicted for the more crowded carbons of the cis isomer.[16] Hydrolysis of either cycloadduct (**11** or **12**) or a mixture of both with 3 *N* hydrochloric acid gave the same mixture of *cis*- and *trans*-6,7-dimethyl(7*H*)azepine-2,5-diones (**13** and **14**) in 98% yield. The NMR spectrum of the major

Table II. Photoproduct Ratios as a Function of *cis*- and *trans*-2-Butene Concentration

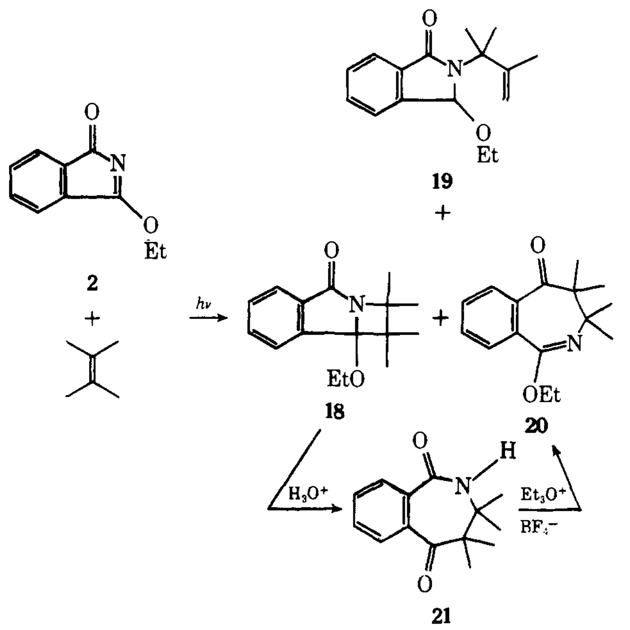
Olefin	Olefin concn, mol/l.	11/12	15/16	(11 + 12)/(15 + 16)
cis-2-Butene	0.92	2.0	3.1	0.72
cis-2-Butene	0.37	2.1	2.9	0.73
trans-2-Butene	0.92	2.1	0.69	1.7
trans-2-Butene	0.37	2.0	0.71	1.8

fraction from the irradiation mixture suggested that it consisted of a mixture of diastereomeric ene products with structures **15** and **16**. Olefinic proton absorptions were observed in the NMR spectrum in the region δ 5.0 to 6.50 ppm, and two methyl doublets of unequal intensity were observed at δ 1.51 and 1.54 ppm. Integration of the methyl doublets gave a diastereomer ratio of 3.0. The ^{13}C NMR spectral data (Table I) are also consistent with a mixture of diastereoisomeric ene products. The structures **15** and **16** were further substantiated by lithium aluminum hydride reduction to a single dihydroisoindolone product **17**.



Identical products in different proportions were obtained when *trans*-2-butene was used as the olefin. The two cycloadducts **11** and **12** were formed in 27 and 13% yields, respectively, and the mixture of diastereomeric ene products were obtained in 24% yield. Integration of the methyl doublets in the NMR spectrum of the ene products gave a diastereomer ratio of 0.70. With both *cis*- and *trans*-2-butene, the product ratios were independent of olefin concentration (see Table II for a summary of the product ratios from *cis*- and *trans*-2-butene).

Three products in 20, 28, and 12% yields were formed when 3-ethoxyisoindolone was irradiated in the presence of tetramethylethylene in methylene chloride solvent. The product in 20% yield was spectroscopically identified as the (2 + 2) photocycloadduct **18**. Its NMR spectrum contained the usual ABX_3 pattern for the ethoxy protons and four methyl singlets. Similarly the product in 28% yield was identified as the ene product **19** from its spectroscopic data.



The product formed in 12% yield was unique with ethoxy protons appearing in the simple triplet-quartet pattern and four methyl groups appearing as one singlet in the NMR spectrum. The benzoazepinone structure **20** was assigned from the spectroscopic data and was confirmed by synthesis from the cycloadduct **18**. Hydrolysis of **18** with 3 *N* hydrochloric acid gave the azepinedione **21** in 95% yield, and *O*-alkylation of **21** with triethyloxonium fluoroborate yielded the benzoazepinone **20** in 44% yield.

Irradition of 3-ethoxyisoindolone in the presence of fumaronitrile gave no cycloadduct formation. Isomerization of the fumaronitrile to maleonitrile did occur. Gas chromatographic comparison of the reaction mixture from this irradiation with that from the benzophenone sensitized fumaronitrile cis-trans isomerization established the identity of maleonitrile in the reaction mixture.

Quantum Yield Measurements. Quantum yields were measured at 3130 Å at 20 ± 0.1° (unless otherwise specified) in a rotating photochemical apparatus. The 3130-Å mercury band was isolated using a Pyrex glass filter and cobaltous sulfate and potassium chromate solution filters. The light was measured with potassium ferrioxalate actinometry,[17] and analyses were obtained by gas chromatography.

The photoreactions of 3-ethoxyisoindolone with 1,1-dimethoxyethene and tetramethylethylene in methylene chloride solvent were chosen for quantum yield studies. Over the concentration range 0.06–2.00 *M*, the quantum yields of product formation were inversely related to the olefin concentration for 1,1-dimethoxyethene and tetramethylethylene (see Table III), and plots of reciprocal of quantum of product formation vs. reciprocal of olefin concentration were nonlinear (Figure 1). For the tetramethylethylene 3-ethoxyisoindolone photoreaction, the product ratios (**18**;**19**; **20**) were also independent of olefin concentration. When reciprocal of total quantum yields for either photoreaction was plotted vs. olefin concentration, linear plots were obtained with the following least-squares slopes and intercepts: 1,1-dimethoxyethene, slope = 0.45 ± 0.04 l./(mol/sec^{-1}), intercept = 1.90 ± 0.04; tetramethylethylene, slope = 0.93 ± 0.03 l./(mol/sec^{-1}), intercept = 1.92 ± 0.02.

3,3,4,4-Tetramethyl-1,2-diazetidine 1,2-dioxide (triplet energy in the range 35.6–42.4 kcal/mol)[18] was employed as a photochemical quencher of the photoreaction of 3-ethoxyisoindolone with tetramethylethylene. Over the concentration range 0.001 to 0.01 *M* of quencher, a linear Stern–Volmer plot was obtained with least-squares slope 87.5 ± 5.1

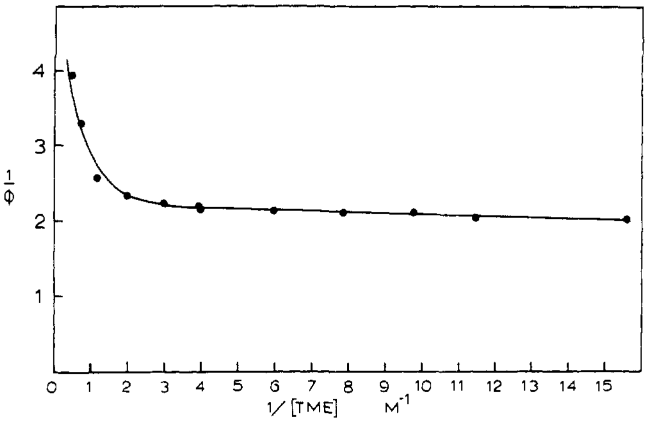


Figure 1. Reciprocal of total quantum yield of product formation vs. reciprocal of tetramethylethylene concentration.

Table III. Quantum Yields of Product Formation as a Function of Olefin Concentration[a]

1,1-Dimethoxyethene		Tetramethylethylene			
[Olefin][b]	ϕ(3)	[Olefin]	ϕ(18)	ϕ(19)	ϕ(20)
0.060	0.52	0.064	0.17	0.25	0.09
0.100	0.47	0.085	0.16	0.24	0.10
0.200	0.49	0.102	0.16	0.22	0.09
0.300	0.50	0.127	0.16	0.23	0.09
0.500	0.48	0.169	0.16	0.22	0.09
0.600	0.48	0.250	0.16	0.21	0.09
0.750	0.46	0.254	0.16	0.21	0.09
1.00	0.45	0.330	0.16	0.21	0.09
1.15	0.42	0.508	0.15	0.20	0.09
1.33	0.40	0.847	0.14	0.18	0.08
1.50	0.38	1.33	0.10	0.15	0.06
2.00	0.35	2.00	0.09	0.12	0.05

[a] The concentration of 3-ethoxyisoindolone was 0.06 *M*, and the solvent was methylene chloride. [b] Olefin concentrations are given in mol/l.

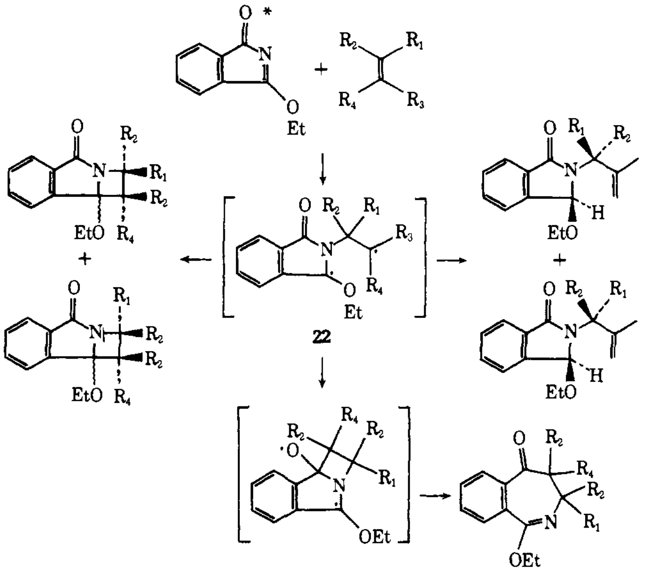
l./mol, and the product ratios **18**:**19**:**20** were independent of quencher concentration.

Discussion

A sufficient mechanism for the photoreactions of 3-ethoxyisoindolone with olefins must account for the formation of cycloadducts, ene products, and azepinone **20**, the regiochemistry, partial stereospecificity observed with *cis*- and *trans*-2-butene (Table II), and the quantum yield data. The photoproduct structures with the exception of **20**, the regiochemistry, and the lack of stereospecificity in cycloaddition are reminiscent of the photoreactions of cyclic α,β-unsaturated ketones with olefins[11] and the triplet state Paterno-Büchi reaction.[3b] The mechanism proposed for the photoreactions of 3-ethoxyisoindolone will be compared with the mechanisms proposed for these now classic cycloaddition reactions.

The product structures and the stereochemical data in Table II suggest the intermediacy of a long-lived 1,4-biradical. A 1,4-biradical such as **22** from reaction of excited 3-ethoxyisoindolone with an olefin could cyclize with complete loss of the stereochemistry of the starting olefin to give azetidine products, undergo intramolecular hydrogen atom transfer to give the ene products, or cyclize at the carbonyl carbon with subsequent or simultaneous carbon-nitrogen bond fragmentation to give the azepinone **20** (see Scheme I) Regiochemistry may then be governed by biradical stability. For both the photoreactions of α,β-unsaturated ketones with olefins and the triplet state Paterno-Büchi reaction,[3] similar 1,4-biradical intermediates have been proposed.[11]

Scheme I



Scheme I does not, however, explain all the stereochemical results. Although there is complete stereochemical scrambling in formation of the cycloadducts **11** and **12**, there is a partial stereospecificity in formation of the ene products **15** and **16**, and the ratio of cycloadducts to ene products is olefin dependent. A single intermediate such as **22** cannot explain both the stereospecificity in formation of the ene products and the lack of stereospecificity in formation of the cycloadducts.

Involvement of two 3-ethoxyisoindolone reactive excited states is one possible explanation of the stereochemical data. However, since photoproduct ratios are olefin concentration independent under all photochemical conditions examined, the two excited states would have to have nearly identical life-times, an unlikely possibility. A kinetic mechanism which explains all the stereochemical data and utilizes one reactive excited state will be presented after a discussion of the quantum yield results.

Initially, the nonlinearity of the plots of reciprocal of quantum yield vs. reciprocal of olefin concentration (Figure 1) was suspected to result from an olefin solvent effect. At high olefin concentrations, the olefin might be affecting the solvent properties of methylene chloride. This possibility was eliminated by quantum yield experiments in which tetramethylethylene concentration was held constant at 0.73 *M*, while cyclohexane was added to imitate higher hydrocarbon concentrations. Over the cyclohexane concentration range 0.0 to 1.18 *M*, the quantum yield of total product formation remained constant at 0.40.

Olefin 3-ethoxyisoindolone ground state complexing was also considered as a possible explanation for the nonlinearity of the plots in Figure 1. The uv absorption spectrum of **2** was independent of the presence of tetramethylethylene over the concentration range 0 to 1.0 *M*. Ground state complexing, then, must not be significant unless the uv spectra of the complex and **2** are virtually identical, an unlikely occurrence.

In the absence of a solvent effect on quantum yield and ground state complexing, the nonlinearity of the plots of reciprocal of quantum yield vs. reciprocal of olefin concentration (Figure 1) and the linearity of the plots of reciprocal of quantum yield vs. olefin concentration indicated that (a) the photoreactions occur from the triplet state of 3-ethoxyisoindolone, (b) all the triplets formed are captured by olefin over the olefin concentration range examined, and (c) olefin is a quencher of the singlet state of 3-ethoxyisoindolone. It is interesting to note that nonlinear quantum yield plots of the type shown in Figure 1 indicate the multiplicity of the reactive excited state without the application of additional energy transfer techniques. The triplet multiplicity of the reactive excited state was further substantiated by the linear Stern–Volmer plot with 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide which is reported not to be an effective singlet quencher.[18] Lack of reaction with fumaronitrile (triplet energy < 60 kcal/mol)[3b] coupled with isomerization to maleonitrile is also consistent with quenching of a 3-ethoxyisoindolone triplet excited state.[3b,19]

A triplet reaction mechanism with singlet quenching consistent with all the experimental data is shown in Scheme II. The partial stereospecificity in formation of the ene product and lack of stereospecificity in formation of the cycloadducts is explained by two reaction paths for ene product formation, one partially stereospecific path via an exciplex and one nonstereospecific path via a long-lived biradical. The path to ene product via the exciplex (k_{ep}) may actually be completely stereospecific.

Scheme II

$$\text{isoindolone} + h\nu \longrightarrow {}^1\text{isoindolone}^*$$

$${}^1\text{isoindolone}^* \xrightarrow{k_d} \text{isoindolone}$$

$${}^1\text{isoindolone}^* + \text{olefin} \xrightarrow{k_{qs}} \text{isoindolone} + \text{olefin}$$

$${}^1\text{isoindolone}^* \xrightarrow{k_{isc}} {}^3\text{isoindolone}^*$$

$${}^3\text{isoindolone}^* + \text{olefin} \xrightarrow{k_e} \text{exciplex}$$

$$\text{exciplex} \xrightarrow{k_{ed}} \text{isoindolone} + \text{olefin}$$

$$\text{exciplex} \xrightarrow{k_{eb}} \text{biradical}$$

$$\text{exciplex} \xrightarrow{k_{ep}} \text{ene product}$$

$$\text{biradical} \xrightarrow{k_{bp}} \text{cycloadduct} + \text{ene product} + \text{azepinone}$$

$$\text{biradical} \xrightarrow{k_{bd}} \text{isoindolone} + \text{olefin}$$

$${}^3\text{isoindolone}^* + \text{quencher} \xrightarrow{k_{qt}} \text{isoindolone} + {}^3\text{quencher}^*$$

$$\frac{1}{\phi(\text{total})} = \left(\frac{1}{\phi_{isc}} + \frac{k_{qs}[\text{olefin}]}{k_{isc}}\right)\left(\frac{(k_{ep} + k_{eb} + k_{ed})(k_{bp} + k_{bd})}{k_{eb}k_{bp} + k_{ep}(k_{bp} + k_{bd})}\right)$$

$$\frac{\phi_0}{\phi_q}(\text{total}) = 1 + \frac{k_{qt}[\text{quencher}]}{k_e[\text{olefin}]}$$

In the proposed mechanism, both exciplex decay (k_{ed}) and biradical decay (k_{bd}) are probably inefficient processes. The intercepts of the plots of reciprocal of quantum yield vs. olefin concentration are olefin independent. If k_{ed} and k_{bd} are both negligible, then the expression for reciprocal of quantum yield simplifies to $1/\phi = 1/\phi_{isc} + k_{qs}[\text{olefin}]/k_{isc}$, and the intercept would be $1/\phi_{isc}$ and olefin independent. The inefficiency of biradical decay is also suggested by the fact that *cis*-2-butene is only isomerized to a small extent (see Experimental Section) to *trans*-2-butene during the course of the photoreaction.

Assuming the mechanism in Scheme II, several physical constants can be estimated. The ratio k_{qs}(tetramethylethylene/k_{qs}(1,1-dimethoxyethene) can be calculated from the ratio of the slopes of the plots of reciprocal of quantum yield vs. olefin concentration and is equal to 2.08. The intercepts of the plots of $1/\phi$ vs. olefin concentration give an intersystem crossing efficiency of 3-ethoxyisoindolone in the absence of olefin equal to 0.52 assuming k_{ed} and k_{bd} are small. If this assumption is incorrect, 0.52 is a minimum value for the intersystem crossing efficiency. If we assume that triplet quenching occurs at a diffusion-controlled rate (8×10^9 l./mol/sec for diffusion in methylene chloride at 20°),[20] the Stern–Volmer slope gives a value for $k_e = 7 \times 10^8$ l./mol/sec.

The mechanism of singlet quenching of 3-ethoxyisoindolone by olefins may actually be more complex than indicated in Scheme II. Exciplexes have been proposed as intermediates in singlet quenching processes[21] and in singlet (2 + 2) cycloadditions[22] from indirect evidence (fluorescence quenching studies) and in some cases from direct observation of exciplex emission. Fluorescence quenching studies were not possible here since 3-ethoxyisoindolone does not fluoresce in the presence or absence of tetramethylethylene.

Chapman and Lura have proposed the existence of a reversibly formed singlet exciplex in the photocycloaddition reaction of excited *trans*-stilbene with tetramethylethylene.[23] The intermediacy of a singlet exciplex was suggested by a negative temperature dependence of quantum yield. The quantum yield of stilbene cycloaddition increased by almost a factor of 3 as the temperature was lowered from 65 to 5°, and assumption of a simple mechanism without reversible exciplex formation gave a rate constant for cycloaddition which decreased with increasing temperature.

To gain some experimental evidence for the possible existence of a singlet exciplex in the quenching of 3-ethoxyisoindolone singlets, the quantum efficiency was examined as a function of temperature. The quantum yield of cycloaddition to tetramethylethylene was measured as a function of olefin concentration at 40°. The plot of reciprocal of quantum yield vs. olefin concentration was linear with slope 1.59 ± 0.17 l./mol/sec and intercept 2.46 ± 0.15. If we assume that k_d and k_{isc} are temperature independent and if we apply the mechanism in Scheme II, then $k_{qs}(40°)/k_{qs}(20°) = 1.33 \pm 0.29$ can be calculated from the slopes and intercepts of the plots of reciprocal of quantum yield vs. tetramethylethylene concentration. If k_d and/or k_{isc} increase with temperature, then 1.33 is a minimum value for $k_{qs}(40°)/k_{qs}(20°)$. Clearly the data do not indicate a negative temperature dependence for k_{qs} and do not demand a more complex mechanism such as reversible singlet exciplex quenching.

The data presented also do not demand the formation of a triplet exciplex. However, at the very least the reaction mechanism must include a path to ene products in which there is restricted rotation about the original olefin double bond and a path to cycloadducts in which there is free rotation about the original olefin double bond, both paths occurring from a common triplet state. Although not demanded, a triplet exciplex mechanism is not an unreasonable mechanistic pathway and is thought to be important in (2 + 2) cycloadditions to carbon–carbon[11,24] and carbon–oxygen double bonds.[3b] The calculated rate constant $k_c = 7 \times 10^8$ l./mol/sec is the same order of magnitude as the rate constants 6.6×10^8 and 1.1×10^8 l./mol/sec calculated for the proposed triplet excimer formation in the (2 + 2) photodimerization of 2-cyclopentenone and 2-cyclohexenone, respectively.[24] If an exciplex precedes a biradical intermediate (such as **22**) as indicated in Scheme II, the regiochemistry of the photoreactions may be governed by the exciplex and not by the biradical. Olefin and excited 3-ethoxyisoindolone dipoles and/or coefficients of the LUMO and HOMO wavefunctions of the reactants may then determine regiochemistry.[25] The fact that cycloadducts **3** and **7** have opposite regiochemistry suggests that dipoles are not the only factor to be considered.

In summary we have reported the photoreactions of 3-ethoxyisoindolone with olefins. The modes of photochemical reactivity include the elusive (2 + 2) cycloaddition reaction to a carbon–nitrogen double bond, a photochemical ene reaction, and a novel cycloaddition of an olefin at the 2–3 positions of a conjugated system. The ene reaction is partially stereospecific; whereas the cycloaddition is not. All of the photoreactions occur from a common 3-ethoxyisoindolone triplet state, and the olefins are quenchers of the 3-ethoxyisoindolone singlet state. A possible mechanism which explains the data in terms of a triplet exciplex is shown in Schemes I and II.

Experimental Section

Melting points and boiling points are uncorrected. Melting points were measured with a Thomas-Hoover Unimelt apparatus. Perkin-Elmer 337 and Cary 14 spectrophotometers were used to determine ir and uv spectra, respectively. NMR spectra were recorded with Varian A-60A and HA-100 and JEOL PS-100 spectrometers, and chemical shifts are reported in parts per million on the δ scale from internal tetramethylsilane. The mass spectra were obtained at 70 eV with a Varian Mat CH-5 spectrometer. GLC analyses and isolations were performed with a Varian Aerograph Model 1700 gas chromatograph equipped with a thermal conductivity detector, and peak areas were measured by disc integration. Gas chromatographic yields were corrected for differences in detector response using an internal standard. Preparative irradiations were conducted with a Hanovia 450-W mercury lamp in a water-cooled immersion well. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

3-Ethoxyisoindolone (2). The synthesis described is a modification of the procedure described for the synthesis of 2-ethoxypyrrolin-5-one.[13] A solution containing 72.0 g (0.42 mol) of silver nitrate in 100 ml of distilled water was added to a stirred aqueous solution of 26.0 g (0.24 mol) of sodium carbonate. The resultant yellow precipitate was collected by vacuum filtration and thoroughly washed with distilled water. This silver carbonate and succeeding silver salts were maintained in the dark to avoid light catalyzed decomposition. A 500-ml three-necked flask was charged with the freshly prepared silver carbonate, 20.0 g (0.12 mol) of freshly sublimed phthalimide, 0.5 g of silver nitrate catalyst, and 250 ml of 95% ethanol. The reaction mixture was refluxed with stirring for 48 hr. Solvent was then removed by distillation at 80–85°, and the salt was dried under vacuum at 85° (0.02 mm) for 12 hr. To the flask containing the dried silver salt were added 250 ml of reagent grade chloroform (distilled from calcium hydride) and 42.4 g (0.27 mol) of ethyl iodide. The mixture was refluxed with stirring for 72 hr. The silver salts were removed by vacuum filtration, and the filtrate was concentrated by rotary evaporation until crystallization ensued. A crystalline product (14.9 g, mp 130–135°) was collected by vacuum filtration in successive fractions. Vacuum sublimation [100° (0.02 mm)] afforded 14.1 g (59%) of 3-ethoxyisoindolone (mp 131–134°). The 3-ethoxyisoindolone gave the following spectroscopic absorptions: ir (KBr), 5.68, 5.72, and 6.46 μ; NMR ($DCCl_3$) δ 1.55 (t, J = 7 Hz, 3 H), 4.77 (q, J = 7 Hz, 2 H), and 7.42–7.92 ppm (m, 4 H); uv λ_{max} (cyclohexane) 216 nm (ϵ 38000), 288 (1900), and 298 (2200); mass spectrum *m/e* 175 (M^+, 9) 148 (13), 147 (17), 130 (19), 105 (16), 104 (85), 103 (base), 102 (20), 77 (13), and 76 (36).

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.54; H, 5.16; N, 8.05.

Photocycloaddition of 3-Ethoxyisoindolone (2) to 1,1-Dimethoxyethene. A solution containing 2.0 g (0.011 mol) of 3-ethoxyisoindolene, 4.0 g (0.045 mol) of 1,1-dimethoxyethene, and 140 ml of reagent grade *tert*-butyl alcohol (distilled from sodium) was irradiated for 30 min with a nitrogen atmosphere in a Pyrex immersion well with a 450-W mercury lamp. Analysis by TLC on basic alumina eluting with benzene indicated complete destruction of starting material and a single product. Rotary evaporation of the solvent and excess dimethoxyethene yielded 1.8 g of an impure solid. Recrystallization from Skelly solve B afforded 1.5 g (50%) of 3,4-benzo-6,6-dimethoxy-5-ethoxyazabicyclo[3.2.0]hept-3-en-2-one (**3**) (mp 62–65°). The cycloadduct gave the following spectroscopic data: ir (KBr) 5.82 and 6.86 μ; NMR ($DCCl_3$) δ 1.18 (t, J = 7.1 Hz, 3 H), 3.12 and 3.45 (AB of ABX_3 pattern, $J_{AX} = J_{BX}$ = 7.1, J_{AB} = 9.0 Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 3.17 (s, 3 H), 3.45 (s, 3 H), 3.86 (d, J = 10 Hz, 1 H), 4.04 (d, J = 10 Hz, 1 H), and 7.30–7.95 ppm (m, 4 H); mass spectrum *m/e* 263 (M^+, 21), 235 (9), 234 (53), 204 (12), 176 (11), 163 (19), 160 (69), 149 (29), 133 (11), 130 (12), 105 (15), 104 (20), 89 (11), 88 (base), 71 (31), and 76 (19).

Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.94; H, 6.54; N, 5.36.

Photocycloaddition of 3-Ethoxyisoindolone (2) to Cyclohexene, A Pyrex immersion well was charged with 1.3 g (0.0074 mol) of 3-ethoxyisoindolone, 3.9 g (0.037 mol) of Baker reagent grade cyclohexene, and 140 ml of reagent grade methylene chloride (distilled from calcium hydride). After degassing for 30 min with nitrogen, the stirred solution was irradiated for 0.5 hr. The solvent and excess cyclohexene were removed by rotary evaporation yielding two fractions of crystalline material (0.65 g, mp 84–86°). The residue was placed in a 50-ml round-bottomed flask and sublimed [100° (8 mm)] into an 8-mm tube using a Büchi 200-W Kugelrohr oven. The flask was removed, the tube was sealed at the bottom, and the material was then resublimed. The sublimed material was combined with the fractions from crystallization and the total sublimed to yield 0.98 g (51%, mp 84–85°) of the cis–anti–cis isomer of 4,5-benzo-6-ethoxy-2-azatricyclo[5.4.0.0^{2,6}]undec-4-en-3-one (**5**). The cycloadduct gave the following spectroscopic data: ir (KBr) 5.90 and 6.21 μ; NMR ($DCCl_3$), δ 1.18 (t, J = 7.1 Hz, 3 H), 2.97 and 3.37 (AB of ABX_3 pattern, $J_{AX} = J_{BX}$ = 7.1, J_{AB} = 8.8 Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 1.1–2.5 (m, 8 H), 2.53–2.84 (m, 1 H), 4.05 (q, J = 8.5 Hz, 1 H), and 7.3–8.1 ppm (m, 4 H); mass spectrum *m/e* 257 (M^+, 3), 229 (10), 228 (53), 177 (10), 176 (85), 149 (10), 148 (base), and 130 (52).

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.58; H, 7.49; N, 5.50.

Photoreaction of 3-Ethoxyisoindolone (2) with Isobutylene, A 2.0-g quantity (0.011 mol) of 3-ethoxyisoindolone and 125 ml of methylene chloride (distilled from calcium hydride) were placed in a dry Pyrex immersion well, and the solution was degassed with nitrogen. The well was immersed in a bath maintained at −12°. A dry ice cold finger condenser was added, and approximately 13 ml of isobutylene was condensed into the solution. The mixture was then irradiated for 30 min with a 450-W mercury lamp while nitrogen was bubbled through the reaction mixture. Complete destruction of starting material was indicated by alumina TLC analysis eluting with benzene. Rotary evaporation of the solvent followed by high vacuum trap-to-trap distillation [120° (10^{-5} mm)] of the concentrate resulted in the isolation of a mixture of two products as indicated by NMR and GLC. A total of 2.27 g (86%) of the mixture was recovered and analyzed by GLC using a 7 ft × 0.25 in. column of 5% Apiezon L on 60–80 mesh Diatoport S at 195° (injection port and column oven) (He flow, 60 ml/min). The products appeared in the ratio of 1:2.78 (uncorrected for differences in GLC response) with retention times of 6 and 10.2 min, respectively. Analytical samples were obtained by collection from a 9.3 ft × 0.375 in. column of identical packing using the same conditions as those described for the analysis. The major product (63%, uncorrected gas chromatographic yield), a viscous clear liquid, was identified as 2,3-dihydro-3-ethoxy-2-[3′-(2′-methylpropenyl)]isoindolone (**8**) and gave the following spectroscopic data: ir (neat) 5.86 μ; NMR ($DCCl_3$) δ 1.14 (t, J = 7 Hz, 3 H), 1.75 (s, 3 H), 3.06 and 3.21 (AB of an ABX_3 pattern, $J_{AX} = J_{BX}$ = 7.0, J_{AB} = 9.0 Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 3.70 (d, J = 15.2 Hz, 1 H), 4.55 (d, J = 15.2 Hz, 1 H), 4.83 (m, 1 H), 5.00 (m, 1 H), 5.85 (s, 1 H), and 7.30–8.05 ppm (m, 4 H); mass spectrum *m/e* 231 (M^+, 79), 202 (58), 187 (36), 186 (base), 185 (22), 160 (17), 148 (26), 146 (38), 145 (28), 133 (60), 132 (34), 130 (19), 127 (13), 105 (30), 104 (55), 99 (19), 90 (17), and 77 (34).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.74; H, 7.44; N, 6.08.

The minor product (23%, uncorrected gas chromatographic yield) was identified as 3,4-benzo-6,6-dimethyl-5-ethoxyazabicyclo[3.2.0]hept-3-en-2-one (**9**) (mp 35–37°) and gave the following spectroscopic data: ir ($CHCl_3$) 5.90 μ; NMR ($DCCl_3$) δ 0.66 (s, 3 H), 1.17 (t, J = 7.0 Hz, 3 H), 1.40 (s, 3 H), 2.93 and 3.29 (AB of an ABX_3 pattern $J_{AX} = J_{BX} = 7.0$, $J_{AB} = 9.5$ Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 3.50 (d, J = 9.0 Hz, 1 H), 3.94 (d, J = 9.0 Hz, 1 H), and 7.23–8.15 ppm (m, 4 H); mass spectrum *m/e* 231 (M^+, 2), 203 (30), 202 (base), 186 (14), 176 (25), 160 (25), 148 (78), 130 (68), 104 (22), 103 (28), 102 (17), and 77 (22).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.60; H, 7.45; N, 6.10.

Photocycloaddition of 3-Ethoxyisoindolone (2) to Furan. A solution containing 1.0 g (0.0057 mol) of 3-ethoxyisoindolone and 1.55 g (0.023 mol) of reagent grade furan in 140 ml of reagent grade methylene chloride (distilled from calcium hydride) was degassed for 30 min with nitrogen and irradiated in a Pyrex immersion well with a 450-W mercury lamp. Alumina TLC analysis eluting with benzene showed complete destruction of starting material after 0.5 hr of irradiation. Rotary evaporation of the solvent and excess furan yielded an impure solid retaining some solvent. Attempted purification of the product by GLC using an Apiezon L on Diatoport S column failed. 3-Ethoxyisoindolone was the only product collected, suggesting thermal fragmentation to starting material on the column. Attempted high vacuum sublimation at 100° (10^{-5} mm) resulted in similar contamination of the adduct with starting material. The product was dissolved in benzene and concentrated to a viscous solution. Then the volume was increased 50% by the addition of anhydrous ether. Crystallization was allowed to proceed for 14 hr. Two fractions totaling 0.75 g (54%) of a slightly yellow crystalline material were collected and identified as 4,5-benzo-6-ethoxy-10-ox-2-azatricyclo[$5.3.0.0^{2,6}$]deca-4,8-dien-3-one (**7**). The cycloadduct gave the following spectral absorptions: ir (KBr) 5.84 and 6.20 μ; NMR ($DCCl_3$) δ 1.08 (t, J = 7.0 Hz, 3 H), 2.79 and 3.22 (AB of an ABX_3 pattern, $J_{AX} = J_{BX} = 7.0$, J_{AB} = 9.0 Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 4.06 (d of d of d, J = 6.2, 2.9, and 1.2 Hz, 1 H), 5.35 (t, J = 2.9 Hz, 1 H), 5.63 (d, J = 6.2 Hz, 1 H), 6.68 (d of d, J = 2.9 and 1.2 Hz, 1 H), and 7.28–8.13 ppm (m, 4 H); mass spectrum *m/e* 243 (M^+, 11), 214 (27), 186 (72), 147 (base), 130 (26), 105 (10), 104 (27), 103 (38), 78 (22), 77 (42), and 76 (20).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.27; H, 5.39; N, 5.76.

Photoreaction of 3-Ethoxyisoindolone (2) with Fumaronitrile, A Pyrex immersion well was charged with 1.0 g (0.0057 mol) of 3-ethoxyisoindolone, 1.8 g (0.023 mol) of fumaronitrile, and 140 ml of reagent grade methylene chloride (distilled from calcium hydride). The solution was degassed with nitrogen prior to and during irradiation with a 450-W mercury lamp for 3.5 hr. The solvent was removed by rotary evaporation and an NMR spectrum of the crude sample obtained. The NMR spectrum showed the presence of maleonitrile in addition to 3-ethoxyisoindolone and fumaronitrile. Maleonitrile was identified by comparison of its NMR spectrum and GLC retention time with a sample prepared by benzophenone sensitized cis-trans isomerization of fumaronitrile.

Photoreaction of 3-Ethoxyisoindolene (2) with *cis*- and *trans*-2-Butene, A 2.0-g quantity (0.0057 mol) of 3-ethoxyisoindolone and 125 ml of reagent grade methylene chloride (distilled from calcium hydride) were placed in a dry Pyrex immersion well, and the solution was degassed with nitrogen. The well was immersed in a calcium chloride–water bath (20 g of calcium chloride–100 g of water) maintained as an ice slurry at −15° by addition of dry ice. Approximately 15 ml of *cis*-2-butene (Matheson) was condensed into the solution, and the mixture was irradiated with a 450-W mercury lamp for 30 min maintaining a nitrogen atmosphere. Complete destruction of isoindolone was indicated by alumina TLC analysis eluting with benzene. Rotary evaporation of the solvent and filtration to remove polymer yielded 2.11 g (80%) of a mixture of four products. Analysis by GLC using a 7 ft × 0.25 in. column of 5% Apiezon L on 60–80 mesh Diatoport S at 200° (injection port and column oven) (He flow, 60 ml/min) showed three peaks at retention times 4.8, 6.1, and 7.8 min in the ratio of 2.0:1.0:4.0, respectively (corrected for differences in GLC response). The peak at retention time (7.8 min) was shown to consist of a mixture of diastereoisomers by NMR analysis (vide infra). Analytical samples were obtained by collection from a 9.3 ft × 0.375 in. GLC column of identical packing and under identical conditions as described for the analysis.

The experimental quantities and conditions of the irradiation were duplicated substituting *trans*-2-butene for *cis*-2-butene. A 2.19-g (83%) yield of the mixture of the same four products was obtained. GLC analysis of the mixture indicated that the products at retention times 4.8, 6.1, and 7.8 min were formed in the ratio of 1.9:1.0:1.7, respectively (corrected for differences in GLC response).

The 4.8-min retention time product (18% from *cis*-2-butene, 27% from *trans*-2-butene, GLC yields), a viscous, clear liquid, was identified as 3,4-benzo-*trans*-6,7-dimethyl-5-ethoxyazabicyclo-[3.2.0]hept-3-en-2-one (**11**) and gave the following spectroscopic data: ir ($CHCl_3$) 5.91 μ; NMR ($DCCl_3$) δ 0.71 (d, J = 7.3 Hz, 3 H), 1.17 (t, J = 7.0 Hz, 3 H), 1.68 (d, J = 6.6 Hz, 3 H), 2.58 (d of q, J = 7.3 and 3.3 Hz, 1 H), 2.93 and 3.32 (AB of an ABX_3 pattern, $J_{AX} = J_{BX} = 7.0$, J_{AB} = 9.2 Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 3.53 (d of q, J = 6.6 and 3.3 Hz, 1 H), and 7.3–8.1 ppm (m, 4 H); mass spectrum *m/e* 231 (M^+, 1) 202)19), 176 (13), 148 (27), 130 (20), 85 (65), and 83 (base).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.72; H, 7.36; N, 6.06. Found: C, 72.68; H, 7.33; N, 6.15.

The 6.1-min retention time product (8% from *cis*-2-butene, 13% from *trans*-2-butene, GLC yields), a viscous, clear liquid, was identified as 3,4-benzo-*cis*-6,7-dimethyl-5-ethoxyazabicyclo-[3.2.0]hept-3-en-2-one (**12**) and gave the following spectroscopic data: ir ($CHCl_3$) 5.90 μ; NMR ($DCCl_3$) δ 1.12 (t, J = 7.1 Hz, 3 H), 1.18 (d, J = 7.4 Hz, 3 H), 1.51 (d, J = 7.0 Hz, 3 H), 2.80 (d of q. J = 8.5 and 7.4 Hz, 1 H), 2.97 and 3.32 (AB of an ABX_3 pattern, $J_{AX} = J_{BX} = 7.1$, J_{AB} = 9.0 Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 4.08 (d of q, J = 8.5 and 7.0 Hz, 1 H), and 7.2–8.1 ppm (m, 4 H); mass spectrum *m/e* 231 (M^+, 2), 202 (15), 176 (10), 148 (20), 130 (14), 87 (11), 85 (69), and 83 (base).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.72; H, 7.36; N, 6.06. Found: C, 72.65; H, 7.39; N, 6.04.

The 7.8-min retention time product (36% from *cis*-2-butene, 24% from *trans*-2-butene, GLC yields) was identified as a mixture of the diastereoisomers of 2,3-dihydro-3-ethoxy-2-[3′-(1′-butenyl)]isoindolone (**15** and **16**) and gave the following spectroscopic data: ir ($CHCl_3$) 5.93 μ; NMR ($DCCl_3$) δ 1.10 (t, J = 7.0 Hz, 3 H), 1.51 and 1.54 (doublets from diastereomers, J = 7.0 Hz, total area 3 H), 2.99 and 3.28 (AB of ABX_3 pattern, $J_{AX} = J_{BX} = 7.0$, J_{AB} = 9.0 Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign, 2 H), 4.85 (broad q, J = 7.0 Hz, 1 H), 5.07–5.50 (m, 2 H), 6.01 (s, 1 H), 5.85–6.50 (m, 1 H), and 7.40–8.05 ppm (m, 4 H); mass spectrum *m/e* 231 (M^+, 5), 132 (12), 87 (11), 85 (64), and 83 (base).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.72; H, 7.36; N, 6.06. Found: C, 72.89; H, 7.46; N, 6.12.

Integrated peak areas from 100-MHz NMR spectra in the region of 1.53 ppm showed a consistent variance in diastereomer ratio with alkene used. Using *cis*-2-butene or *trans*-2-butene, this ratio was 3.0 or 0.70, respectively.

Effect of 2-Butene Concentration on Diastereomer Ratio, A solution of 8.0 g of *cis*-2-butene in 140 ml of spectrograde methylene chloride (distilled from calcium hydride) was prepared in a cold room maintained at −10°. Two 100-ml volumetric flasks were charged with 0.50 g of 3-ethoxyisoindolone and 100 or 40 ml, respectively, of the above solution. The solutions were diluted to the mark with additional solvent as needed. The solutions of olefin and isoindolone were then irradiated to completion in a Pyrex immersion well (45 min) with a 450-W mercury lamp. During the irradiation, the temperature was maintained at −15° with a refrigerated bath. The above procedure was duplicated using *trans*-2-butene. The products **15** and **16** from each irradiation were collected with a preparative GLC column as previously described, and NMR spectra were obtained. Integration of the NMR spectra gave the diastereomer ratios shown in Table II.

Test for Isomerization of *cis*-2-Butene by 3-Ethoxyisoindolone (2), A Pyrex immersion well was charged with 0.67 g (0.012 mol) of *cis*-2-butene, 1.05 g (0.0060 mol) of 3-ethoxyisoindolone, and 100 ml of spectrograde methylene chloride (distilled from calcium hydride). The solution was degassed with nitrogen and irradiated to completion at −15°. The resultant reaction mixture was analyzed with a 14 ft × 0.25 in., 25% β,β-oxydipropionitrile on 80–100 mesh Chromosorb P, GLC column maintained at 25° (detector 100°, He flow 60 ml/min). A 14% conversion of *cis*-2-butene to *trans*-2-butene was determined by approximating GLC peak areas as height times width at half-height.

A solution containing 0.067 g (0.0012 mol) of *cis*-2-butene and 0.105 g (0.0060 mol) of 3-ethoxyisoindolone in 100 ml of spectrograde methylene chloride (distilled from calcium hydride) was prepared. Three quantum yield sample tubes (vide infra) were charged with 3.0 ml each of the above solution, freeze–thaw degassed, sealed, and irradiated for 4 hr under quantum yield conditions (vide infra). GLC analysis as described indicated negligible cis-trans isomerization. Under these conditions, 9.3% of the 3-ethoxyisoindolone was destroyed.

Photoreaction of 3-Ethoxyisoindolone (2) with Tetramethylethylene. A solution containing 1.0 g (0.0057 mol) of 3-ethoxyisoindolone, 2.0 g (0.024 mol) of tetramethylethylene (Aldrich, gold label), and 120 ml of reagent grade methylene chloride distilled from calcium hydride was degassed with nitrogen. The mixture was irradiated in a Pyrex immersion well for 45 min with a nitrogen atmosphere. Complete destruction of 3-ethoxyisoindolone was indicated by both alumina TLC eluting with benzene and GLC. Rotary evaporation and filtration to remove polymer gave 1.26 g (85%) of a mixture of three products. Analysis by GLC using a 7 ft × 0.25 in. column of 5% Apiezon L on 60–80 mesh Diatoport S at 200° (injection port and column oven) (He flow, 60 ml/min) indicated the products were formed in the ratio of 2.0:1.0:2.6 (corrected for differences in GLC response) at retention times 7.13, 8.15, and 11.25 min, respectively. Products were isolated by preparative GLC using a 9.3 ft × 0.375 in. column of identical packing material using the same elution conditions.

The 7.13-min retention time product, a viscous clear liquid, was identified as 3,4-benzo-6,6,7,7-tetramethyl-5-ethoxyazabicyclo[3.2.0]hept-3-en-2-one (**18,** 20% GLC yield) and gave the following spectral absorptions: ir ($CHCl_3$) 5.96 μ; NMR ($DCCl_3$) δ 0.70 (s, 3 H), 1.12 (t, J = 6.3 Hz, 3 H), 1.21 (s, 3 H), 1.36 (s, 3 H), 1.61 (s, 3 H), 2.85 and 3.23 (AB of an ABX_3 pattern, $J_{AX} = J_{BX} = 6.3$, $J_{AB} = 9.0$ Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), and 7.37–8.15 ppm (m, 4 H); mass spectrum *m/e* 259 (M^+, 34) 230 (50), 203 (32), 202 (35), 176 (37), 175 (41), 174 (21), 173 (base), 172 (12), 159 (18), 148 (39), 145 (34), 131 (14), 130 (32), 129 (12), 115 (21), 104 (21), 84 (23), and 77 (21).

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.13; H, 8.11; N, 5.41. Found: C, 74.05; H, 8.15; N, 5.38.

The 8.15-min retention time product, a viscous clear liquid, was identified as 3,4-benzo-6,7-dihydro-2-ethoxy-6,6,7,7-tetramethyl-(7*H*)azepin-5-one (**20,** 12% GLC yield) and gave the following spectroscopic data: ir ($CHCl_3$) 5.96 μ; NMR ($DCCl_3$) δ 1.23 (s, 12 H), 1.36 (t, J = 6.9 Hz, 3 H), 4.22 (q, J = 6.9 Hz, 2 H), and 7.37–8.17 ppm (m, 4 H); mass spectrum *m/e* 259 (M^+, 28), 230 (12), 204 (12), 203 (80), 176 (17), 175 (base), 173 (21), 159 (12), 145 (14), 130 (26), 104 (19), and 77 (18).

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.13; H, 8.11; N, 5.41. Found: C, 74.09; H, 8.03; N, 5.44.

The 11.25-min retention time product, a viscous clear liquid, was identified as 2,3-dihydro-3-ethoxy-2-[3′-(2′,3′-dimethyl-1′-butenyl)]isoindolone (**19,** 28% GLC yield) and gave the following spectroscopic data: ir ($CHCl_3$) 5.90 μ; NMR ($DCCl_3$) δ 1.13 (t, J = 7.4 Hz, 3 H), 1.67 (s, 3 H), 1.77 (s, 6 H), 2.96 and 334 (AB of an ABX_3 pattern, $J_{AX} = J_{BX} = 7.4$, $J_{AB} = 9.3$ Hz, $J_{AX} = J_{BX}$ and J_{AB} are of opposite sign), 4.95 (m, 2 H), 6.12 (s, 1 H), and 7.41–7.90 ppm (m, 4 H); mass spectrum *m/e* 259 (M^+, 61), 230 (15), 218 (43), 215 (13), 203 (13), 198 (25), 176 (19), 175 (16), 174 (13), 173 (21), 161 (32), 160 (19), 148 (22), 133 (87), 132 (base), 130 (25), 105 (23), 104 (20), 99 (12), and 77 (32).

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.13; H, 8.11; N, 5.41. Found: C, 73.93; H, 8.15; N, 5.40.

Hydrolysis of Photocycloadducts. The photocycloadducts obtained from the irradiation of 3-ethoxyisoindolone (**2**) in the presence of olefins were hydrolyzed by the following procedure. Less than 1 g of the photocycloadduct was placed in a 25-ml round-bottomed flask fitted with reflux condenser and magnetic stirring apparatus, and 13 ml of 3 *N* hydrochloric acid solution was added. The solution was stirred for 8–16 hr with slight warming of the flask to promote solubility. The water was then rotary evaporated and the product collected for recrystallization.

The 1,1-dimethoxyethene 3-ethoxyisoindolone cycloadduct (**3**) was hydrolyzed and recrystallized from acetonitrile yielding 0.34 g (76%) of a white crystalline solid (mp 235–236°). The product was identified as 3,4-benzo-6,7-dihydro-6,6-dimethoxy(1*H*)azepine-2,5-dione (**4**) from the following spectral data: ir (KBr) 3.07, 5.88, 5.99, and 6.14 μ; NMR (Me_2SO-d_6) δ 3.28 (s, 6 H), 3.45 (d, J = 6.5 Hz, 2 H, coupling disappeared with D_2O exchange), 7.3–7.9 (m, 4 H), and 8.2 ppm (broad, 1 H, disappeared with D_2O exchange); mass spectrum *m/e* 235 (M^+, 0.2), 163 (14), 160 (10), 106 (31), 104 (19), 88 (base), 77 (35), and 76 (38).

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.27; H, 5.63; N, 5.96.

A 0.29-g quantity of the cyclohexene photocycloadduct **5** was hydrolyzed and recrystallized from acetonitrile to yield 0.169 g (95%) of a white crystalline material (mp 235°). The product was identified as 3,4-benzo-6,7-dihydro-6,7-tetramethylene(1*H*)azepine-2,5-dione (**6**) from the following spectral data: ir (KBr) 3.18, 3.29, and 6.04 μ; NMR (Me_2SO-d_6) δ 1.1–2.35 (m, 8 H), 2.35–2.8 (m, 1 H), 4.1–4.4 (m, 1 H), 6.8 (broad, 1 H, disappeared with D_2O exchange), and 7.4–8.1 ppm (m, 4 H); mass spectrum *m/e* 229 (M^+, 37), 201 (38), 186 (11), 174 (12), 159 (16), 148 (base), 147 (34), 131 (13), 130 (16), 105 (13), 104 (14), 103 (17), 96 (13), 82 (55), 77 (38), and 76 (40).

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.20; H, 6.72; N, 6.11.

The isobutylene photocycloadduct (**9**, 70 mg, isolated by preparative GLC) was hydrolyzed, and the product was purified by sublimation [100° (0.02 mm)] to give 59 mg (96%) of a white crystalline product (mp 167°). The product was identified as 3,4-benzo-6,7-dihydro-6,6-dimethyl(1*H*)azepine-2,5-dione (**10**) from the following spectral data: ir (KBr) 3.22, 5.94, 6.00, and 6.07 μ; NMR (Me_2SO-d_6) δ 1.13 (s, 6 H), 3.17 (d, J = 6.0 Hz, 2 H, collapsed to a singlet with D_2O exchange), and 7.50–8.50 ppm (m, 5 H); mass spectrum *m/e* 203 (M^+, 2), 174 (18), 159 (18), 149 (74), 148 (57), 130 (34), 104 (23), 77 (19), 76 (36), and 56 (base).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.74; H, 6.37; N, 7.02.

A 0.3-g sample of a mixture of **11** and **12** from the photocycloaddition of 3-ethoxyisoindolone (**2**) to *trans*-2-butene was purified by preparative GLC and hydrolyzed. Recrystallization of the product from benzene–Skelly solve B yielded 0.279 g (98%) of a mixture of the cis and trans isomers of 3,4-benzo-6,7-dihydro-6,7-dimethyl(1*H*)azepine-2,5-dione (**14** and **13**) (mp 173–210°). The ratio of *cis:trans*-azepinedione obtained (0.5) was independent of the starting azabicyclic isomer or mixture of azabicyclic isomers (**11** and **12**) as shown by NMR. The products were identified from the following spectral data: ir ($CHCl_3$) 3.16, 5.98, and 6.05 μ; NMR (Me_2SO-d_6) trans isomer δ 1.32 (d, J = 7.0 Hz, 3 H), 1.35 (d, J = 7.0 Hz, 3 H), 2.67 (d of q, J = 7.0 and 2.3 Hz, 1 H), 4.24 (d of p, J = 7.0, 7.0, and 2.3 Hz, 1 H, pattern collapsed to d of q with D_2O exchange), and 7.3–8.2 ppm (m, 5 H); NMR (Me_2SO-d_6) cis isomer δ 1.18 (d, J = 7.0 Hz, 3 H), 1.35 (d, J = 7.0 Hz, 3 H), 2.81 (d of q, J = 10.1 and 7.0 Hz, 1 H), 3.59 (m, collapses to a d of q with D_2O exchange, J = 10.1 and 7.0 Hz, 1 H), and 7.3–8.2 ppm (m, 5 H); mass spectrum *m/e* 203 (M^+, 7), 161 (16), 160 (96), 148 (51), 132 (33), 131 (21), 130 (33), 105 (37), 104 (base), 103 (27), 102 (58), 78 (52), and 77 (48).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.59. Found: C, 70.85; H, 6.40; N, 6.62.

The tetramethylethylene photocycloadduct (**18,** 0.4 g) was isolated by preparative GLC and hydrolyzed yielding 0.34 g (95%) of a white crystalline solid. The product was identified as 3,4-benzo-6,7-dihydro-6,6,7,7-tetramethyl(1*H*)azepine-2,5-dione (**21,** mp 165°) from the following spectroscopic data: ir ($CHCl_3$) 3.15, 5.97, 6.07, and 7.13 μ; NMR ($DCCl_3$) δ 1.29 (s, 6 H), 1.33 (s, 6 H), 6.95 (broad, 1 H, disappeared with D_2O exchange), and 7.55–8.30 ppm (m, 4 H); mass spectrum *m/e* 216 (2), 175 (16), 174 (86), 159 (88), 146 (24), 131 (17), 105 (16), 104 (30), 77 (21), and 76 (24).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.86; H, 7.36; N, 6.13.

Synthesis of 3,4-Benzo-2-ethoxy-6,6,7,7-tetramethyl(7*H*)-azepin-5-one (20). A 50-ml round-bottomed flask was oven dried and charged with 0.15 g (0.0083 mol) of triethyloxonium fluoroborate, 25 ml of methylene chloride (freshly distilled from calcium hydride), and 0.082 g (0.004 mol) of 3,4-benzo-6,7-dihydro-6,6,7,7-tetramethyl(1*H*)azepine-2,5-dione (**21**) obtained from the hydrolysis of 3,4-benzo-6,6,7,7-tetramethyl-5-ethoxyazabicyclo[3.2.0]hept-3-en-2-one (**18**). The flask was fitted with a magnetic stirring apparatus, and the solution was stirred and refluxed for 19 hr. After cooling to room temperature, 50% potassium hydroxide solution was added dropwise with stirring until precipitation was observed (33 drops). The solution was filtered and concentrated to a viscous oil by rotary evaporation. NMR analysis of the crude product indicated that there was no more than 10% unreacted dione (**21**). The product was dissolved in 0.5 ml of benzene and 1.5 ml of Skelly solve B and placed under a stream of nitrogen. When a precipitate formed, the mother liquor was pipetted off and the crystals formed were washed with Skelly solve B. The crystalline precipitate proved to be nearly pure azepinedione while the mother liquor was enriched in the desired azepine-5-one (**20**). The separation procedure was repeated twice until 0.041 g (44%) of nearly pure product was obtained. GLC collection of the product using a 10.5 ft × 0.25 in. column of 5% lac 446 on 60-80 mesh Diatoport S at 185° (injection port and column oven) (He flow, 60 ml/min) yielded 0.025 g of pure 3,4-benzo-2-ethoxy-6,6,7,7-tetramethyl(7*H*)azepine-5-one (**20**). The product exhibited ir and NMR spectra identical with those of the product (**20**) obtained from the irradiation of 3-ethoxyisoindolone in the presence of tetramethylethylene.

Reduction of 2,3-Dihydro-3-ethoxy-2-[3′-(1′-butenyl)]-isoindolone (15 and 16). An oven-dried 25-ml two-necked flask was fitted with reflux condenser, addition funnel, and drying tubes. The flask was charged with 0.043 g (0.0012 mol) of lithium aluminum hydride (Alfa Inorganics) and 12 ml of absolute ether. A solution of 0.24 g (0.0010 mol) of 2,3-dihydro-3-ethoxy-2-[3′-(1′-butenyl)]-isoindolone (**15** and **16**) in 6 ml of absolute ether was added over a 15-min period. The reaction mixture was then allowed to reflux gently for 24 hr. After cooling, distilled water was added dropwise until precipitation was observed. The solution was allowed to stir for an additional 3 hr and then was vacuum filtered through Celite (Johns-Mansville 512). Drying over anhydrous magnesium sulfate, rotary evaporation of solvent, and collection from a 9.25 ft × 0.375 in. 5% Apiezon L on 60-80 mesh Diatoport S GLC column at 175° (injection port and column oven) (He flow 60 ml/min) afforded an analytical sample. The principal product, a viscous, unstable liquid, was identified as 1,2-dihydro-2-[3′-(1′-butenyl)]isoindole (**17**) from the following spectroscopic data: ir ($CHCl_3$), no significant bands; NMR ($CDCl_3$) δ 1.28 (d, $J = 6.4$ Hz, 3 H), 3.21 (q, $J = 6.4$ Hz, 1 H), 3.98 (s, 4 H), 5.0-5.45 (m, 2 H), 5.65-6.27 (m, 1 H), and 7.18-7.38 ppm (m, 4 H); mass spectrum *m/e* 173 (M^+, 14), 159 (11), 158 (76), 146 (14), 118 (31), 117 (16), 91 (12), and 90 (10); decomposition made elemental analysis unfeasible.

Thermal Test of Olefin Reactivity. In order to verify that the photocycloaddition of 1,1-dimethoxyethene to 3-ethoxyisoindolone was not a ground state process, the following thermal test reaction was run. A solution containing 0.25 g of 3-ethoxyisoindolone (**2**) and 0.50 g of 1,1-dimethoxyethene in 25 ml of sodium metal dried *tert*-butyl alcohol was placed in a 50-ml round-bottomed flask. The solution was stirred for 30 min at room temperature. Rotary evaporation of solvent and 1,1-dimethoxyethene resulted in the recovery of 0.24 g of 3-ethoxyisoindolone established spectroscopically.

Reagents Used for Quantum Yield Measurements. Spectrograde methylene chloride (Fisher) was distilled from calcium hydride prior to use. 3-Ethoxyisoindolone was recrystallized from Skelly solve B (mp 134-136°) and 1,1-dimethoxyethene was distilled through an annular spinning band column [bp 85-86° (630 mm)]. Tetramethylethylene (Aldrich, gold label) was used without further purification. 3,3,4,4-Tetramethyl-1,2-diazetine 1,2-dioxide (mp 190-192°) was prepared according to the procedure of Ullman and Singh.[18]

Quantum Yield Measurements. Quantum yield experiments were performed with a rotating photochemical apparatus as described by Moses and co-workers.[26] The light source was a 550-W Hanovia mercury lamp in a water-cooled Pyrex immersion well. The voltage of the electrical power to the lamp transformer was stabilized with a Sola 2000 VA constant voltage transformer. The 3130-Å mercury band was isolated using a two-compartment, cylindrical, quartz, solution cell. The solution filter was modeled after that described by Hunt and Davis.[27] The inside cell compartment with a path length of 1.25 ± 0.05 cm contained a 0.80 *M* cobaltous sulfate solution, and the outside compartment with a path length of 1.65 ± 0.05 cm contained a 6.06×10^{-3} *M* potassium chromate solution. The solution filter was stable over a period of 28 hr to irradiation from the 550-W mercury lamp when the lamp was in a Pyrex immersion well. It was not stable, however, when a quartz immersion well was used. The filter solutions were replaced after 20 hr of irradiation. The entire quantum yield apparatus was immersed in a 15-gal water bath maintained at 20 ± 0.10° unless otherwise stated.

Samples (3.0 ml) of the appropriate concentrations of 3-ethoxyisoindolone (**2**), tetramethylethylene, 1,1-dimethoxyethene, and 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide in methylene chloride solvent were placed in oven-dried 13-mm Pyrex test tubes, degassed by four freeze (liqiuid nitrogen)-pump (10^{-5} mm)-thaw cycles, and sealed. The concentration of 3-ethoxyisoindolone (**2**) was 0.060 *M* and greater than 99% of the incident 3130-Å light was absorbed. During the irradiations, the lamp intensity was monitored with potassium ferrioxalate actinometry and averaged 1.65×10^{15} quanta/sec. Analyses of product formation from irradiation of 3-ethoxyisoindolone with tetramethylethylene were obtained by GLC with a 10.5 ft × 0.25 in. column of 5% LAC 446 on 60-80 mesh Diatoport S at 185° relative to external benzophenone. The photocycloadduct from irradiation with 1,1-dimethoxyethene was analyzed relative to external benzophenone by GLC using a 7.5 ft × 0.25 in. column of 5% Apiezon L on 60-80 mesh Diatoport S at 150°. On column injection was used for all analyses with identical injection port and column oven temperatures, and the helium flow was 60 ml/min. Gas chromatographic data were corrected for differences in detector response, and quantum yield irradiation times were adjusted such that no more than 10% of the starting materials was destroyed during the irradiation.

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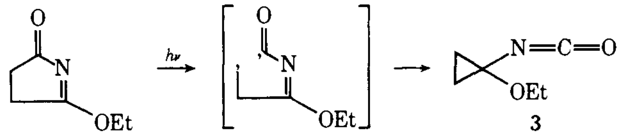
Photochemical Reactivity of Keto Imino Ethers. VI.[1] Type I Rearrangement and (2 + 2) Photocycloaddition to the Carbon–Nitrogen Double Bond of 2-Oxazolin-4-ones

Ronald M. Rodehorst and Tad H. Koch*

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received October 19, 1974*

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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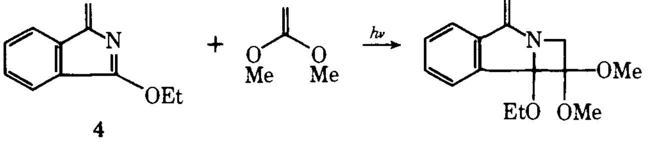
We have subsequently reported on the photoreactivity of 2-ethoxyisoindolone (**4**). The keto imino ether **4** was prepared with the idea of blocking the Norrish type I cleavage by strengthening the carbon–carbon bond α to the carbonyl with the anticipation of then observing the novel (2 + 2) photocycloaddition 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 $n-\pi^*$ bands at 265 nm (ϵ 45) and 275 (60), respectively, with strong end absorption for the $\pi-\pi^*$ bands; whereas, **4** has no resolved $n-\pi^*$ band with $\pi-\pi^*$ bands at 216 nm (ϵ 38000), 288 (1900), and 298 (2100).



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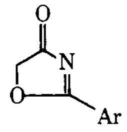
The photochemical reactivity of a series of 2-aryl-2-oxazolin-4-ones (**5**) was then examined with the idea of determining the effect of the additional conjugation of the keto imino ether chromophore with the benzo group of **4** on reactivity in (2 + 2) cycloaddition. The oxazolinones **5** are keto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



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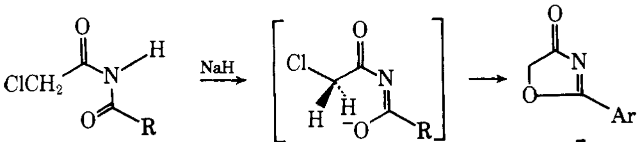
Results

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-



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