2-methyl-1-pentene, 763-29-1; cyclohexene, 110-83-8; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; 2-methylcyclopentanone, 1120-72-5; cyclohexanone, 108-94-1; 2,6-dimethylcyclohexanone, 2816-57-1; 2-butanone, 78-93-3; pinacolone, 75-97-8; *p*-nitrobenzyl alcohol, 619-73-8; 3,4,5-trimethoxybenzyl alcohol, 3840-31-1; benzyl alcohol, 100-51-6; benzhydrol, 91-01-0; benzoin, 119-53-9; xanthen-9-ol, 90-46-0; 1-phenyl-1,5-pentanediol, 1011-61-6; cinnamyl alcohol, 104-54-1; 3,4,5-trimethoxycinnamyl alcohol, 1504-56-9; *cis*-1,4-but-2-enediol, 6117-80-2; cyclopentanol, 96-41-3; hydroquinone, 123-31-9; catechol, 120-80-9; 1,3-cyclohexadiene, 592-57-4; flavanone, 487-26-3; 1,3,5-cycloheptatriene, 544-25-2; phenol, 108-95-2; 1,5-cyclooctadiene, 111-78-4; 1,2-hexanediol, 6920-22-5; 2-methyl-1,2-pentanediol, 20667-05-4; *trans*-1,2-cyclohexanediol, 1460-57-7; 2-methyl-2,3-butanediol, 5396-58-7; 2,3-dimethyl-2-butene oxide, 5076-20-0; γ-butyrolactone, 96-48-0; δ-valerolactone, 542-28-9; β-methyl-δ-valerolactone, 1121-84-2; γ-methyl-δ-valerolactone, 3123-98-6; 6-hydroxyhexanoic acid, 1191-25-9; 2,6-dimethyl-ε-caprolactone, 55879-32-8; *p*-nitrobenzaldehyde, 555-16-8; 3,4,5-trimethoxybenzaldehyde, 86-81-7; benzaldehyde, 100-52-7; benzophenone, 119-61-9; benzil, 134-81-6; xanthone, 90-47-1; 5-hydroxy-1-phenyl-1-pentanone, 1011-62-7; cinnamaldehyde, 104-55-2; 3,4,5-trimethoxycinnamaldehyde, 34346-90-2; *p*-benzoquinone, 106-51-4; *o*-benzoquinone, 583-63-1.

Photolytic Dehydrochlorination of *N*-Chloro-*N*-alkyl Amides: Formation of *N*-(α-Methoxyalkyl) Amides

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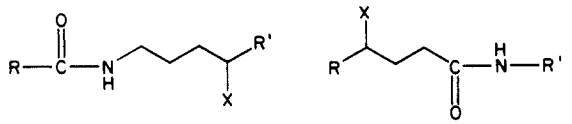
The photoinduced dehydrochlorination, in methanol, of *N*-chloro-*N*-alkyl amides with one substituent at the α position to nitrogen gave good yields of *N*-(α-methoxyalkyl) amides and the parent amides as secondary products. *N*-Chloro amides disubstituted at the α position gave mostly parent amides. In most cases no products resulting from 1,5 hydrogen transfer of amidyl radicals were observed. The quantum yields of decomposition of *N*-chloro-*N*-methylpentanamide (**1a**) were significantly greater than unity, indicative of a chain process for dehydrochlorination. The reaction was affected by the solvent, addition of base or radical inhibitors, concentration of *N*-chloro amide, light intensity, and irradiation wavelength.

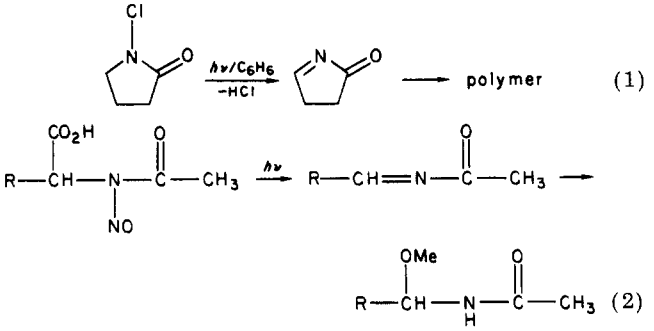
The photolysis of *N*-halo amides is known to give products arising from both amidyl radical and halogen atom intermediates.[1,2] Typical products of amidyl radical intermediates are δ-halo amides I and 4-haloacyl isomers II, which result from regiospecific 1,5 hydrogen abstraction



I II

from the *N*-alkyl moiety and the acyl chain, respectively.[2-6] When both the *N*-alkyl and acyl moieties of the *N*-halo amide are small, precluding normal 1,5 hydrogen transfer, a product arising from 1,4 hydrogen transfer has been observed.[2] Amidyl radicals also have been found to undergo efficient intramolecular addition to olefinic bonds.[7-9] All of these pathways are believed to involve amidyl radical chain processes with quantum yields greater than unity. In cases where intramolecular processes are impossible, such as with *N*-chloro-*N*-*tert*-butylacetamide, a slow intermolecular hydrogen abstraction predominates in solvents of poor hydrogen-donating ability.[3,6] In good hydrogen-donating solvents such as cyclohexane, an efficient radical-chain process produces the parent amide and chlorinated solvent.[2]

The photolysis in benzene of *N*-chloro amides bearing a hydrogen α to nitrogen, such as *N*-chloropyrrolidone, is complicated by the formation of gummy polymeric products.[6] These products are thought to result from polymerization of intermediate acyl imines derived from dehydrochlorination of *N*-chloro amides (eq 1). Although the



(1)

(2)

quantum yields were not reported, the dehydrochlorination is rapid and probably involves a radical-chain process. Products characteristic of intermediate acyl imines are also formed in the photolysis of *N*-chloro-*N*-methylcarbamates,[1c] *N*-nitroso-*N*-alkyl amides,[10-14] and *N*-acyl-*N*-nitroso-α-amino acids.[15,16] In the latter case, photolysis

(1) (a) R. S. Neale, *Synthesis*, 1 (1971); (b) P. Mackiewicz and R. Furstoss, *Tetrahedron*, 34, 3241 (1978); (c) J. Lessard, M. Mondon, and D. Touchard, *Can. J. Chem.*, 59, 431 (1981).
(2) R. A. Johnson and F. D. Greene, *J. Org. Chem.*, 40, 2186 (1975).
(3) Y. L. Chow and T. C. Joseph, *J. Chem. Soc., Chem. Commun.*, 490 (1969).
(4) A. L. J. Beckwith and A. Goodrich, *Aust. J. Chem.*, 18, 747 (1965).
(5) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965).
(6) R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Am. Chem. Soc.*, 88, 3051 (1966).
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(9) Lessard et al. have shown that intramolecular addition to olefins by amidyl radicals also can be promoted with benzoyl peroxide initiation or chromous chloride reduction: P. Mackiewicz, R. Furstoss, B. Waegell, R. Cote, and J. Lessard, *J. Org. Chem.*, 43, 3746, 3750 (1978).
(10) Y. L. Chow and A. C. H. Lee, *Chem. Ind.*, 827 (1967).
(11) Y. L. Chow, N. S. Tam, and A. C. H. Lee, *Can. J. Chem.*, 47, 2441 (1969).
(12) Y. L. Chow and A. C. H. Lee, *Can. J. Chem.*, 45, 321 (1967).
(13) Y. L. Chow and N. S. Tam, *J. Chem. Soc. C*, 1138 (1970).
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(15) J. Polo and Y. L. Chow, *Heterocycles*, 11, 101 (1978).

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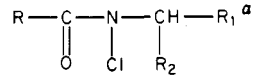
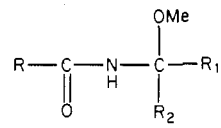
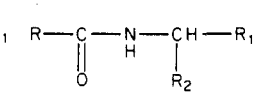
Table I. Photolysis of *N*-Chloro Amides in Methanol

	 [a]			products,[b] %	
					
compd	R	R_1	R_2	2	3
1a	C_4H_9	H	H	84 (72)	16 (13)
1b	C_5H_{11}	CH_3	H	80 (69)	15 (11)
1c	CH_3	*i*-Pr	H	85 (50)	15 (14)
1d	CH_3	C_5H_{11}	H	81 (71)	11 (10)
1e	CH_3	C_6H_5	H	37 (26)	63 (51)
1f	$-(CH_2)_2-$		H	(64)	(3)
1g	$-(CH_2)_3-$		H	(69)	5
1h	$-(CH_2)_4-$		H	77 (66)	18 (9)
1i	CH_3	CH_3	CH_3	*c*	56 (53)
1j	CH_3	$-(CH_2)_4-$		*d*	(60)
1k	CH_3	$-(CH_2)_5-$		*c,e*	(76)
1l	C_4H_9	CH_3	CH_3	*f*	(38)
1m	3-cyclohexenyl	H	H	5[g]	7

[a] 0.075–0.1 M. [b] Yields determined by GC analysis; isolated yields in parentheses. [c] Acetamide was detected. [d] Two minor products were also detected. [e] 1,1-Dimethoxycyclohexane (24%) was detected. [f] Valeramide (49%) and *N*-isopropyl-4-chlorovaleramide (**41**; 7%) were detected. [g] 6-Methyl-4-*exo*-chloro-6-azabicyclo[3.2.1]octan-7-one (**6a**; 28%) and endo isomer **6b** (45%) were isolated.

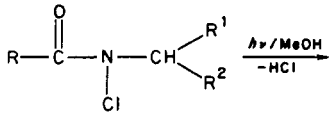
Table II. Effect of Solvent on Photolysis of *N*-Chloro-*N*-methylpentanamide[a] (1a)

			products,[b] %		
entry	solvent	$t_{1/2}$, min	n-$C_4H_9C(O)$-$NHCH_2OR$	parent amide 3a	4a
1	methanol[c]	<0.5	84(Me)	16	
2	ethanol[c]	<0.5	44(Et)	47	
3	2-propanol[c,d]	<0.5		79	10
4	*tert*-butyl alcohol	<1	14(*t*-Bu)	30	46
5	methanol–acetonitrile (35:65)	2		73	10

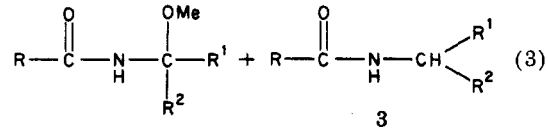
[a] 0.075 M. [b] Determined by GC analysis with internal standards. [c] Photolysis of 1a in methanol, ethanol and isopropanol also gave dimethoxymethane (4%), 1,1-diethoxyethane (56%), and acetone (60%), respectively. [d] The half-life of 1a in isopropanol (dark reaction) was 15 minutes.

in methanol gave moderate yields of *N*-(α-methoxyalkyl) amides by addition of solvent to intermediate acyl imines (eq 2).

We report here that the photoinduced dehydrochlorination of *N*-chloro-*N*-alkyl amides in methanol is an efficient process and provides a new method for synthesis of *N*-(α-methoxyalkyl) amides (eq 3). With one exception,



1

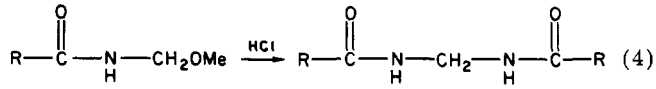


2 3 (3)

no products resulting from 1,5 hydrogen transfer of amidyl radicals were observed, and in several cases the only other products were the parent amides.

Results and Discussion

Irradiation of *N*-chloro-*N*-alkyl amides 1 in methanol with a 450-W medium-pressure mercury arc, filtered through Vycor, resulted in rapid formation of the corresponding *N*-(α-methoxyalkyl) amides **2**, some parent amides **3**, and 1 equiv of HCl (Table I). The methoxyalkyl amides **2** were stable under neutral or basic conditions and could be isolated from parent amides by flash chromatography[17] on silica gel. When the workup was performed under acidic conditions, the methoxyalkyl amides **2** underwent further transformations. For example, *N*-(α-methoxymethyl)valeramide (**2a**) underwent further reaction in the presence of HCl generated in situ from the photolysis to give the bisamide **5** (eq 4).[18]



2a 5 (4)

R = n-C_4H_9

As Table I indicates, the number of substituents on the carbon adjacent to nitrogen has substantial influence on the course of the reaction. Photolysis of *N*-chloro-*N*-alkyl amides with one substituent at the position α to nitrogen (**1b–h**) gave *N*-(α-methoxyalkyl) amides in high yield. *N*-Chloro-*N*-alkyl amides disubstituted at the α position (**1i–k**) gave the corresponding parent amides and small amounts of acetamide but no *N*-(α-methoxyalkyl) amides. An exception, in part, was *N*-chloro-*N*-isopropylvaleramide (**1l**), which gave valeramide as the major product (49%)

(16) Y. L. Chow, *Tetrahedron Lett.*, 2473 (1965).

(17) W. C. Stille, M. Kahn, and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).

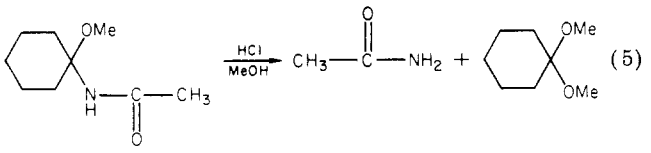
(18) The dimerization of methoxyalkyl amides under acidic conditions is well-known: H. E. Zaugg and W. B. Martin, *Org. React.*, **14**, 52 (1965).

Table III. Effect of Additives on Photolysis of *N*-Chloro-*N*-methylpentanamide[a] (1a) in Methanol

entry	additive	concn, M	$t_{1/2}$, min	products,[b] % 2a	3a	4a
1			<0.5	84	16	
2	KOAc	0.15	<0.5		62	18
3	TMP[c]	0.15	8		52	16
4	HCl[d]	0.15	<0.5		100	
5	H_2SO_4	1.0		37	60	
6	CH_3CO_2H	1.0		63	35	
7	CF_3CO_2H	1.0		55	40	
8	oxygen[e]		5	28	57	
9	dodecanethiol	0.15	1	33	58	
10	trichloroethylene	0.15	2	84	16	
11	1-methoxycyclohexene[f]	0.07	<0.5	23	66	

[a] 0.075 M. [b] Determined bt GC analysis with internal standards. [c] 2,4,6-Trimethylpyridine. [d] In the form of acetyl chloride; the half-life of 1a in methanol with 1 equiv of HCl (dark reaction) was 6 min. [e] Oxygen bubbled through solution at least 15 min before irradiation and maintained thereafter. [f] 2-Chloro-1,1-dimethoxycyclohexane was detected in 46% yield.

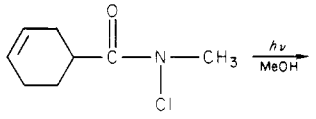
and some *N*-isopropyl-4-chlorovaleramide (**4l**, 7%). Acetamide and cyclohexanone dimethyl ketal (24%) were detected in the photolysis of *N*-chloro-*N*-cyclohexylacetamide (eq 5). These results indicated that *N*-(α-methoxyalkyl) amides possessing two alkyl substituents at the α position to nitrogen may be formed but undergo subsequent solvolysis in acidic methanol.



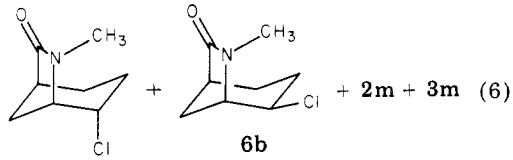
(5)

2k

Surprisingly, C-chlorinated products characteristic of amidyl radical intermediates were not formed in the photolysis of **1a–d** in methanol. This suggested that photolytic dehydrochlorination was more favorable than the intramolecular hydrogen transfer of amidyl radicals under the reaction conditions. It was of interest to determine whether dehydrochlorination could compete effectively with intramolecular addition of amidyl radical to an olefinic bond (eq 6). The photolysis of the unsaturated *N*-chloro amide **1m** in benzene has been shown to give a 1:1 ratio of exo and endo bicyclic lactams **6a** and **6b**.[7,8] In methanol, photolysis of **1m** gave a mixture of **6a** and **6b** (1:1.6, 73%), some parent amide **3m**, and a small amount of methoxyalkyl amide **2m**. Thus intramolecular addition of amidyl radical to an olefinic bond on the acyl chain was a more favorable process than dehydrochlorination.[19]



1m



(6)

6a 6b

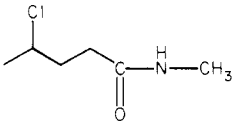
(19) Intramolecular addition of amidyl radicals to an olefinic bond on the acyl chain is more favorable than intramolecular addition to an olefinic bond on a *N*-alkyl chain.[9] We have not investigated the efficiency of the latter system in relation to dehydrochlorination.

Table IV. Quantum Yields[a] of the Photolysis of *N*-Chloro-*N*-methylpentanamide[b] (1a) in Methanol

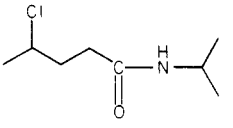
wavelength, nm	φ(2a)	φ(3a)
254	64	36
300	22	30

[a] Based on potassium ferrioxalate actinometry.[20] [b] 0.10 M.

The photolysis of *N*-chloro-*N*-methylvaleramide (**1a**) was carried out under several conditions to determine the factors influencing the dehydrochlorination (Tables II and III). The degradation of **1a** in methanol was complete in less than 2 min; the quantum yields of formation of **2a** and **3a** were much greater than unity (Table IV), and **2a** was formed in 84% yield. Dehydrochlorination in ethanol was less efficient, the ethoxymethyl amide and parent amide being formed in a 1:1 ratio. 2-Propanol reduced **1a** to parent amide **3a** rapidly in the dark, and the reduction was catalyzed further by light. Photolysis of **1a** in *tert*-butyl alcohol gave a considerable amount of C-chlorinated amide **4a**, along with parent amide **3a** and a minor amount of the *tert*-butoxymethyl amide.



4a



4l

Johnson and Greene used 2,4,6-trimethylpyridine (TMP) to suppress the effect of HCl in the light-initiated chlorination of alkanes by a number of *N*-chloro amides.[2] Photolysis of **1a** in methanol, in the presence of TMP or potassium acetate as HCl scavengers, afforded a mixture of parent amide and *C*-chloro amide **4a** but no *N*-(α-methoxymethyl) amide **2a**. These results indicated that free HCl generated in situ was necessary for the formation of *N*-(α-methoxyalkyl) amides. However, addition of HCl or other acids such as trifluoroacetic acid to a methanolic solution of **1a** just prior to photolysis did not increase the yield of **2a**. This may be expected as HCl is known to catalyze the decomposition of *N*-chloro amides to the corresponding parent amides.[6]

Radical scavengers such as oxygen and dodecanethiol decreased the rate of decomposition of **1a** and favored the formation of the parent amide over **2a**. Although trichloroethylene, a chlorine radical trapping agent under certain conditions,[21] had no effect on the ratio of the

Table V. Effect of Light Intensity[a] on Photolysis of 1a[b] in Methanol

wavelength, nm	no. of lamps	products, % 2a	3a
254	1	72	21
	3	78	15
	6	84	12
300	1	47	53
	2	63	22
	6	61	22

[a] Photolysis carried out in a Rayonet reactor (Model RPR-100) fitted with RPR-2537 Å lamps or with RPR-3000 Å lamps. [b] 0.075 M.

Table VI. Effect of Wavelength on Photolysis[a] of 1a in Methanol

filter	wavelength, nm	products, % 2a	3a
Vycor	>210	84	12
Pyrex	>280	61	39
uranium	>330	32	56

[a] Photolysis of 1a (0.075 M) was carried out with 450-W medium-pressure mercury lamp.

products, 1-methoxycyclohexene (1 equiv) significantly decreased the amount of **2a** produced in the photolysis.[22]

Low light intensity was found to favor the formation of parent amide **3a**, and the effect was found more pronounced at 300 nm than at 254 nm (Table V). The UV absorption of **1a** in methanol has maxima in the region of 260 nm (n–π^*) with broad tailing to 350 nm. Reactions performed at longer wavelengths using Pyrex or uranium glass filters also favored the formation of parent amide **3a** (Table VI). The initial concentration of the *N*-chloro amide **1a** had a strong influence on the course of the photolysis. As Figure 1 demonstrates, when the initial concentration of **1a** was increased above 0.1 M in methanol, the yield of the parent amide **3a** increased dramatically at the expense of the α-methoxyalkyl amide **2a**.

By the proper choice of conditions, one can exercise considerable control over the course of the photolytic degradation of *N*-chloro amides. The effects of solvents and additives listed in Tables III and IV indicated that *tert*-butyl alcohol solvent or the addition of base (TMP or potassium acetate) favors the formation of C-chlorinated products. We found that the photolysis of *N*-chloro-*N*-methylvaleramide (**1a**) and *N*-chloro-*N*-isopropylvaleramide (**1l**), using the combination of *tert*-butyl alcohol solvent and potassium acetate, produced the C-chlorinated amides **4a** and **4l** in high yields.

The photochemical decomposition of *N*-chloro amides in cyclohexane has been demonstrated to consist of at least two radical-chain processes.[2] A chlorine atom–HCl chain process, strongly inhibited by 2,4,6-trimethylpyridine, resulted in chlorinated solvent, and a competing amidyl radical chain process gave both chlorinated solvent and products from intramolecular 1,5 hydrogen transfer. The high quantum yields and the effects of inhibitors observed in the photolysis of *N*-chloro amides in methanol indicate that the dehydrochlorination is a radical-chain process.

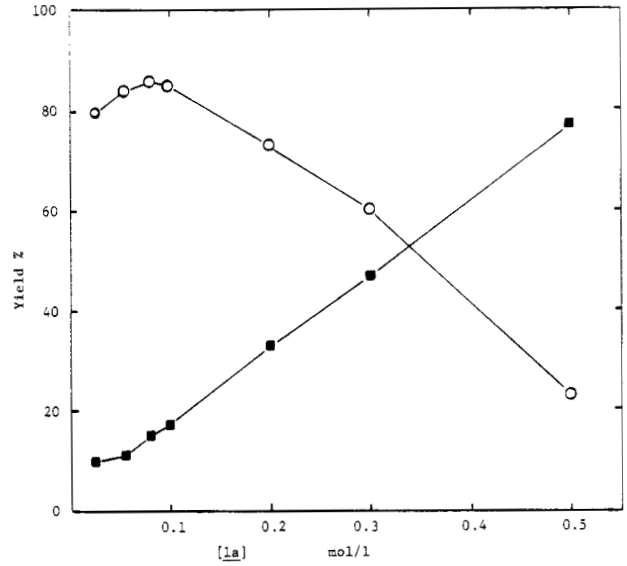


Figure 1. Effect of concentration of *N*-chloro-*N*-methylpentanamide (**1a**) on product yields [(○) *N*-(α-methoxymethyl)pentanamide (**2a**), (■) *N*-methylpentanamide (**3a**)] in photolysis of **1a** in methanol.

The inhibiting effect of TMP or potassium acetate on the formation of **2a** indicates that this reaction involves a chlorine atom–HCl chain process. A reasonable pathway is outlined in Scheme I. A chlorine atom, the chain propagator, abstracts a hydrogen α to nitrogen on the *N*-chloro-*N*-alkyl amide (eq 8). The resulting radical undergoes subsequent β scission to regenerate chlorine atom and an acyl imine intermediate, which adds methanol to give the observed product (eq 9, 10). In competing processes, the chlorine atom chain may result in chlorination of solvent according to the Goldfinger mechanism (eq 11–13)[2,23] and the amidyl radical chain may produce parent amide, chloro-rearranged products, and chlorinated solvent (eq 14–17).[24]

In most cases listed in Table I, no chloro rearrangement was observed, and the amidyl radical chain process is believed to play a minor role in the photolytic decomposition. However, under conditions where the chlorine atom–HCl chain process is inhibited, the amidyl radical chain would be expected to play a greater part in product formation, as it does in the presence of TMP, potassium acetate, or acetonitrile solvent. The effects of base and the initial concentration of *N*-chloro amide on the course of the photolysis can be understood in terms of eq 11–13. In the presence of base, HCl is scavenged and eq 11 will act effectively as a chlorine atom chain terminator. At high initial concentration of *N*-chloro amide, a corresponding high concentration of HCl is produced during the photolysis and the decomposition of *N*-chloro amide would proceed with a greater contribution from HCl-catalyzed reactions (eq 12).

The photolysis of *N*-chloro-*N*-alkyl amides in methanol may be a useful alternative to other methods for the preparation of methoxyalkyl amides. Condensation of primary amides with formaldehyde in methanol gives *N*-methoxymethyl amides, but the method is not useful for preparation of *N*-(α-methoxyalkyl) amides of most higher aldehydes.[18] Methoxyalkyl amides and hydroxyalkyl amides have been prepared by anodic oxidation of

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(21) C. Walling and J. A. McGuinness, *J. Am. Chem. Soc.*, **91**, 2053 (1969).
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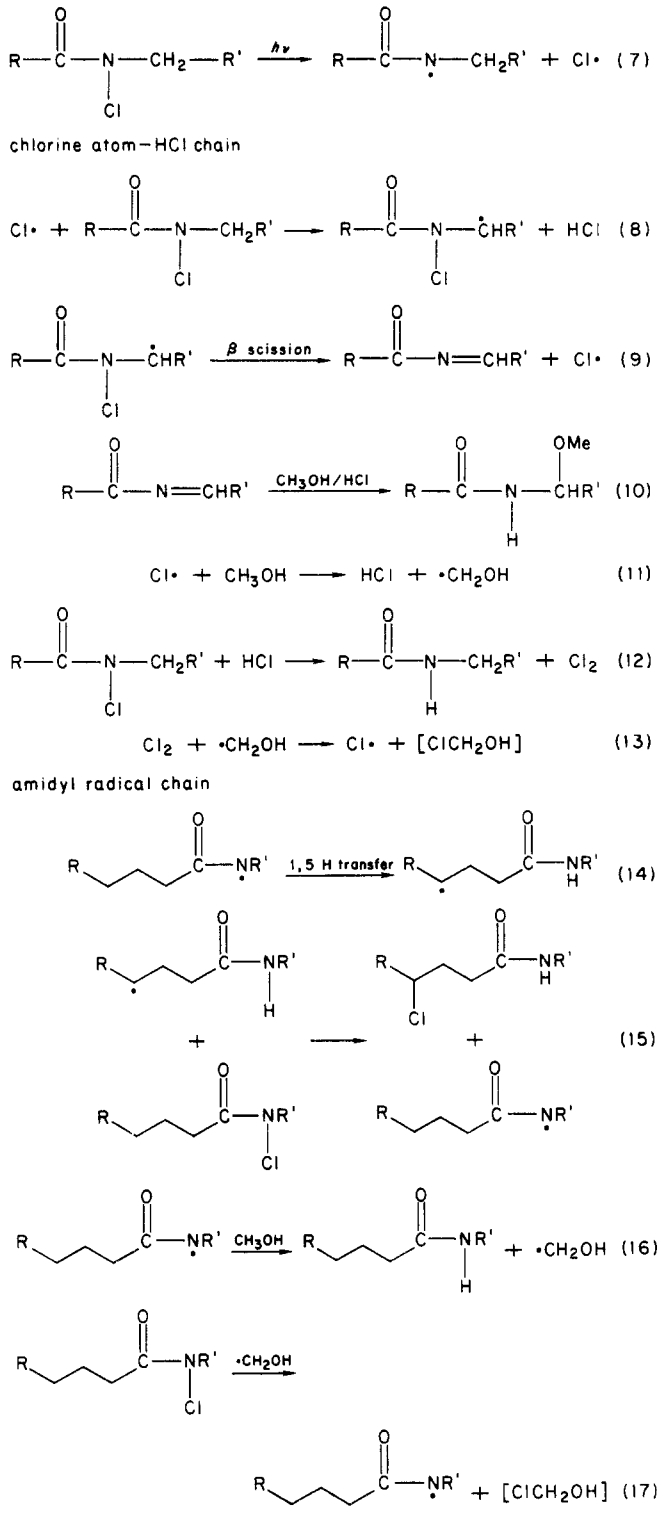
(24) Products resulting from chlorination of solvent were detected (see Table II, footnote *c*).

Scheme I



amides and carbamates in methanol[25,26] and by the partial reduction of imides with sodium borohydride[27] or diisobutylaluminum hydride.[28] They have been shown to be useful intermediates in carbon bond formation α to nitrogen in amidoalkylations,[29] *N*-acyl iminium ion cyclizations,[30] and imino Diels–Alder reactions.[31]

Experimental Section

General Procedures. Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. Boiling points for products distilled under vacuum in a Kugelrohr apparatus refer to the oven temperatures. The ^{1}H NMR and ^{13}C NMR spectra were obtained with a JEOL FX-90Q spectrometer with tetramethylsilane internal standard. The IR spectra were determined with Perkin-Elmer Models 337 and 457 spectrometers. The UV spectra were measured with a Perkin-Elmer Model 552 spectrophotometer. Gas chromatographic separations were carried out on a Hewlett-Packard Model 5710A gas chromatograph equipped with dual flame-ionization detectors. A 20 × 0.125 in. stainless steel column containing 10% UCW-982 on 80–100-mesh Chromosorb WAW DMCS was used. Photolysis samples were taken at intervals of time, neutralized with potassium acetate, and analyzed by GC with saturated hydrocarbon internal standards. Each sample was analyzed at least twice. Peak areas were determined by cutting and weighing. Flash column chromatography was performed with Baker silica gel (40 μm). Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN. Analytical TLC was run on Merck silica gel 60F-254 plates (0.2 mm).

***N*-Chloro-*N*-alkyl Amides.** Most of the *N*-chloro amides were prepared by treatment of a solution of the parent amide (0.02 mol) in methanol (25 mL) with *tert*-butyl hypochlorite (0.03 mol) (Frinton Laboratories) under nitrogen for 30 min.[32,33] Concentration of the solution under reduced pressure afforded the *N*-chloro amides as colorless or slightly yellow liquids. They were purified by vacuum distillation with a Kugelrohr apparatus. The purity of *N*-chloro amides was checked by TLC, NMR, or GC analysis. The following *N*-chloro amides were prepared: *N*-chloro-*N*-methylpentanamide (**1a**), bp 50–53 °C (2.2 mm) [lit.[6] bp 71 °C (10 mm)]; *N*-chloro-*N*-ethylhexanamide (**1b**), bp 54 °C (0.08 mm); *N*-chloro-*N*-(2-methylpropyl)acetamide (**1c**), bp 107–110 °C (15 mm); *N*-chloro-*N*-hexylacetamide (**1d**), bp 57–60 °C (0.2 mm); *N*-chloro-*N*-benzylacetamide (**1e**), bp 100–102 °C (0.9 mm); *N*-chloro-*N*-isopropylacetamide (**1i**), bp 69–72 °C (15 mm); the *N*-chloro lactams **1f–h** were used without distillation;[34] *N*-chloro-*N*-isopropylpentanamide (**1l**); bp 55–58 °C (0.15 mm); *N*-chloro-*N*-cyclopentylacetamide (**1j**), bp 60–62 °C (0.2 mm); *N*-chloro-*N*-cyclohexylacetamide (**1k**), bp 77–80 °C (0.4 mm). *N*-chloro-*N*-methyl-3-cyclohexenecarboxamide (**1m**) was prepared according to method of Kuehne and Horne.[8]

***N*-(Methoxymethyl)pentanamide 2a. Typical Procedure.** A solution of *N*-chloro-*N*-methylpentanamide (**1a**; 3.70 g, 24.75 mmol) in methanol (330 mL) in a water-cooled quartz immersion well fitted with a Vycor filter was purged with nitrogen for 15 min followed by irradiation with a Hanovia 450-W medium-pressure mercury lamp for 15 min.

The irradiated solution was made slightly basic (pH 8–9) by addition of 1 N sodium hydroxide (25 mL), concentrated to a volume of 35 mL, and extracted with dichloromethane (5 × 40 mL). The extracts were dried over magnesium sulfate and con-

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centrated to an oil, which was separated by flash chromatography[17] on silica gel (petroleum ether–ethyl acetate–methanol, 3:1:0.1) to give **2a** (2.62 g, 72%), bp 115–120 °C (0.2 mm); IR ($CHCl_3$) 3450, 3340, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 1.15–1.80 (m, 4 H), 2.25 (t, 2 H), 3.31 (s, 3 H), 4.46 (d, 2 H), 7.05 (brs, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.4, 71.4, 55.8, 36.4, 27.7, 22.4, 13.8. Anal. Calcd for $C_7H_{15}NO_2$: C, 57.90; H, 10.41. Found C, 58.56; H, 10.44.

Further elution gave *N*-methylpentanamide (**3a**; 0.36 g, 13%).[35]

***N*-(α-Methoxyethyl)hexanamide (2b).** Photolysis of *N*-chloro-*N*-ethylhexanamide (**1b**; 4.41 g, 24.7 mmol) yielded an oil fractionated by flash chromatography (petroleum ether–ethyl acetate–methanol, 3:1:0.1) to give **2b** (2.93 g, 69%): melting point at room temperature; bp 100–105 °C (0.1 mm); IR (neat) 3290, 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.15–1.80 (m, 9 H), 2.20 (t, 2 H), 3.32 (s, 3 H), 5.30 (m, 1 H), 6.10 (brs, 1 H); ^{13}C NMR ($CDCl_3$) δ 173.3, 77.6, 55.5, 36.8, 31.5, 25.3, 22.4, 21.6, 13.9. Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05. Found: C, 62.51; H, 11.09.

Further elution of the column gave *N*-ethylhexanamide (**3b**; 0.39 g, 11%).[35]

***N*-(1-Methoxy-2-methylpropyl)acetamide (2c).** Photolysis of *N*-chloro-*N*-isobutylacetamide (**1c**; 3.57 g, 23.7 mmol) gave an oil purified by flash chromatography (petroleum ether–ethyl acetate–methanol, 1:1:0.05) to give **2c** (1.70 g, 50%): mp 56.5–57.2 °C; IR ($CHCl_3$) 3440, 3325, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (2 d, 6 H), 1.77 (m, 1 H), 2.05 (s, 3 H), 3.32 (s, 3 H), 4.85 (dd, 1 H), 6.50 (brd, 1 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 85.4, 55.9, 23.1, 17.8, 17.4. Anal. Calcd for $C_7H_{15}NO_2$: C, 57.90; H, 10.41. Found: C, 57.79; H, 10.26.

Further elution afforded *N*-(2-methylpropyl)acetamide (**3c**; 0.38 g, 14%).[35]

***N*-(α-Methoxyhexyl)acetamide (2d).** Photolysis of *N*-chloro-*N*-hexylacetamide (**1d**; 4.39 g, 24.8 mmol) gave an oil separated by flash chromatography (petroleum ether–ethyl acetate–methanol, 1:1:0.05) to give **2d** (3.08 g, 71%): mp 33–36 °C; IR ($CHCl_3$) 3440, 3325, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.15–1.70 (m, 8 H), 2.03 (s, 3 H), 3.30 (s, 3 H), 5.10 (m, 1 H), 7.05 (brd, 1 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 81.3, 55.5, 35.3, 31.5, 24.6, 23.1, 22.6, 14.0. Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05. Found: C, 62.27; H, 10.79.

Further elution of the column yielded *N*-hexylacetamide (**3d**; 0.27 g, 10%).[35]

***N*-(α-Methoxybenzyl)acetamide (2e).** Photolysis of *N*-chloro-*N*-benzylacetamide (**1e**; 4.58 g, 25 mmol) afforded a solid separated by flash chromatography (petroleum ether–ethyl acetate–methanol, 2:1:0.15) to yield **2e** (1.16 g, 26%): mp 89–91 °C; IR (KBr) 3300, 1715, 1695, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (s, 3 H), 3.34 (s, 3 H), 6.05 (d, 1 H), 7.05 (brd, 1 H), 7.35 (m, 5 H). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31. Found: C, 67.10; H, 7.31.

Further elution of the column yielded *N*-benzylacetamide (**3e**; 1.90 g, 51%).[35]

5-Methoxy-2-pyrrolidone (2f). Photolysis of *N*-chloro-2-pyrrolidone (**1f**; 6.59 g, 55.1 mmol) gave a solid separated by flash chromatography (petroleum ether–ethyl acetate–methanol, 1:1:0.1) to give **2f** (4.03 g, 64%): mp 60–62 °C; IR ($CHCl_3$) 3440, 3225, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00–2.65 (m, 4 H), 3.28 (s, 3 H), 4.90 (m, 1 H), 8.68 (brs, 1 H). Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88. Found: C, 51.85; H, 7.65.

Further elution yielded 2-pyrrolidone (**3f**; 0.14 g, 3%).[35]

6-Methoxy-2-piperidinone (2g). Photolysis of *N*-chloro-δ-valerolactam (**1g**; 4.42 g, 33 mmol) afforded a solid purified by flash chromatography (ether–methanol, 15:1) to give **2g** (2.90 g, 69%): mp 111–113 °C; IR ($CHCl_3$) 3405, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–2.50 (m, 6 H), 3.35 (s, 3 H), 4.58 (m, 1 H), 8.52 (brs, 1 H). Anal. Calcd for $C_6H_{11}NO_2$: C, 55.79; H, 8.59. Found: C, 55.99; H, 8.30.

7-Methoxycaprolactam (2h). A solution containing *N*-chloro-ε-caprolactam (**1h**; 3.65 g, 24.8 mmol) gave a solid separated by flash chromatography (petroleum ether–ethyl acetate–methanol, 1:1:0.1) to give **2h** (2.35 g, 66%): mp 69–71 °C; IR ($CHCl_3$) 3415, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–2.80 (m, 8 H), 3.35 (s, 3 H), 4.32 (t, 1 H), 8.02 (brs, 1 H); ^{13}C NMR ($CDCl_3$) δ 179.4, 83.3, 55.1, 37.4, 34.1, 23.7, 23.3. Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15. Found: C, 58.96; H, 9.11.

Further elution of column afforded ε-caprolactam (**3h**; 0.25 g, 9%).[35]

Photolysis of *N*-Chloro-*N*-isopropylacetamide (1i). Photolysis of **1i** (4.49 g, 33 mmol) gave an oil purified by chromatography (petroleum ether–ethyl acetate–methanol, 3:1:0.1) to give *N*-isopropylacetamide (**3i**; 1.73 g, 53%).[35] GC analysis also indicated the presence of acetamide (t_R 0.5 min at 85 °C) in the photolysis mixture.

Photolysis of *N*-Chloro-*N*-cyclopentylacetamide (1j). Photolysis of **1j** (4.01 g, 24.9 mmol) gave a semisolid, which was shown by GC analysis to consist of *N*-cyclopentylacetamide (**3j**; 60%, t_R 7.3 min at 100 °C) and two minor components. Attempts to isolate these components by chromatography resulted in decomposition.

Photolysis of *N*-Chloro-*N*-cyclohexylacetamide (1k). Photolysis of **1k** (4.06 g, 23.2 mmol) gave a semisolid, which was shown by GC analysis to consist of acetamide (t_R 4.5 min at 60 °C), 1,1-dimethoxycyclohexane (24%, t_R 3.2 min at 90 °C), and *N*-cyclohexylacetamide (**3k**; isolated by recrystallization; 2.50 g, 76%).[35]

Photolysis of *N*-Chloro-*N*-isopropylpentanamide (1l). Photolysis of **1l** (5.87 g, 33 mmol) afforded a liquid (3.92 g), which was partitioned by flash chromatography (petroleum ether–ether–methanol, 4:6:0.1). The first fraction (2.05 g) was shown by GC to be a mixture of *N*-isopropylpentanamide (**3l**; 38%, t_R 8.6 min at 95 °C) and *N*-isopropyl-4-chloropentanamide (**4l**; 7%, t_R 16.8 min).

Further elution of the column afforded valeramide (1.63 g, 49%), mp 104–106 °C (lit. mp 106 °C).

Photolysis of *N*-Chloro-*N*-methyl-3-cyclohexenecarboxamide (1m). Photolysis of **1m** (3.43 g, 19.8 mmol) gave a solution that was shown by GC analysis to contain **1m** (4%, t_R 6.2 min), *N*-methyl-3-cyclohexenecarboxamide (**3m**; 7%, t_R 7.5 min), 6-methyl-4-*exo*-chloro-6-azabicyclo[3.2.1]octan-7-one (**6a**; 28%, t_R 11.7 min), 6-methyl-4-*endo*-chloro-6-azabicyclo[3.2.1]octan-7-one (**6b**; 45%, t_R 13.8 min), and *N*-(methoxymethyl)-3-cyclohexenecarboxamide (**2m**; 5%, t_R 14.5 min). The slightly acidic solution was neutralized with 1 N sodium hydroxide and worked up in a usual manner to provide an oil (3.28 g) that was partitioned by flash chromatography (petroleum ether–ether–methanol, 2:2:0.1).

The first fraction (0.17 g) was shown by ^1H NMR and GC analysis to be a mixture of **6a** and **2m** (2:1).

The second fraction gave **6a** (0.50 g, 15%): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65–2.60 (m, 7 H), 2.87 (s, 3 H), 3.70 (t, 1 H), 4.30 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 176.7, 62.2, 53.1, 39.9, 31.3, 27.7, 21.0.

The third fraction (0.35 g) was shown by GC to be a mixture of **6a** and **3m** (1:1).

The fourth fraction gave **6b** (1.06 g, 31%): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.5 (m, 7 H), 3.07 (s, 3 H), 3.85 (d, 1 H), 4.15 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 176.4, 64.3, 59.0, 39.0, 37.7, 30.3, 27.3.

The relative ^{13}C NMR chemical shifts of isomers **6a** and **6b** were in accord with their previous stereochemical assignments.[7,8]

***N,N'*-Methylenebis(pentanamide) (5).** Photolysis of *N*-chloro-*N*-methylpentanamide (**1a**; 2.51 g, 16.8 mmol) gave an acidic solution, which was concentrated without neutralization. The resulting liquid solidified upon warming under vacuum and was recrystallized from acetone to give **5** (1.43 g, 79%): mp 184–186 °C; IR (Nujol) 3315, 1635 cm^{-1}; ^1H NMR ($CDCl_3$ + Me_2SO-d_6) δ 0.79–1.05 (t, 6 H), 1.10–1.80 (m, 8 H), 2.06–2.32 (t, 4 H), 4.40–4.60 (t, 2 H), 7.66 (brs, 1 H), 8.00 (brs, 1 H). Anal. Calcd for $C_{11}H_{22}N_2O_2$: C, 61.6; H, 10.4. Found: C, 61.4; H, 10.5.

***N*-Methyl-4-chloropentanamide (4a).** A solution containing *N*-chloro-*N*-methylpentanamide (**1a**; 3.70 g, 24.7 mmol) and potassium acetate (4.40 g) in *tert*-butyl alcohol (330 mL) was irradiated for 15 min. GC analysis of the irradiated solution showed a mixture (8:1) of **4a** and *N*-methylpentanamide (**3a**). The workup gave a liquid that was eluted through a silica gel column with ethyl acetate–methanol (19:1) to give **4a** (2.53 g, 68%): IR ($CHCl_3$) 3465, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (d, 3 H), 1.70–2.69 (m, 4 H), 2.78 (d, 3 H), 3.87–4.28 (m, 1 H), 7.10 (brs, 1 H); ^{13}C NMR ($CDCl_3$) δ 173.1, 58.2, 35.9, 33.2, 26.2, 25.4.

(35) The parent amide was identified by comparison with an authentic sample.

Attempts to purify **4a** by distillation resulted in decomposition.

***N*-Isopropyl-4-chloropentanamide (4l).** A solution containing *N*-chloro-*N*-isopropylpentanamide (**1l**; 4.39 g, 24.7 mmol) and potassium acetate (4.4 g) in *tert*-butyl alcohol (330 mL) was irradiated for 15 min. The workup gave a solid that was recrystallized from petroleum ether to give **4l** as colorless needles (3.58 g, 81%): mp 55–56 °C; IR ($CHCl_3$) 3445, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (d, 6 H), 1.55 (d, 3 H), 1.74–2.20 (m, 2 H), 2.20–2.45 (m, 2 H), 3.84–4.29 (m, 2 H), 5.60 (brs, 1 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 58.4, 41.4, 35.9, 33.8, 25.5, 22.8. Anal. Calcd for $C_8H_{16}NOCl$: C, 54.08; H, 9.08; N, 7.89. Found: C, 53.93; H, 8.92; N, 7.96.

Quantitative Irradiations. A Rayonet Model RPR-100 photoreactor fitted with eight PRP-2537 Å lamps was used for all analytical-scale photolyses at 254 nm. The photoreactor was equipped with a Rayonet Model MGR-100 merry-go-round, supporting up to eight test tubes and providing the same light intensity for each tube.

Solutions of *N*-chloro amides (with additives) were normally 7.5×10^{-2} M in methanol. The solutions (2 mL) in 13 mm × 10 mm quartz tubes were deaerated with nitrogen for 15 min prior to irradiation and maintained under a nitrogen atmosphere thereafter. The irradiated samples were neutralized with potassium acetate and yields determined by GC analysis relative to a saturated hydrocarbon standard added after photolysis.

Quantum yields for the decomposition of **1a** (0.1 M) in methanol solution were determined with three PRP-2537 Å lamps. The amount of light absorbed by a sample during the course of an irradiation was determined with use of potassium ferrioxalate actinometry.[20]

Acknowledgment. We thank J. L. Edwards and A. L. Schwartz for technical assistance and A. G. Geigley for ^1H NMR and ^{13}C NMR spectra.

Registry No. **1a**, 10271-71-3; **1b**, 87740-37-2; **1c**, 87740-38-3; **1d**, 87740-39-4; **1e**, 23624-82-0; **1f**, 33744-04-6; **1g**, 54468-04-1; **1h**, 19434-64-1; **1i**, 44639-55-6; **1j**, 87740-40-7; **1k**, 5014-42-6; **1l**, 87740-41-8; **1m**, 36393-98-3; **2a**, 74802-84-9; **2b**, 87740-42-9; **2c**, 87740-43-0; **2d**, 87740-44-1; **2e**, 39057-61-9; **2f**, 63853-74-7; **2g**, 63853-82-7; **2h**, 63853-81-6; **3a**, 6225-10-1; **3b**, 13092-79-0; **3c**, 1540-94-9; **3d**, 7501-79-3; **3e**, 588-46-5; **3h**, 105-60-2; **3i**, 1118-69-0; **3j**, 25291-41-2; **3k**, 1124-53-4; **3l**, 87740-45-2; **3m**, 54385-24-9; **4a**, 10336-07-9; **4l**, 87740-46-3; **5**, 87740-47-4; **6a**, 36394-04-4; **6b**, 36394-03-3; MeOH, 67-56-1; EtOH, 64-17-5; *t*-BuOH, 75-65-0; KOAc, 127-08-2; TMP, 108-75-8; HCl, 7647-01-0; H_2SO_4, 7664-93-9; CH_3CO_2H, 64-19-7; CF_3CO_2H, 76-05-1; O_2, 7782-44-7; 1-dodecanethiol, 112-55-0; trichloroethylene, 79-01-6; 1-methoxycyclohexene, 931-57-7; *N*-(ethoxymethyl)valeramide, 87740-48-5; *N*-(*tert*-butoxymethyl)valeramide, 87740-49-6; 1,1-dimethoxycyclohexane, 933-40-4; valeramide, 626-97-1; 2-chloro-1,1-dimethoxycyclohexane, 65933-44-0.

Aspects of the Intramolecular Diels–Alder Reactions of Some 1,3,9-Trienic Amides, Amines, and Esters. An Approach to the Pentacyclic Skeleton of the Yohimboid Alkaloids

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The intramolecular cycloadditions of a number of 1,3,9-trienes containing an amide, amine, or ester function in the chain linking the dienophile and the diene were examined, and a general preference for the formation of cis cycloadducts was observed. Thus, the aza trienes **7b–h** were found to undergo intramolecular Diels–Alder reaction upon thermolysis at temperatures ranging from 25 to 275 °C to give mixtures of the *cis*- and *trans*-hydroisoquinolines **9b–h** and **10b–h**, respectively, in ratios that varied from about 1.1:1 to 8:1. Thermolysis of the pentadienamide **34** produced the *cis*- and *trans*-hydroisoquinolines **35** and **36** (1.6:1). Interestingly, the aza trienes **13** and **14** in which the internal double bond is *Z* appear to suffer extensive isomerization, presumably via 1,5 hydrogen migration, prior to cyclization to provide isomeric trienes, which have not been isolated but have been tentatively identified as **22** and **25** since they afford corresponding mixtures of the *cis*- and *trans*-hydroisoindoles **20/21** and **23/24** as the principal cycloadducts; only small amounts of the expected *cis*-hydroisoquinolines **9e** and **9h** were obtained in these thermolyses. In order to demonstrate the feasibility of applying intramolecular Diels–Alder reactions of aza trienes to the syntheses of alkaloids containing a hydroisoquinoline ring, the *trans*-hydroisoquinoline **10d** was converted to the yohimbine-related compounds **38** and **39** by cyclization with $POCl_3$ followed by either catalytic hydrogenation or hydride reduction of the intermediate iminium salt. The reactivity of the related esters **40–42** toward intramolecular [4 + 2] cycloaddition was also briefly examined, and it was found that only the acrylate **41** underwent cyclization at temperatures below 275 °C.

Introduction

During the course of a general investigation directed toward the development of new strategies for alkaloid synthesis, we have examined the feasibility of employing intramolecular Diels–Alder reactions[2] for the construction of fused, functionalized nitrogen heterocycles. Our investigations coupled with those of others have now clearly established that the intramolecular [4 + 2] cycloadditions of suitably substituted aza trienes may be utilized for the expeditious construction of hydroindoles, hydroisoindoles, hydroquinolines, indolizidines, and quinolizidines,[3] which are important structural elements common to many al-

(1) Recipient of a National Institutes of Health (National Cancer Institute) Research Career Development Award, 1980–1985.

(2) For reviews of intramolecular Diels–Alder reactions, see: (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10; *Synthesis* **1978**, 793; *Heterocycles* **1980**, *14*, 1615. (b) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (c) Ciganek, E. *Org. React.*, in press. We thank Dr. Ciganek, for a preprint of this manuscript prior to publication.

(3) For a leading reference of the intramolecular cycloadditions of various aza trienes, see: Martin, S. F.; Tu, C.; Kimura, M.; Simonsen, S. H. *J. Org. Chem.* **1982**, *47*, 3634 and references cited therein. For other recent examples, also see: (a) Takebayashi, T.; Iwasawa, N.; Mukaiyama, T. *Chem. Lett.* **1982**, 579. (b) Exon, C.; Gallagher, T.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1982**, 613. (c) Bremmer, M. L.; Weinreb, S. M. *Tetrahedron Lett.* **1983**, *24*, 261. (d) Gallagher, T.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2086.

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