2.03 and 5.87 ppm characteristic of 19. A quartet at 3.63 ppm (J =7 Hz) was now observed which was probably due to liberated free ethanol.

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Registry No.-1, 41205-09-8; 2a, 53042-55-0; 3, 5988-91-0; 4, 53042-56-1; 5a, 53042-57-2; 5b, 53042-58-3; 5c, 53042-59-4; 5d, 53042-60-7; 5e, 53042-61-8; 8, 53042-62-9; 9b, 53042-63-0; 9b free acid, 53042-64-1; 9c isomer A, 53042-65-2; 9c isomer B, 53109-13-0; 9c isomer C, 53109-14-1; 9c isomer D, 53109-15-2; 10, 53042-66-3; 11a, 53042-67-4; 11b, 53042-68-5; 11c, 53042-69-6; 11d, 53042-70-9; 12, 53042-71-0; 13, 40770-70-5; 14, 40770-71-6; 15a, 53042-72-1; 15b, 53042-73-2; 19, 53042-74-3; diethyl 2-oxopropylphosphonate, 1067-71-6: 1-ethyl-3-p-tolyltriazene, 50707-40-9; 3-methyl-2-butenoic acid, 541-47-9; triethyl orthoacetate, 78-39-7.

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Photochemical Reactivity of Imino Lactones. Photoreduction and Photoelimination

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The photochemical reactivity of three imino lactones, 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (3a), 5,6dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (3b), and 3-butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (3c), is described. Oxazinones 3a and 3b are photostable with respect to the [2 + 2] photocycloaddition reaction to the carbon-nitrogen double bond. Oxazinone 3a undergoes photoreductive dimerization in 2-propanol solvent, oxazinone 3c photoeliminates propene to give 3a, and 3b is photostable. Possible mechanisms for the reductive dimerization and elimination reactions are discussed.

In our exploration of the photochemical reactivity of conjugated imines and imino ethers, we have synthesized

and studied three imino lactones. These chromophores were prepared as systems which might illustrate the elusive [2 + 2] photocycloaddition reaction of carbon-nitrogen double bonds to olefins. We have reported this mode of photoreactivity with keto imino ethers such as 2-phenyloxazolin-4-one (1),¹ and Hyatt and Swenton have observed similar reactivity with 1,3-dimethyl-6-azauracil (2).² Al-



though the imino lactones described here, 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**3a**), 5,6-dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (**3b**), and 3-butyl-5,6dihydro-5,5-dimethyl-1,4-oxazin-2-one (**3c**), resemble the azauracil of Hyatt and Swenton, their photochemical reactivity with olefins is not competitive with decay processes and photoreduction.

Results and Discussion

Synthesis of Reactants. 5,6-Dihydro-5,5-dimethyl-3phenyl-1,4-oxazin-2-one (3b) was prepared by the reaction of ethyl benzoylformate with 2-amino-2-methylpropanol as described by Biekert and Sonnenbichler.³ 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (3a) and 3-butýl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (3c) were prepared by an analogous procedure from the reaction of 2-amino-2methylpropanol with ethyl pyruvate and ethyl hexan-2onate, respectively, in refluxing toluene. Products 3a and 3c were characterized by strong carboxyl and medium intensity imine stretching bands at 1735 and 1640 cm⁻¹ in the infrared, strong mass spectral parent ions at m/e 141 and 183, respectively, and the nmr data reported in the Experimental Section. In the uv in ethanol solvent, 3a, 3b, and 3c gave n- π * bands at 322 (ϵ 120), 332 (ϵ 282), and 322



nm (ϵ 135), respectively. The π - π * band of **3b** appeared at 266 nm (ϵ 7560) and **3a** and **3c** showed only strong end absorption for the π - π * transitions.

As noted by Biekert and Sonnenbichler,³ 5,5-dimethyl-2-hydroxy-2-phenylmorpholin-3-one (4b) was a by-product of the synthesis of 3b. Similarly, 2-hydroxy-2,5,5-trimethylmorpholin-3-one (4a) was obtained as a by-product of the synthesis of 3a. An additional by-product, 5a, was also isolated. It was characterized from the spectroscopic data reported in the Experimental Section and by synthesis from 4a and 2-amino-2-methylpropanol. Like 4b, the hemiketal 4a exists in equilibrium with an isomeric, acyclic, hydroxy ketoamide as shown by nmr analysis.

Photochemical Reactions. Irradiation of 3a or 3b with a 450-W, mercury lamp through a Pyrex filter in nonhydrogen donating solvents of varying polarity such as 2-methyl-2-propanol, benzene, and cyclohexane resulted only in recovered starting material as indicated by ir, nmr, and glpc. Similarly, irradiation of 3a and 3b in the presence of electron rich and electron neutral olefins such as 1,1-dimethoxyethene and cyclohexene, respectively, in these solvents gave only recovered starting materials. At 77°K, irradiation of a glass of 3a or 3b in a low-temperature infrared cell⁴ with a 200-W Bausch and Lomb, super pressure, mercury source through a Corning CSO-54 filter gave no destruction of starting material as evidenced by infrared analysis.

When 3a was irradiated at -15° with a 450-W, mercury lamp through a Pyrex filter in a hydrogen-donating solvent such as 2-propanol, reductive type dimers were isolated in 57% yield. These were assigned the meso and dl structures 6 and 7 and were formed in the ratio of 3:2 (meso:dl). The



meso and dl dimers were separated using a Chromatronix liquid chromatography column of tlc grade alumina eluting at medium pressure. They were characterized by the nmr data shown in Table I, carboxyl and N-H stretching bands at 1710 and 3360 $\rm cm^{-1}$ in the infrared, and a weak parent ion in the mass spectrum at m/e 284 with a base peak at m/e 142 corresponding to homolytic cleavage of the 3-3' bond. The assignment of stereochemistry was accomplished by observing changes in the nmr spectra of 6 and 7 in the presence of the optically active europium shift reagent, tris(3-(trifluoromethylhydroxymethylene)-d-camphorato)europium(III).⁵ As shown in Table I the nmr absorption by the methyl protons at ring positions 3(3') and the methylene protons at 6(6') of the d and the l isomers were separated in the presence of the optically active shift reagent, thus distinguishing the dl from the meso dimer. Irradiation of 3b under similar conditions in reducing solvents did not lead to reductive dimerization and only starting material was recovered.

The photoreduction of **3a** occurs with a quantum yield of destruction of 0.005 and is quenched by *cis*-piperylene. When the quantum yield data in the presence and absence of quencher (Table II) were plotted in the Stern-Volmer fashion a linear plot was obtained with a slope of 10 l./mol. Analysis of the piperylene by glpc indicated that it was isomerized to *trans*-piperylene during the quantum yield experiments. These results suggest that the photoreduction of **3a** occurs *via* a triplet state.

Compd	Solvent	2(27)		
			5(5')	δ(6')
	CDCl ₃	1.53 s (3 H)	1.12 s (3 H), 1.31 s (3 H)	3.90 d (1 H), 4.27 d (1 H),
6 + shift reagent	\mathbf{CDCl}_3	1.62 s (3 H)	1.17 s (3 H), 1.38 s (3 H)	J = 10 Hz 3.99 d (1 H), 4.38 d (1 H), L = 10 Hz
	CDCl ₃	1.68 s (3 H)	1.15 s (3 H), 1.30 s (3 H)	3.94 d (1 H), 4.46 d (1 H),
7 - shift reagent	CDC1 ₃	2.07 s (1.5 H), 2.09 s (1.5 H)	1.23 s (3 H), 1.40 s (3 H)	J = 10 Hz 4.08 d (0.5 H), 4.71 d (0.5 H), J = 10 Hz

Tabla

Table II Quantum Yield of Destruction of 3a in 2-Propand						
	[cis-					
[3a] ^a	Piperylene] ^a	A _{initial}	A _{final} ⁰	φ		
0.021	0.00	2.549	2.320	0.0049		
0.021	0.01	2.618	2.417	0.0043		
0.021	0.05	2.565	2.432	0.0028		
0.021	0.10	2.601	2.492	0.0023		
0.021	0.15	2576	2,483	0.0020		

^a Concentrations are given in moles/liter. ^b Average of six measurements of the initial and final optical densities at 322 nm of the oxazinone (3a) solutions.

There are two reasonable photochemical events which might ultimately lead to the reductive dimers 6 and 7. Excited 3a might abstract a hydrogen atom from 2-propanol at the nitrogen of the imine functional group (path a, Scheme I) or at the carbonyl oxygen of the carboxyl func-



tional group (path b, Scheme I). If initial hydrogen atom abstraction occurred at the carboxyl group, a subsequent intra- or intermolecular hydrogen atom transfer would be required prior to radical combination. The latter path is similar to the chemical sensitization mechanism proposed by Padwa⁶ and others⁷ to explain the photoreduction of imines in the presence of carbonyl compounds.

3-Butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (3c) was studied in order to gain some evidence for distin-

Table III
Quantum Yield of Formation of 3a from 3c

[3c] ^a	¢	[3c] ^a	¢
0.0255	0.0011	0.102	0.0021
0.0408	0.0013	0.204	0.0023
a Compensation	a ana airran in na	alag /litan	

^a Concentrations are given in moles/liter.

guishing between these two pathways for reductive dimerization. It was theorized that if the nitrogen of the imine functional group of **3a** had a propensity for hydrogen atom abstraction (*i.e.*, path a, Scheme I), **3c** would undergo a photoreaction analogous to the Norrish Type II photoelimination reaction of ketones. This would occur via intramolecular γ -hydrogen abstraction from the butyl side chain by the nitrogen of the imine functional group followed by elimination of propene.

Oxazinone (3c) was irradiated in 2-methyl-2-propanol solvent with a 450-W, mercury lamp through a Pyrex filter. 2-Methyl-2-propanol was chosen as the solvent for this experiment because it has a polarity similar to 2-propanol without being a reducing solvent. Under these conditions the only product isolated was 3a, the product of photoelimination, in 44% yield. Propene was identified as a by-product of the irradiation by nmr and mass spectrometry.



The formation of 3a and propene from irradiation of 3c was in itself most consistent with initial hydrogen atom abstraction by the nitrogen of the imine functional group. Hydrogen atom abstraction from the side chain of 3c by the carbonyl oxygen of the carboxyl functional group would most likely lead to a cyclization product rather than the products of elimination.⁸

If the photoreaction of 3c occurred by a Norrish Type II mechanism involving initial hydrogen atom abstraction by the nitrogen of the imine functional group, the quantum yield of 3a formation should be independent of the concentration of starting 3c. The quantum yield data for this experiment are reported in Table III. Contrary to the result



predicted by the imine Norrish Type II mechanism, the quantum yield of product formation was concentration dependent and the reciprocal of quantum yield was linear in reciprocal of 3c concentration, least-squares slope $1.54 \pm 0.17 \times 10^{-5}$ mol/l. This result coupled with the low quantum yield prompts us to reconsider the chemical sensitization mechanism and other more complex mechanisms for the elimination reaction as well as for the reductive dimerization. A possible chemical sensitization route to photoelimination consistent with the results of Table III is shown in Scheme II. A rationale for the second step of this mechanism is the documented stability of radicals such as $8.^9$

It is interesting to speculate about the photostability of **3a** and **3b** with respect to the [2 + 2] photocycloaddition reaction with olefins. Danilov and coworkers¹⁰ have suggested that the photostability of the 6-aza analogs of thymine to [2 + 2] dimerization results from an unreactive low-energy n,π^* state. This suggestion has been challenged by the work of Hyatt and Swenton.² However, in our exploration of the photoreactivity of keto imino ethers, we have concluded that molecules which are reactive in the [2 + 2] photocycloaddition to carbon-nitrogen double bonds have low-energy n,π^* states and those which are unreactive have low-energy n,π^* states.^{1,11,12} At least in the singlet manifold, **3a**, **3b**, and **3c** have lowest energy n,π^* states.

Experimental Section

Apparatus and Instruments. Melting points and boiling points are uncorrected. Melting points were measured with a Thomas-Hoover Unimelt apparatus. A Perkin-Elmer 337 spectrophotometer was used to determine ir spectra. Uv spectra were measured with Cary 14 and 17 spectrophotometers, and nmr spectra were recorded with a JEOL PS-100 and Varian A-60A and HA-100 spectrometers. Chemical shifts are reported in parts per million on the δ scale from internal tetramethylsilane. Mass spectra were obtained with a Varian Mat CH-5 spectrometer. Glpc analyses and isolations were performed with Varian Aerograph (Model 200 and 1500) gas chromatographs equipped with thermal conductivity detectors, and peak areas were measured by Disc integration. Microanalyses were performed by Atlantic Microlab, Atlanta, Georgia.

Synthesis of 5,6-Dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (3b). 5,6-Dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one was prepared by the method of Biekert and Sonnenbichler.³ The oxazinone (3b) was purified by glpc using a 10 ft \times 0.375 in. column of 5% SE-30 on 60-80 mesh Chromosorb W at 185° (He 80 cm³/min) and gave the following spectral data: nmr (CDCl₃) δ 1.32 (s, 6 H), 4.18 (s, 2 H), 7.35 (m, 3 H), and 7.92 ppm (m, 2 H); ir (neat) 1740 and 1605 cm⁻¹; mass spectrum (70 eV) *m/e* 203 (60), 159 (27), 146 (12), 145 (92), 105 (52), 104 (base), 103 (35), 77 (65); uv λ_{max} (95% EtOH) 332 sh (282), 330 sh (271), and 266 nm (7560). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.00; H, 6.45; N, 6.88.

In addition to the oxazinone (3b), a precipitate was formed during the reaction which was removed by suction filtration and recrystallized from 2-propanol, mp 125-126° (lit.3 mp 122°). and identified as 5,5-dimethyl-2-hydroxy-2-phenylmorpholin-3-one (4b). In dimethyl sulfoxide solution at ambient temperature 4b existed in equilibrium with N-(2-(1-hydroxy-2-methylpropyl)) benzoylformamide as a 86:14 mixture (4b:formamide) as indicated by the nmr spectrum. As the temperature of the solution was increased, the percentage of formamide in the mixture increased. At 140° the ratio was 33:67. The following spectral data were obtained: nmr (DMSO- d_6) morpholinone 4b δ 1.17 (s, 3 H), 1.36 (s, 3 H), 3.49 and 4.03 (AB pattern, J = 12 Hz), 7.14 (s, 1 H), 7.2-7.6 (m, 5 H), and 7.92 ppm (broad, 1 H); the peaks at δ 7.14 and 7.92 ppm disappeared upon exchange with D_2O ; formamide δ 1.31 (s, 6 (\dot{H}) , 3.50 $(\dot{d}, J = 6 \text{ Hz}, 2 \text{ H})$, 4.90 (t, J = 6 Hz, 1 H), 7.52 (m, 3 H), 7.89 (m, 2 H), and 8.2 ppm (broad, 1 H); upon addition of D₂O the peaks at δ 4.90 and 8.2 ppm disappeared and the doublet at δ 3.50 ppm collapsed to a singlet; ir (KBr) 3190 and 1645 cm⁻¹; mass spectrum (70 eV) m/e 204 (0.5), 193 (2.5), 190 (3.8), 123 (9.5), 116 (15), 105 (65), 77 (41), 73 (17), 58 (base), and 56 (20).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.13; H, 6.92; N, 6.27.

Synthesis of 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (3a). 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one was prepared by a procedure similar to the one described for 3b. A solution of 58 g (0.50 mol) of ethyl pyruvate in 75 ml of toluene was added dropwise to 44.5 g (0.50 mol) of 2-amino-2-methylpropanol in 200 ml of refluxing toluene. The reaction was carried out under a nitrogen atmosphere and a Dean-Stark trap was used to remove the water. After completion of the addition (3 hr), the refluxing was continued overnight. The reaction mixture was transferred to a distillation apparatus and the toluene was removed by distillation through a 20-cm Vigreux column. After the theoretical amount of toluene was collected the pressure was reduced and the product was distilled. Oxazinone (20.0 g) distilling at 90° (25 mm) was collected. Redistillation of the recovered toluene yielded an additional 8.7 g of product for a total yield of 36.7%. Nmr (CDCl₃) showed δ 1.30 (s, 6 H), 2.27 (s, 3 H), and 4.23 ppm (s, 2 H); ir (neat) 1735 and 1640 cm⁻¹; uv λ_{max} (95% EtOH) 322 nm (120); mass spectrum (70 eV) m/e 141 (52), 83 (91), 56 (68), 42 (72), 41 (base).

Anal. Calcd for C₇H₁₁NO₂: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.65; H, 7.88; N, 9.95.

Continued distillation of the reaction residue gave 13.1 g (0.057 mol) of 2-N- (1'-hydroxy-2'-methyl-2'-propyl)amino-2,5,5-trimethylmorpholin-3-one (**5a**), bp 90° (0.02 mm). The viscous liquid gradually crystallized and was recrystallized twice from ether: mp 90–92°; nmr (CCl₄) δ 1.20 (s, 3 H), 1.22 (s, 3 H), 1.30 (s, 6 H), 1.42 (s, 3 H), 3.40 and 3.61 (AB pattern, J = 8 Hz), 3.50 (s, 2 H), and 6.85 ppm (broad, 1 H); nmr (DMSO- d_6) δ 1.10 (s, 3 H), 1.19 (s, 3 H), 1.22 (s, 6 H), 1.37 (s, 3 H), 3.01 (s, 1 H), 3.36 (d, J = 5 Hz, 2 H), 3.46 (s, 2 H), 5.01 (t, J = 5 Hz, 1 H), and 7.53 ppm (broad, 1 H); upon treatment with D₂O the latter spectrum changed as follows, δ 3.01, 5.01, and 7.53 ppm disappeared while δ 3.36 ppm collapsed to a singlet; ir (CCl₄) 3380, 3300, and 1668 cm⁻¹; mass spectrum (70 eV) *m/e* 200 (4.2), 199 (68), 143 (2.7), 127 (2.7), 115 (32), 114 (base), 98 (5.5), 83 (8.2), 72 (64).

Anal. Calcd for C₁₁H₂₂N₂O₃: C, 57.37, H, 9.63; N, 12.16. Found: C, 57.43; H, 9.70; N, 12.11.

Another compound formed in low yields in this reaction was identified as 2-hydroxy-2,5,5-trimethylmorpholin-3-one (4a), mp 168-170° (sealed tube), after recrystallization from 2-propanol. As the temperature of a solution of 4a in dimethyl sulfoxide was increased to 80° new peaks appeared in the nmr spectrum which were assigned to the compound N- (2-(1-hydroxy-2-methylpropyl))acetylformamide. At 140° the composition of the mixture was 66:34 (4a:formamide) as determined by nmr. The following spectral data were obtained: nmr (DMSO- d_6) morpholinone (4a) $\delta 1.07$ (s, 3 H), 1.19 (s, 3 H), 1.35 (s, 3 H), 3.30 and 3.81 (AB pattern, J =(a) 5 Hz), 2.639 (c) 1 H), and 7.7 ppm (broad, 1 H); the peaks at δ 6.39 and 7.7 ppm disappeared upon exchange with D₂O; formamide δ 1.22 (s, 6 H), 2.30 (s, 3 H), 3.38 (d, J = 6 Hz, 2 H), 4.97 (t, J = 6 Hz, 1 H), and 7.5 ppm (broad, 1 H); upon addition of D₂O the peaks at δ 4.97 and 7.5 ppm disappeared and the doublet at δ 3.38 ppm collapsed to a singlet; ir (KBr) 3190 and 1650 cm⁻¹; mass spectrum (70 eV) m/e 142 (3), 131 (2), 116 (3), 114 (2), 74 (9), 61 (6), 58 (base), 56 (32).

Anal. Calcd for C₇H₁₃NO₃: C, 52.82; H, 8.23; N, 8.80. Found: C, 52.89; H, 8.29; N, 8.89.

The addition of ethyl pyruvate to 2-amino-2-methylpropanol in refluxing benzene yielded 16% 5,6-dihydro-3,5,5-trimethyl-1,4oxazin-2-one (3a), 33% 2-hydroxy-2,5,5-trimethylmorpholin-3-one (4a), and none of product 5a. Reaction of 2-Hydroxy-2,5,5-trimethylmorpholin-3-one

Reaction of 2-Hydroxy-2,5,5-trimethylmorpholin-3-one (4a) with 2-Amino-2-methylpropanol. 2-Hydroxy-2,5,5-trimethylmorpholin-3-one (2.0 g, 0.013 mol) was dissolved in 50 ml of dry toluene. 2-Amino-2-methylpropanol (2.3 g, 0.026 mol) was added and the mixture was refluxed for 24 hr using a Dean-Stark trap for removal of water. Analysis by glpc using a 5 ft × 0.25 in. column of 5% SE-30 on 60-80 mesh Chromosorb W at 140° (He 60 cm³/min) showed some unreacted alcohol and a large peak with the same retention time as the morpholinone 5a. Distillation under vacuum gave 1.85 g of a slightly yellow viscous liquid, bp 85–90° (0.02 mm), which crystallized when seeded with a crystal of 5a. Recrystallization from ether gave 1.6 g (54%) of white crystals, mp 89–91°, mixture melting point with morpholinone 5a, 89–91°. The spectra of this compound were identical with those of the previously isolated 5a.

Synthesis of 3-Butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (3c). 3-Butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one was synthesized in a manner similar to the synthesis of oxazinone **3b.** A 1000-ml three-neck flask, equipped with a Dean-Stark trap, stirrer, dropping funnel, and nitrogen inlet, was charged with 350 ml of toluene and 32 ml (0.34 mol) of 2-amino-2-methylpropanol and brought to reflux. Ethyl hexan-2-onate¹³ (38.1 g, 0.24 mol) was added dropwise over a period of 2 hr to the mixture and the reaction refluxed overnight. The toluene was distilled off at atmospheric pressure and the product was distilled at 110° (8 mm), yielding 27.5 g (63%) of pure product. Nmr (CCl₄) showed δ 0.83 to 1.82 (m, 7 H), 1.29 (s, 6 H), 2.54 (t, J = 7 Hz, 2 H), and 4.19 ppm (s, 2 H); ir (neat) 1735 and 1640 cm⁻¹; mass spectrum (70 eV) m/e183 (8.4), 141 (28), 126 (14), 125 (58), 84 (37), 83 (29), 82 (11), 68 (13), 58 (17), 57 (19), 56 (base); uv λ_{max} (95% EtOH) 322 nm (135). Anal. Calcd for C₁₀H₁₇NO₂: C, 65.54; H, 9.35; N, 7.64. Found: C,

65.53; H, 9.39; N, 7.69. **Photodimerization of 5,6-Dihydro-3,5,5-trimethyl-1,4-oxa zin-2-one (3a) in 2-Propanol.** Oxazinone **3a** (25.3 g) dissolved in 500 ml of 2-propanol, distilled from anhydrous calcium sulfate, was degassed with nitrogen and irradiated with a 450-W, mercury, immersion lamp through Pyrex under a nitrogen atmosphere. Throughout the reaction the photochemical apparatus was immersed in a bath kept at -15° . At this temperature the dimers formed a thick, gelatinous precipitate during the reaction. Every 24 hr the photolysis was interrupted, the precipitate removed by vacuum filtration, and the filtrate returned for continued irradiation. After 5 days no more precipitate formed and the solvent was removed on a rotary evaporator using a Dry Ice-acetone condenser, maintaining the water bath at 10°. Combined yield was 14.4 g

(57%) of mixed reductive dimers (6 and 7), mp 142–143°, in the ratio of 3:2, meso to dl. The meso and dl dimers were separated using medium pressure liquid abarmatorscape. A Chromateonic class column 23 × 0.5 in

liquid chromatography. A Chromatronix glass column, 23×0.5 in. was packed with Woelm, neutral, tlc grade alumina and activated by first eluting with methanol and then with benzene followed by Skelly B. Solvent was pumped by means of a Milton Roy mini-Pump, and fractions were collected with a time-controlled fraction collector. The entire apparatus was kept in a cold room at 7°. In a typical run, 100 mg of crude dimer mixture was dissolved in 4.5 ml of 5% MeOH in benzene and injected onto the column using a Chromatronix injection system. The eluting solvent was 1% MeOH and 5% Skelly B in benzene at a flow rate of 60 cm³/hr with fractions changing every 5 min. The fastest moving of the dimers was eluted in 70 min and the slower moving in 85 min. Fractions were analyzed using 4×7 cm Brinkmann silica gel N-HR tlc sheets, developing with 10% MeOH in benzene at 7° and visualizing with iodine vapor. $R_{\rm f}$ values were 0.15 and 0.4 for meso and dl dimers, respectively. Total recovery of material was better than 95%.

Physical properties of the dimers were as follows: meso dimer, mp 148–150°, dl dimer, mp 155–156°; nmr, see Table I; meso and dl dimers, ir (KBr) 3360 and 1710 cm⁻¹; meso and dl dimers, mass spectrum (70 eV) m/e 284 (1), 253 (24), 144 (20), 143 (60), 142 (base), 88 (41), 56 (44), 55 (31).

Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.13; H, 8.51; N, 9.85. Found for meso: C, 59.26; H, 8.46; N, 9.79. Found for dl: C, 59.33; H, 8.59; N, 9.80.

Irradiation of 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (3a) in Ethanol. 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (1.4 g) in 130 ml of absolute ethanol was degassed with nitrogen for 0.5 hr and irradiated with a 450-W mercury lamp with a Pyrex immersion well for 26 hr under nitrogen. Throughout the reaction the water bath was kept at 20°. The irradiation mixture was then concentrated on a rotary evaporator keeping the water bath at about 15°. After most of the ethanol was removed 40 ml of cold Skelly B was added and the precipitate of dimers was collected by suction filtration. The filtrate was washed with another 20-ml portion of cold Skelly B, and 0.64 g (45%) of mixed reductive dimers (6 and 7), mp 138–140°, was obtained. Nmr analysis showed the meso to *dl* ratio to be 2:1.

Irradiation of 5,6-Dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (3b). A 0.2-mm path length ir solution cell was filled with a benzene solution of 5,6-dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one of a concentration such that the carboxyl stretching band at 1740 cm⁻¹ gave an absorbance of 1. The solution was irradiated at ambient temperature with a Bausch and Lomb, 200 W, super pressure mercury lamp through a Corning CSO-54 filter for 30 min. Subsequent scanning of the ir showed no change in the spectrum. A solution of 3b and 1,1-dimethoxyethene was similarly prepared and irradiated for 90 min with the CSO-54 filtered light. Again irradiation resulted in no change of the infrared absorption spectrum of 3b. When a solution of 3b was irradiated with a 450-W, mercury lamp with a Pyrex immersion well in ethanol or 2-propanol solvent as described for 3a, no destruction of starting material occurred.

Irradiation of 3-Butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (3c). 3-Butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (1.0 g) mixed with 150 ml of 2-methyl-2-propanol was irradiated with a 450-W, mercury lamp through Pyrex for 48 hr at 30°. The reaction was monitored by glpc using a 5 ft \times 0.25 in. column of 5% SE-30 on 60-80 mesh Chromosorb W at 120° (He 60 cm³/min). A steady decrease in starting oxazinone and a simultaneous formation of a new product at shorter retention time was observed. The solvent was removed by distillation at atmospheric pressure and the product was distilled at 65° (12 mm), yielding 0.34 g (44%). The physical properties of the product were identical with those of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (3a).

Irradiation of 3-Butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (3c) in an Nmr Tube. 3-Butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one, 0.25 g, and 0.5 cm³ of benzene- d_6 were placed in an nmr tube, freeze-thaw degassed to a residual pressure of 10^{-4} mm. The tube was sealed and attached to the Pyrex water jacket of a 450-W, medium pressure, mercury lamp and irradiated for 24 hr. The terminal nmr spectrum showed that there was about 50% conversion to 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (3a) by integration of the gem-dimethyl singlets at δ 1.29 (3c) and 1.30 (3a) ppm. In addition to the appearance of absorptions due to (3a), peaks were observed which were due to dissolved propene, as identified by comparison with an authentic sample.

The gaseous product from the nmr tube was collected in a liquid nitrogen trap and identified as propene by comparison of the mass spectral fragmentation patterns with those reported in the literature. 14

Reagents Used for Quantum Yield Experiments. 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**3a**) and 3-butyl-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (**3c**) were purified by preparative glpc using a 10 ft \times 0.375 in. column of 5% SE-30 on 60-80 mesh Chromosorb W at 140 and 165°, respectively (He 80 cm³/min). Spectrograde 2-propanol and Spectrograde benzene were used without further purification. *cis*-Piperylene (Chemical Samples) was purified by glpc collection from a 1t ft \times 0.25 in. column of 25% $\beta\beta'$ -oxydipropionitrile on 80-100 mesh Chromosorb P at ambient temperature (He 60 cm³/min).

Quantum Yield Measurements. Quantum yield measurements were performed in a rotating photochemical apparatus¹⁵ immersed in a 15 gal constant temperature bath held at 25.0 \pm 0.5°. Light from a Hanovia, 550-W, mercury lamp contained in a Pyrex immersion well was passed through a solution filtering system to isolate the 313-nm band. The filter was constructed from three concentric quartz cylinders, 12.5, 8.8, and 6.0 cm in diameter, sealed between two anodized aluminum disks with Neoprene rubber gaskets. The path length in the inner cell was 1.25 ± 0.5 cm and was filled with 0.8 *M* cobalt sulfate solution. The outer cell had a path length of 1.65 ± 0.05 cm and was filled with $6 \times 10^{-4} M$ potassium chromate solution. The chemical filters were found to be stable to the conditions of the experiment. Potassium ferrioxalate actinometry was used to measure the light output of the system during the experiments.¹⁶

Quantum yield calculations for destruction of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one were based on the change in the optical density of the oxazinone (3a) solutions after irradiation. Photochemistry of Acid Hydrazides

Samples of 3a in 2-propanol solvent (3.0 ml) were placed in the round-tube portion of a two-compartment cell and freeze-thaw degassed to a residual pressure of 10^{-4} mm. The cell was constructed from Pyrex glass tubing with a tubular compartment 13 mm o.d. by 55 mm and a cuvette compartment from 10 mm i.d. by 55 mm Trubore square tubing. Irradiations were carried out with the solution in the 13-mm tube and uv analyses were performed after transfer of the solution to the cuvette portion. cis-Piperylene, present at the concentrations shown in Table II, was employed as a triplet quencher for the photoreduction. At the end of the experiment formation of trans- piperylene was detected by glpc using the β,β' -oxydipropionitrile column (vide supra). Samples of 3c in benzene solvent (3.00 ml) of the various concentrations shown in Table III were placed in Pyrex tubes (13×70 mm) and freezethaw degassed to a residual pressure of 10^{-5} mm. After irradiation in the quantum yield apparatus formation of 5.6-dihydro-3,5.5-trimethyl-1,4-oxazin-2-one (3a) was measured by glpc using a 6 ft \times 0.25 in. column of 5% FS-1265 on 30-60 mesh Haloport F at 115° (He 60 cm³/min) using benzisoxazole as an internal standard. The quantum yields of formation of 3a as a function of the initial concentration of 3c are reported in Table III.

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Registry No-3a, 53153-46-1; 3b, 53153-47-2; 3c, 53153-48-3; 4a, 53153-49-4; 4b, 53153-50-7; 5a, 53153-51-8; 6, 53153-52-9; 7, 53153-53-0; N - (2 - (1 - hydroxy-2-methylpropyl))benzoylformamide, 53153-54-1; ethyl pyruvate, 617-35-6; N - (2-(1-hydroxy-2methylpropyl)acetylformamide, 53153-55-2; 2-amino-2-methylpropanol, 124-68-5; ethyl hexan-2-onate, 5753-96-8.

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Photochemistry of Acid Hydrazides. Determination of Modes of Reaction and Identification of Photoproducts^{1a,b}

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The photochemical reaction pathways of a number of benzoic and acetic acid hydrazides of the type $R_1CONZNR_2R_3$ ($R_1 = CH_3$, C_6H_5 ; Z = H, CH_3 , C_6H_5CO , $p - CH_3C_6H_4SO_2$; $R_2R_3 = C_6H_5$, CH_3 , C_6H_5CO , CH_3CO) have been determined with 254-nm light. All reaction products are the result of dissociative processes with the two primary processes being nitrogen-nitrogen and carbonyl carbon-nitrogen cleavage. The first of these processes yields amides and amines, while the second yields aldehydes and acids. The amount and direction of cleavage appear to depend on the relative dissociation energies of the bonds in the vicinity of the carbonyl group of hydrazides. Secondary products of the type R1CONZR2 and R1COR2 are observed and shown to arise via known photochemical processes of the initial photoproducts of the acid hydrazides.

Although the photochemistry of amides² has been well studied, the corresponding aza analogs, acid hydrazides, have received scant attention in the literature.³ Generally, amides undergo photochemical reactions similar to those of ketones, namely α cleavage and Norrish type II cleavage⁴ (Scheme I). The analogous α -amino ketones undergo, almost exclusively, elimination reactions.^{5,6} However, cyclization in very high yields has been reported for α -N-alkylaminoacetophenones to produce 3-azetidinols7 similar to the cyclobutanol formation of ketones.^{8–11}

Scheme I **Photolytic Reactions of Amides**

 $CH_3CH_2CH_2CONH_3 \xrightarrow{h_{\nu}} CH_3CH_2CH_3NH_3 + CO$ α cleavage

type II $CH_3CH_2CH_2CONH_2 \xrightarrow{h_{\nu}} CH_2 \longrightarrow CH_2 \longrightarrow CH_2 CH_2$

Considering the large volume of previous work on the ketones and amides, as well as their variety of photochemical reactions, it appeared reasonable to investigate the photochemistry of acylhydrazides as aza analogs of amides and diaza analogs of ketones to determine their comparative modes of reaction. Of particular interest was the potential for synthetic routes to diazetidinols via an internal cyclization of the hydrazides.

Results and Discussion

The results of the photolysis of the compounds reported in this study are summarized in Table I. Percentage yields are not corrected for unreacted starting material as they could not be assayed via gas chromatography. However, in the preparative runs, analyzed by column chromatography, the unreacted starting material was recovered, accounting for approximately 90-95% of the material balance. There-