Chlorination with N-Chloro Amides. I. Inter- and Intramolecular Chlorination[1a]

Richard A. Johnson[1b] and Frederick D. Greene*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received January 15, 1975

Decomposition of a series of *N*-chloro amides in solution has been examined as a function of the solvent, the structure of the *N*-chloro amide, the mode of initiation, and the effect of additives. The reactions proceed by free-radical chain decomposition, affording products derived from intra- and intermolecular hydrogen abstraction. The light-initiated decompositions of *N*-chloro-*N*-methylacetamide (**1a**), *N*-chloro-*N*-*tert*-butylacetamide (**2a**), and *N*-chloro-*N*-(1,1-dimethyl-2-phenylethyl)acetamide (**3a**) in cyclohexane afforded chlorocyclohexane and the parent amide; the rates were inhibited by 2,4,6-trimethylpyridine. The decomposition of *N*-chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide (**4a**) afforded *N*-*tert*-butyl-3-chloro-2,2-dimethylpropionamide (**4c**) derived from the rarely observed intramolecular 1,4-hydrogen transfer. The decomposition of *N*-chloro-*N*-(1,1-dimethylpentyl)-acetamide (**5a**) afforded *N*-(1,1-dimethyl-4-chloropentyl)acetamide (**5c**) in high yield, derived from 1,5-hydrogen transfer from carbon to nitrogen. The light-initiated decompositions of **4a** and **5a** were not inhibited by trimethylpyridine. The decompositions are interpreted in terms of chlorine atom–HCl chains (repressible by 2,4,6-trimethylpyridine) and of amidyl radical chains. Hydrogen abstraction takes place at the nitrogen and not at the oxygen of an amidyl radical.

Replacement of hydrogen of an amide (RCONHR′) by halogen (RCONXR′) affords a means for selective degradation of the amide under mild conditions. The synthetic utility of *N*-halo amides has been discussed.[2] The amidyl radical derived from the *N*-halo species may abstract a hydrogen atom by an intramolecular process analogous to the 1,5-hydrogen shift from carbon to nitrogen in the Hoffman–Loeffler–Freytag rearrangement.[3] A number of amides[4,5] (X = Cl, Br, I) and a few sulfonamides[6] have been halogenated on the acyl portion (R) by this method. The major products usually are derived from 1,5-hydrogen transfer, with minor products from 1,6 transfer in a few cases. Halogenation of the *N*-alkyl chain (R′) at the δ carbon also occurs by this method.[7] Amidyl radicals generated by the photolysis of *N*-nitroso amides undergo 1,5-hydrogen transfer from the *N*-alkyl chain.[8]

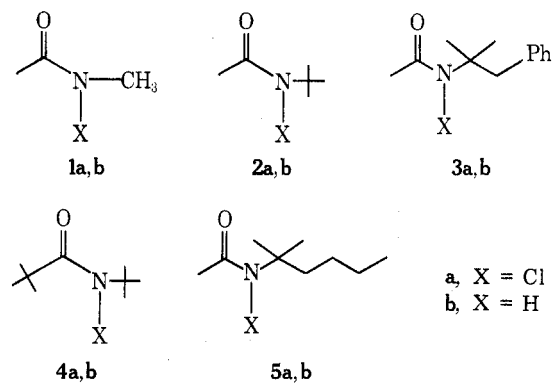
The objective of this work is to broaden our understanding of amidyl radicals, and to elucidate factors which affect the various free-radical chain decomposition paths of several *N*-chloro amides. Selectivity in hydrogen atom abstraction is taken up in Part II.[9]

Results

Preparation and Properties of *N*-Chloro Amides. *N*-Chloro amides **1a, 2a, 3a,** and **5a** were readily prepared by treating the parent amide with *tert*-butyl hypochlorite in methanol.[10] Compound **4a** required the use of chlorine monoxide in CCl_4. The N-tertiary alkyl compounds **2a, 3a, 4a,** and **5a** were stable over a period of months at 5° (in the dark). *N*-Chloro-*N*-methylacetamide (**1a**) was unstable in 2,3-dimethylbutane at 5° over a period of days.

The ultraviolet spectra of the *N*-chloro amides have maxima in the region of 260 mμ with broad tailing up to ca. 360 mμ, which permits light-initiated reactions to be carried out in Pyrex glassware. All of the *N*-chloro amides were stable toward 2,4,6-trimethylpyridine (TMP) under the reaction conditions but not stable to triethylamine or to pyridine. All (except **1a,** which was not tested) were stable toward trichloroethylene (TCE). The *N*-chloro amides **1a–5a** are readily soluble in cyclohexane, 2,2-dimethylbutane, 2,3-dimethylbutane, *n*-hexane, and benzene. The parent amides **1b–5b,** often major products of decomposition, are much less soluble and occasionally crystallize from solution after completion of the reaction.

Decomposition. The *N*-chloro amides are moderately stable in solution at 80° in the dark. In 2,3-dimethylbutane or cyclohexane, the values for $t_{1/2}$ (the time for decomposition of the first 50% of the *N*-chloro amide) follow: **2a** (20 days), **4a** (9 hr), **5a** (10 hr). Rates of decomposition are greatly accelerated by irradiation with a weak ultraviolet source or by use of dibenzoyl peroxide (azobisisobutyronitrile was ineffective). Rates are retarded by oxygen. The chain length for decomposition of *N*-chloro-*N*-*tert*-butylacetamide in cyclohexane at 80° in the dark initiated by dibenzoyl peroxide was ca. 2000.



1a, *N*-chloro-*N*-methylacetamide
2a, *N*-chloro-*tert*-butylacetamide
3a, *N*-chloro-*N*-(1,1-dimethyl-2-phenylethyl)acetamide
4a, *N*-chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide
5a, *N*-chloro-*N*-(1,1-dimethylpentyl)acetamide

The products of decomposition are dependent on the *N*-chloro amide and on the reaction conditions. The results are summarized in the following paragraphs and in Tables I–IV.

***N*-Chloro-*N*-methylacetamide (1a) and *N*-Chloro-*N*-*tert*-butylacetamide (2a) (Table I and Eq 1).** The presence of 2,4,6-trimethylpyridine greatly reduced the rate of decomposition but had little effect on product composition.

$$\underset{\textbf{1a},\ R' = CH_3}{\underset{\textbf{2a},\ R' = \textit{tert}\text{-butyl}}{CH_3CONClR'}} \xrightarrow[h\nu,\ 25°]{\text{cyclohexane}} CH_3CONHR' + C_6H_{11}Cl \qquad (1)$$

***N*-Chloro-*N*-(1,1-dimethyl-2-phenylethyl)acetamide (3a) (Table II and Eq 2 and 3).** The irradiation of **3a** in degassed cyclohexane produced yields of 80–90% of the

Table I
Light-initiated Decomposition of *N*-Chloro Amides in Cyclohexane at 20–25°

N-Chloro amide	[*N*-Chloro amide], *M*	[TMP],[a] *M*	Yield of RCl, %	$t_{1/2}$,[b] min
1a	0.15		97	10
	0.15	0.22	94	320
2a	0.64		97	3
	0.64	0.19	89	125
3a	0.058		79	18
	0.058	0.15	46	430
4a	0.10		48[c,d]	3
	0.10	0.11	3[e]	6
5a	0.063		4[f]	9
	0.066	0.15	0.3[g]	6

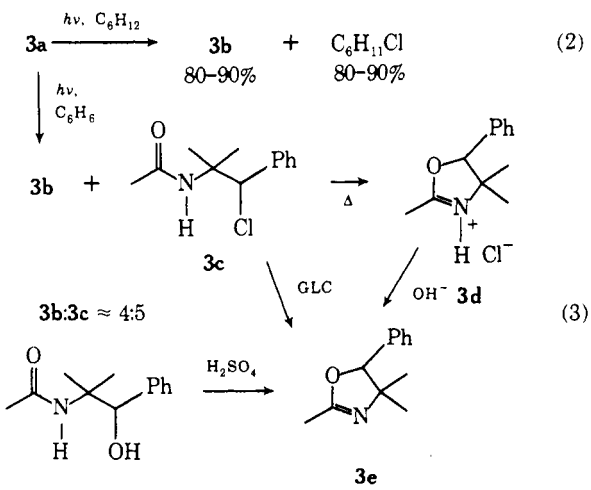
[a] TMP, 2,4,6-trimethylpyridine. [b] $t_{1/2}$ = time for 50% decomposition of *N*-chloro amide. [c] Solvent was a mixture of 2,3-dimethylbutane and cyclohexane. [d] Major product is 4c (52%); see eq 4. [e] Major product is 4c (97%); see eq 4. [f] Major product is 5c (94%); see eq 6. [g] Major product is 5c (100%); see eq 6.

Table II
Product Yields and Values for $t_{1/2}$ in the Light-Initiated Decomposition of *N*-Chloro-*N*-(1,1-dimethyl-2-phenylethyl)acetamide (3a) in Cyclohexane at 25°

			Products[b]	
[**3a**], *M*	Additive (*M*)	$t_{1/2}$, min[a]	**3b**, %	$C_6H_{11}Cl$, %
0.058	None	18	89	79
0.047	None	55	75	80
0.071	None	25	93	83
0.047	Ox[c]	102	90	88
0.058	TMP (0.15)[d]	430	52	46
0.047	TMP (0.05)[d]	430	57	53
0.047	TMP (0.05),[d] Ox	768	75	62

[a] $t_{1/2}$ = time for 50% decomposition of **3a**. [b] Percent yield determined by GLC using internal standards; **3b**, *N*-(1,1-dimethyl-2-phenylethyl)acetamide; $C_6H_{11}Cl$, chlorocyclohexane. [c] Undegassed, oxygen present. [d] TMP, 2,4,6-trimethylpyridine.

parent amide **3b** and chlorocyclohexane (Table II). The irradiation of **3a** in degassed benzene produced **3b** and *N*-(1,1-dimethyl-2-chloro-2-phenylethyl)acetamide (**3c**) in a ratio of ca. 4:5. On warming the benzene solution, **3c** isomerized to the hydrochloride salt **3d**. On washing with base,



3d gave 5-phenyl-2,4,4-trimethyl-2-oxazoline (**3e**), which was also collected from the GLC analysis of **3c**. An authentic sample of **3e** was prepared by an alternate route. Neither **3c** nor **3e** was a product in the irradiation of **3a** in cyclohexane.

Table III
Products and Values for $t_{1/2}$ in the Decomposition of 0.10 *M* *N*-Chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide (4a) in 2,3-Dimethylbutane and Cyclohexane (1.57:1 Molar Ratio)

		Products, %	
Conditions[a]	$t_{1/2}$, min[b]	**4b**	**4c**
hν, 21°	3	48	52
hν, 21°, TMP[c] (0.11 *M*)	6	3	97
Dark, 80°	~600	6	94
Dark, 80°, DBPO[d] (5.6 mol %)	7	6	94

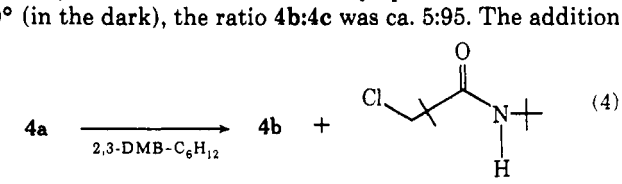
[a] All samples were degassed. [b] Time for 50% decomposition of **4a**. [c] TMP = 2,4,6-trimethylpyridine. [d] DBPO, dibenzoyl peroxide.

Table IV
Light-Initiated Decomposition of *N*-Chloro-*N*-(1,1-dimethylpentyl)acetamide (5a) in Cyclohexane at 25°

			Products, %[b]		
[**5a**], *M*	Additive (*M*)	$t_{1/2}$[a]	**5c**	**5b**	$C_6H_{11}Cl$
0.063	None	9	94	6	4
0.075[c]	None	3	97	3	3
0.063	Ox[d]	89	6	83	78
0.066	TMP[e] (0.15)	6	100	0.3	0.3
0.066	TMP[e] (0.15), Ox[d]	110	86	3	3

[a] $t_{1/2}$ = time for 50% decomposition of **5a**. [b] Determined by GLC using internal standards: **5b**, *N*-(1,1-dimethylpentyl)acetamide; **5c**, *N*-(1,1-dimethyl-4-chloropentyl)acetamide. See eq 6. [c] Irradiated at 15°. [d] Undegassed, oxygen present. [e] TMP, 2,4,6-trimethylpyridine.

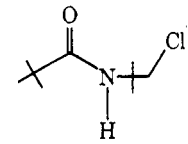
***N*-Chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide (4a).** The irradiation of **4a** in a mixture of 2,3-dimethylbutane and cyclohexane gave the parent amide **4b** and *N*-*tert*-butyl-3-chloro-2,2-dimethylpropionamide (**4c**) in ca. 1:1 ratio (Table III). No other amide products were observed. When **4a** was irradiated with trimethylpyridine present, or initiated with dibenzoyl peroxide (DBPO) at 80° (in the dark), the ratio **4b**:**4c** was ca. 5:95. The addition



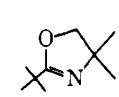
4c

of trimethylpyridine had only a small effect on the rate. The thermolysis was slow ($t_{1/2}$ 600 min), the peroxide-initiated reaction much faster ($t_{1/2}$ 7 min) at 80°.

Assignment of structure for the rearranged product as **4c** (rather than **4d**) was made on the basis of mass spectral

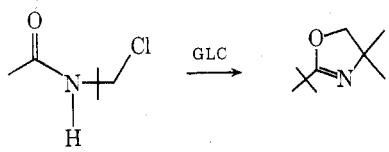


4d



4e

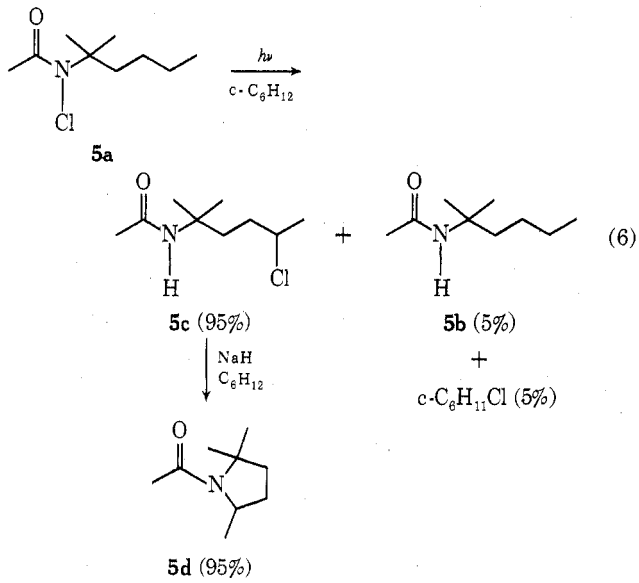
data which place the chlorine on the acyl portion of the amide (see Experimental Section). This assignment is supported by the thermal stability of **4c**, which could be collected unchanged from GLC. Under such conditions, amide **4d** would be expected to cyclize to the oxazoline **4e**,[11] as was found for **3c** (eq 3) and reported[4] for **2c** (eq 5).



(5)

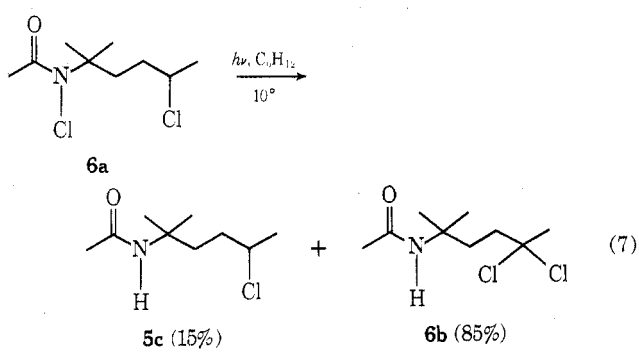
2c

***N*-Chloro-*N*-(1,1-dimethylpentyl)acetamide (5a) (Table IV and Eq 6).** The only chlorinated amide product found was **5c**, based on NMR evidence, on cyclization to acetyl-2,2,5-trimethylpyrrolidine (**5d**) by treatment with sodium hydride in refluxing hexane, and on comparison with an authentic sample of **5c** prepared by an alternate route.



When solutions of **5a** were irradiated without degassing, the yields of the rearranged amide **5c** were greatly reduced (6–10%) and the yields of the parent amide **5b** and chlorocyclohexane correspondingly increased (74–78%) (Table IV). The samples that were not degassed also had a much longer time for 50% decomposition, characteristic of oxygen inhibition of free-radical chain reactions. The addition of trimethylpyridine raised the yield of the rearranged amide **5c** to ca. 100% in degassed samples and to 86% in samples not degassed. The base had very little effect on the rate of decomposition of **5a**.

Treatment of **5c** with *tert*-butyl hypochlorite in methyl alcohol afforded *N*-chloro-*N*-(1,1-dimethyl-4-chloropentyl)acetamide (**6a**), which on irradiation in degassed cyclohexane yielded ca. 15% **5c** and 85% *N*-(1,1-dimethyl-4,4-dichloropentyl)acetamide (**6b**).



Discussion

The sensitivity of the rates of decomposition to inhibition by oxygen and other additives and to acceleration by free-radical initiators and by weak irradiation indicates that the *N*-chloro amides **1a–5a** decompose by free-radical chain reactions of long chain length. The variations in rates and in product compositions as a function of additives point strongly to the operation of more than one kind of chain process.[12] The principal possibilities are summarized in Scheme I.

The "amidyl radical chain" simply involves abstraction of a hydrogen from the solvent or from within the amide (intramolecular) followed by atom transfer of a chlorine from another *N*-chloro amide to the intermediate carbon radical. The chlorine atom chain is essentially the Goldfinger mechanism[12,13] proposed for *N*-chlorosuccinimide. Neale[4] and others have shown that HCl rapidly reacts with *N*-chloro amide to generate Cl_2.

Effects of 2,4,6-Trimethylpyridine and Other Scavengers. The purpose of adding 2,4,6-trimethylpyridine (TMP) was to trap any HCl generated during the photolysis with the hope of limiting the reaction of the *N*-chloro amide to an amidyl radical chain (see Scheme I). This additive has a large inhibiting effect on the rates of decomposition of *N*-chloro-*N*-methylacetamide (**1a**), *N*-chloro-*N*-*tert*-butylacetamide (**2a**), and *N*-chloro-*N*-(1,1-dimethyl-2-phenylethyl)acetamide (**3a**) (see Table I), all of which give products of solvent chlorination. The rates for *N*-chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide (**4a**) and *N*-chloro-*N*-(1,1-dimethylpentyl)acetamide (**5a**) show little or no inhibition when TMP is added (see Table I). Intramolecular hydrogen transfer leading to the *C*-chloro compound **5c** is the primary chain reaction path for **5a**. TMP does not inhibit the reaction, but does increase the yield of rearranged product **5c** (see Table IV), and essentially eliminates chlorination of the cyclohexane. A similar, but more dramatic, effect is observed for the irradiation of **4a** in cyclohexane. Without TMP, approximately 50% of the product is **4c** (intramolecular attack) and 50% is chloroalkane (intermolecular attack). Addition of TMP has little effect on rate but changes the product composition to 97% **4c** (intramolecular) and 3% chloroalkane (intermolecular). The simplest interpretation for cases **4a** and **5a** is (1) irradiation initiates both amidyl radical chains and chlorine atom chains; (2) the amidyl radicals abstract hydrogen intramolecularly, leading on to the *C*-chloro amides **4c** and **5c**; (3) these amidyl radical chains are not affected by TMP; and (4) chlorination of solvent comes from chlorine atom–HCl chains which are repressed by the acid-scavenging action of TMP.

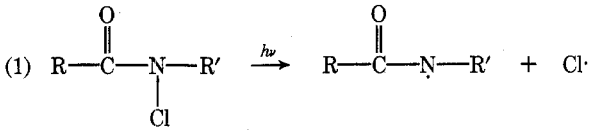
In the light-initiated decomposition of **1a**, **2a**, and **3a** the products indicate that the major reaction is chlorination of the solvent (cyclohexane or 2,3-dimethylbutane). The reaction could proceed by amidyl radical chains, by chlorine atom–HCl chains, or perhaps both. The strong inhibition by TMP suggests that HCl is important in the chain decomposition. In the presence of TMP presumably only the slower amidyl radical chain is available as the principal chlorination path.[14]

Effect of Oxygen on *N*-Chloro Amide Reactions. The rates of decomposition of all five of the *N*-chloro amides were inhibited by oxygen. Different product ratios and chlorination selectivities[9] were also observed, suggesting significant changes in the atom transfer steps involved.

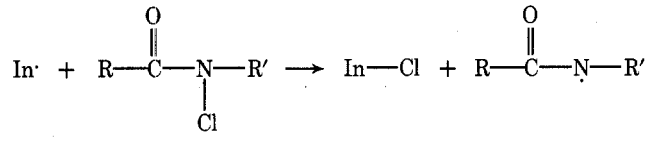
Light-initiated decomposition of **5a** in cyclohexane *in*

Scheme I
Free-Radical Chain Steps of *N*-Chloro Amides

Initiation



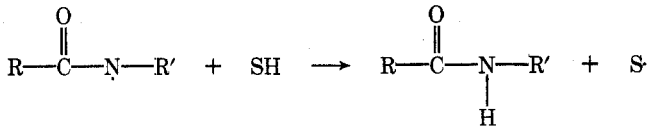
or (2) Initiator → 2In·

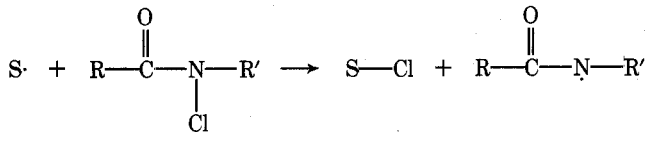


Propagation

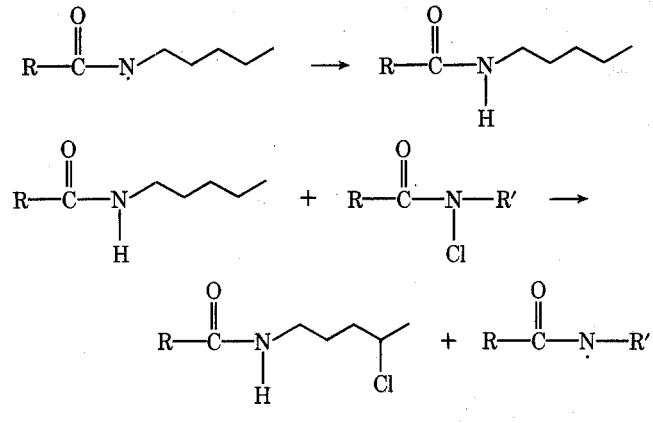
(1) Amidyl radical chain

(a) Intermolecular

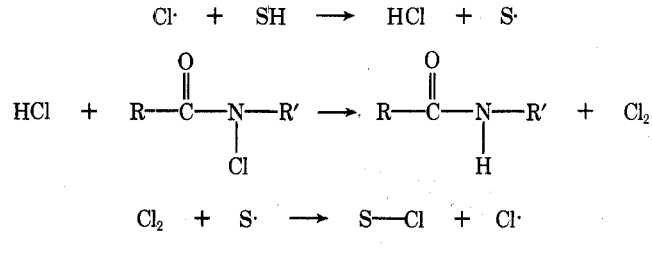




(b) Intramolecular



(2) Chlorine atom–HCl chain

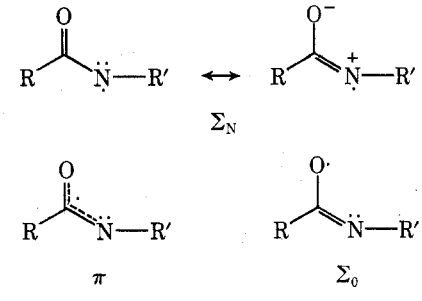


Termination (The results of this study are uninformative on this point; presumably the usual "like-" and "cross-termination" steps are involved.)

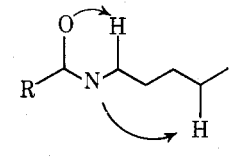
the presence of oxygen and absence of TMP greatly increases the importance of solvent chlorination (Table IV, lines 1 and 2 vs. line 3); in the presence of TMP, solvent chlorination with **5a** is unimportant and remains unimportant when oxygen is present (Table IV, lines 3 and 4). These results suggest that oxygen in some way enhances the chlorine atom–HCl chains. In accord with this, the light-initiated chlorinations of various alkanes with **2a** in the presence of oxygen show selectivities characteristic of chlorine atoms.[9] Again, this suggests that oxygen favors the HCl chain mechanism.

A study[15] of the allylic bromination of cyclohexene by *N*-bromosuccinimide (NBS) in carbon tetrachloride contains several observations relevant to the present case. Cyclohexenyl hydroperoxide increased the rate of allylic bromination, but the presence of oxygen inhibited the reaction. Thus, with the *N*-chloro amides of the present study, oxygen inhibits the free-radical chain reaction, and in the process forms hydroperoxides which react with the *N*-chloro amide to produce HCl and carry on the HCl chain. In this way the rate is inhibited, the yield of intermolecular chlorination products is raised in the case of **5a**, and chlorination with **2a** in the presence of oxygen is characteristic of chlorine atom.[9] The formation of amide peroxides may be the cause of the poor product balance in the irradiation of **5a** in the presence of oxygen.

Reactive Center of an Amidyl Radical. Amidyl radicals might be expected to show reactivity at both oxygen and nitrogen. An amidyl radical has several possible ground states (Σ_N, π, Σ_O). Evidence from ESR favors the π state for simple amidyl radicals.[16]



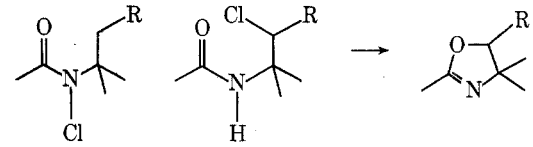
If we only consider the favored six-membered transition state (resulting in 1,5-hydrogen transfer), attack on the *N*-alkyl chain could result in two different products, depending on whether oxygen or nitrogen is the abstracting



species. We concur with Chow and Joseph that reactivity at oxygen is nil,[7] for the reasons given below.

When **5a** was irradiated (with trimethylpyridine to quench the HCl chain) in cyclohexane, a 100% yield of a single chloro amide (**5c**) was obtained, indicating a highly specific 1,5-hydrogen transfer from carbon to nitrogen. The 85% yield of **6b** from **6a** (eq 7) further suggests the preference for 1,5-hydrogen transfer to nitrogen, overcoming the expected low reactivity of the hydrogen at this δ carbon already holding one chlorine.[17-19]

The light-initiated decompositions of **2a** and **3a** in *cyclohexane* did not yield any of the rearrangement product (**2c** or **3c**), even when trimethylpyridine was added to quench

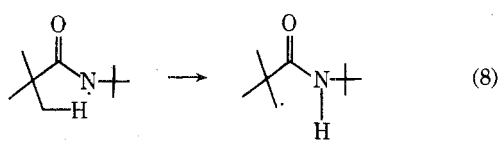


2a, R = H **2c**, R = H
3a, R = Ph **3c**, R = Ph

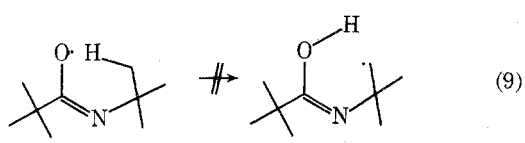
the HCl chain chlorination of cyclohexane. The large rate inhibition by trimethylpyridine on **2a** and **3a** (compared to the negligible inhibition for **4a** and **5a**, see Table I) also is consistent with a lack of intramolecular hydrogen abstraction. The light-initiated decompositions of **2a**[4,7] and **3a** in *benzene* do afford **2c** and **3c**, in all likelihood the result of intermolecular attack by amidyl radical or chlorine atom.

***N-tert*-Butyl-2,2-dimethylpropionamidyl Radical.** The decomposition of **4a**, like that of the other *N*-chloro amides of this study,[1,2] clearly takes place by a free-radical chain reaction (Table III). The major product (~97% from **4a** with $h\nu$, TMP), even in cyclohexane as solvent, is *N-tert*-butyl-3-chloro-2,2-dimethylpropionamide (**4c**) (eq 4). Apparently, the amidyl radical is so hindered that the unfavorable 1,4-hydrogen transfer is preferred over abstraction of hydrogen from the solvent. The 1,4-hydrogen transfer is quite unusual and has not been observed in rearrangements of alkoxy,[20a] aminium,[3] or amidyl[4-8] radicals. The major path where possible is 1,5-hydrogen transfer via a six-membered ring transition state. In some cases low yields of products of 1,6-hydrogen transfer have been observed.[5b] Products derived from 1,4-hydrogen transfer have been reported in some studies of carbonyl compounds.[20b] 1,4-Hydrogen transfer also has been observed in the 2,4,6-tri-*tert*-butylphenyl radical.[20c]

The fact that 1,4-hydrogen transfer from the acyl *tert*-butyl group (eq 8) occurs with **4a** is further evidence that amidyl radicals do not undergo hydrogen abstraction by oxygen (eq 9). Abstraction by an oxygen radical would involve a favorable 1,5-hydrogen transfer by attacking the *N-tert*-butyl group.

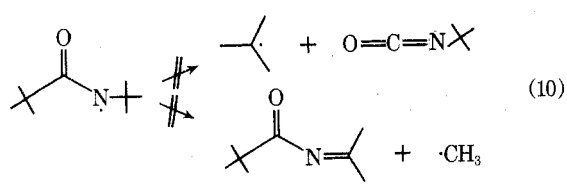


(8)



(9)

An alternative to hydrogen transfer would be β-scission of the amidyl radical (eq 10). This process is commonly observed for alkoxy radicals[20a,21] and has been proposed to explain some of the products from the photolysis of *N*-nitroso amides.[22] However, products of β-scission were not observed in the reactions of **4a**.



(10)

Experimental Section

Melting points are corrected. Reagent grade cyclohexane and 2,3-dimethylbutane were washed with concentrated sulfuric acid (until no discoloration) and distilled from sodium benzophenone ketyl.

Gas–liquid partition chromatographic analyses (GLC) were performed on an Aerograph 220 instrument with a thermal conductivity detector and with glass injection port liners. The following columns were used: column A, 2 ft × 0.25 in. aluminum tube packed with 15% silicone oil (SE-30) and 0.5% diethylene glycol succinate (DEGS) on Chromosorb W; column B, 6 ft × 0.25 in. aluminum tube packed with 15% Versamide 900 on Chromosorb W; column C, 6 ft × 0.25 in. aluminum tube packed with 15% silicone oil (SE-30) and 0.5% diethylene glycol succinate (DEGS) on Chromosorb W; column D, 6 ft × 0.25 in. aluminum tube packed with 20% silicone oil (SE-30) and 2% diethylene glycol succinate (DEGS) on Chromosorb P.

***N*-(1,1-Dimethylpentyl)acetamide (5b)** was prepared by the Ritter reaction[23] with 2-methyl-2-hexanol, acetonitrile, and concentrated H_2SO_4, as colorless needles (hexane): mp 53.0–54.5° (lit.[24] mp 65–67°); ir (CCl_4) 3430 (sh, NH), 3310 (br, NH), 1685 (s, C=O), 1540 (s, -NHC=O), 1385, and 1367 cm^{-1} [$-C(CH_3)_2$]; NMR δ 0.90 (t, J = 6 Hz, 3 H, $-CH_2CH_3$), 1.27 [s, 6 H, $-C(CH_3)_2$], 1.87 (s, 3 H, CH_3CO-), 1.1–1.7 [m, 6 H, $-(CH_2)_3CH_3$], and 5.9 ppm (s, 1 H, NH).

Anal. Calcd for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.90. Found: C, 68.48; H, 12.10; N, 8.95.

***N*-Chloro-*N*-(1,1-dimethylpentyl)acetamide (5a).** To a solution of 10.02 g (0.064 mol) of *N*-(1,1-dimethylpentyl)acetamide in 25 ml of methyl alcohol in a foil-wrapped flask was added 11 ml (10 g, 0.092 mol) of *tert*-butyl hypochlorite. After stirring for 2 hr the solvent and excess hypochlorite were removed on a rotoevaporator, leaving a colorless liquid. Distillation yielded 10.62 g (87%), bp 35.0–36.2° (0.36 mm). Iodometric analysis indicated 99.5 ± 1.5% active chlorine: ir (CCl_4) 1680 (s, C=O) and 1280 cm^{-1} (s); uv (isooctane) λ_{max} 257 mμ (ϵ 356); NMR (CCl_4) δ 0.92 (t, J = 6 Hz, 3 H, $-CH_2CH_3$), 1.41 [s, 6 H, $-C(CH_3)_2$], 2.16 (s, 3 H, CH_3CO-), and 1.1–1.9 ppm [m, 6 H, $-(CH_2)_3CH_3$].

Anal. Calcd for $C_9H_{18}NOCl$: C, 56.39; H, 9.46; N, 7.31. Found: C, 56.52; H, 9.36; N, 7.19.

***N*-Chloro-*N*-methylacetamide (1a)** was prepared by treating the amide with *tert*-butyl hypochlorite in methyl alcohol: bp 35–40° (14–18 mm); $n^{25.5}D$ 1.4563; ir (CCl_4) 1685 (C=O), 1320 cm^{-1} (s) [lit.[4] bp 42° (24 mm), $n^{23.5}D$ 1.4583]; iodometric analysis, 96.5 ± 1.0% active chlorine.

***N*-Chloro-*N*-*tert*-butylacetamide (2a)** was prepared by treating the amide with *tert*-butyl hypochlorite in methyl alcohol: bp 50° (9 mm); $n^{23.0}D$ 1.4506 [lit.[4] bp 44° (9 mm), $n^{23}D$ 1.4510]; ir (CCl_4) 1680 (s, C=O) and 1285 cm^{-1} (s); NMR (CCl_4) δ 1.43 [s, 9 H, $-C(CH_3)_3$] and 2.15 ppm (s, 3 H, CH_3CO-); iodometric analysis, 97.0 ± 1.0% active chlorine.

***N*-(1,1-Dimethyl-2-phenylethyl)acetamide (3b)** was prepared by treating α,α-dimethyl-β-phenethylamine with acetic anhydride in ether: mp 90.0–91.0° (lit.[25] mp 91.5–92.0°); ir (CCl_4) 3440 (sh, NH), 3300 (br, NH), 1682 (s, C=O), and 1502 cm^{-1} (s, -NHC=O); NMR (CCl_4) δ 1.22 [s, 6 H, $-C(CH_3)_2$], 1.69 (s, 3 H, CH_3CO-), 2.92 (s, 2 H, $-CH_2C_6H_5$), 6.16 (s, 1 H, -NH), and 6.97 ppm (s, 5 H, $-C_6H_5$); uv (isooctane) λ_{max} 259 mμ (ϵ 180).

***N*-Chloro-*N*-(1,1-dimethyl-2-phenylethyl)acetamide (3a)** was prepared by treating the amide with *tert*-butyl hypochlorite in methyl alcohol, yielding a viscous, colorless liquid: bp 73–77° (0.10 mm); $n^{26.2}D$ 1.5294; ir (CCl_4) 1663 (s, C=O) and 1290 cm^{-1} (s); NMR (CCl_4) δ 1.43 [s, 6 H, $-C(CH_3)_2$], 2.17 (s, 3 H, CH_3CO-), 3.13 (s, 2 H, $-CH_2C_6H_5$), and 7.14 ppm (s, 5 H, $-C_6H_5$); uv (isooctane) λ_{max} 259 mμ (ϵ 492); iodometric analysis, 98.0 ± 1.0% active chlorine.

Anal. Calcd for $C_{12}H_{16}NOCl$: C, 63.85; H, 7.15; N, 6.21. Found: C, 63.97; H, 7.15; N, 6.31.

***N-tert*-Butyl-2,2-dimethylpropionamide (4b)** was prepared by adding an excess of *tert*-butylamine to 2,2-dimethylpropionyl chloride in ether: mp 118–119° (hexane) (lit.[26] mp 118–119°); ir (CCl_4) 3480 (sh, NH), 1670 cm^{-1} (s, C=O); NMR (CCl_4) δ 1.15 (s, 9 H), 1.35 (s, 9 H), and 5.25 ppm (s, 1 H, NH).

***N*-Chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide (4a).** To 5.9 g (0.038 mol) of the amide in 50 ml of CCl_4 in a foil-wrapped flask was added 115 ml of a 0.37 M solution of chlorine monoxide[27] in CCl_4. After stirring for 3 hr the solution was washed with 300 ml of water and dried ($MgSO_4$), the solvent was removed on a rotoevaporator, and the remaining pale yellow liquid was distilled: 4.32 g; bp 26° (0.04 mm); ir (CCl_4) 1672 (s, C=O), 1262 (s), and 1155 cm^{-1} (s); NMR (CCl_4) δ 1.35 (s, 9 H) and 1.45 ppm (s, 9 H); iodometric analysis, 96.0 ± 1.0% active chlorine. Attempts to N-chlorinate the amide with *tert*-butyl hypochlorite under a variety of conditions were unsuccessful.

Methods for the Decomposition of *N*-Chloro Amides. Some large-scale decompositions were done in 17-mm o.d. Pyrex test tubes which had been washed in a Lakeseal glass cleanser solution, rinsed, and dried. Reactions in which rates, product yields, or relative reactivities were determined were carried out in 5-mm o.d. Pyrex tubes. Lengths (0.4 m) of tubing were soaked in Lakeseal glass cleaner for 1 hr, rinsed with distilled water, soaked in 0.2 N HCl solution for 24 hr, rinsed, soaked in 0.2 N NH_4OH solution for 24 hr, and rinsed; each length was drawn out to make two tubes (each sealed at one end) and dried (150°).

Solutions of *N*-chloro amide (and added scavengers if specified)

were always made with freshly distilled solvents. Aliquots (0.5 ml) were placed in 5-mm o.d. Pyrex tubes, degassed by freezing (liquid nitrogen), evacuating (0.02–0.05 mm), and thawing five times, and then sealed. Sample tubes which were "not degassed" were loosely capped with no-air stoppers. In light-initiated reactions up to 16 sample tubes were rotated (to assure equal light exposure to each sample) in a clear Pyrex Dewar flask filled with water which was kept at a constant temperature during the run. The low-intensity long-wavelength uv light source was either a Blak-Ray uvl-22 lamp (Ultraviolet Products Co.) or a Burton Model 1910 lamp (Burton Manufacturing Co.). To measure the rates of decomposition, usually two sets of eight tubes were irradiated; samples were periodically removed from the light, immediately frozen, later thawed, opened, and analyzed iodometrically for positive chlorine. Samples were analyzed by GLC after disappearance of the *N*-chloro amide; yields were determined by adding an aliquot containing an internal standard after opening the tube. Thermally initiated samples were placed in a dark constant-temperature oil bath at 80.0 ± 0.1°; the rates and products were determined in the same manner as above.

Irradiation of *N*-Chloro-*N*-(1,1-dimethyl-2-phenylethyl)-acetamide in Benzene. Prepurified nitrogen was slowly bubbled through a solution of 6.10 g of the *N*-chloro amide in 65 ml of benzene for 75 min before irradiation, and a positive nitrogen pressure was maintained in the flask during photolysis. The solution was irradiated for 4 days at 20° with a Westinghouse 275-W sunlamp. Analysis by GLC (column B, 190°) indicated two major peaks at 1.2 and 5.3 min (ratio 1.26:1), the latter corresponding to *N*-(1,1-dimethyl-2-phenylethyl)acetamide. Removal of the benzene (rotoevaporator at room temperature) left a brown oil which was dissolved in 25 ml of CCl_4, seeded, and cooled at −22° for several days. The 2.10 g of off-white material collected was recrystallized three times (CCl_4), yielding 0.73 g of fine white crystals: mp 105.0–106.5° (solidified at 108–110°); second mp 176–179°; ir ($CHCl_3$) 3430 (sh, NH), 3300 (w, br, NH), 1678 (s, C=O), and 1505 cm^{-1} (s, –NHC=O); NMR ($CDCl_3$) δ 1.28 (s, 3 H, $-CCH_3$), 1.45 (s, 3 H, $-CCH_3$), 1.90 (s, 3 H, CH_3CO), 5.83 (s, 1 H, –CHClPh), 5.43 (s, 1 H, NH), and 7.38 (s, 5 H, $-C_6H_5$).

Anal. Calcd for $C_{12}H_{16}NOCl$: C, 63.84; H, 7.10; N, 6.21. Found: C, 63.86; H, 7.00; N, 6.09. When collected by GLC it has the same retention time (1.2 min) as 5-phenyl-2,4,4-trimethyl-2-oxazoline, and an identical ir spectrum.

In a separate experiment, attempts to crystallize this material from benzene–hexane resulted in the collection of fine white crystals: mp 170–175°; ir ($CHCl_3$) 3300–3400 (br, $-^+NH$), 2200–2500 (br, $-^+NH$), 1820 (br, NH), 1665 cm^{-1} (sh, C=O) (characteristic of ammonium salts); NMR ($CDCl_3$) δ 1.08 (s, 3 H, $-CCH_3$), 1.72 (s, 3 H, $-CCH_3$), 2.70 (s, 3 H, CH_3CO), 5.88 (s, 1 H, –OCHPh), and 7.50 ppm (s, 5 H, $-C_6H_5$).

Washing a chloroform solution of this material with a Na_2CO_3 solution produced a colorless oil with ir and NMR identical with those of 5-phenyl-2,4,4-trimethyl-2-oxazoline.

***N*-(1,1-Dimethyl-2-hydroxy-2-phenylethyl)acetamide** was prepared by treating 1-phenyl-2-amino-2-methyl-1-propanol (Commercial Solvents Corp.) with acetic anhydride in ether: mp 151.5–153.0° (benzene); ir ($CHCl_3$) 3280 (br) and 3420 (sh) (NH and OH), 1655 (s, C=O), 1510 (s, –NHC=O), and 1055 cm^{-1} (OH); NMR ($CDCl_3$) δ 1.17 (s, 3 H, $-CCH_3$), 1.37 (s, 3 H, $-CCH_3$), 1.70 (s, 3 H, CH_3CO), 4.50 (d, 1 H, J = 6 Hz, –CHOH), 5.83 (s, 1 H, NH), 6.18 (d, 1 H, J = 6 Hz, –CHOH), and 7.25 ppm (s, 5 H, $-C_6H_5$).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.53; H, 8.27; N, 6.76. Found: C, 69.78; H, 7.92; N, 6.65.

5-Phenyl-2,4,4-trimethyl-2-oxazoline was prepared by slowly adding 3.50 g (0.017 mol) of *N*-(1,1-dimethyl-2-hydroxy-2-phenylethyl)acetamide to 10 ml (0.19 mol) of concentrated H_2SO_4. The acid solution was poured onto crushed ice and neutralized (K_2CO_3), the product was extracted with ether and dried (Na_2SO_4), and the ether was removed, leaving 2.88 g (90%) of colorless oil. The ir, NMR, and analysis samples were collected by GLC (column B): ir (CCl_4) 1678 cm^{-1} (s, –OC=N–); NMR (CCl_4) δ 0.63 (s, 3 H, $-CCH_3$), 1.38 (s, 3 H, $-CCH_3$), 2.00 (s, 3 H, CH_3CO), 5.00 (s, 1 H, $-OCHC_6H_5$), and 7.26 ppm (s, 5 H, $-C_6H_5$).

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.56; H, 8.33; N, 7.17.

***N*-*tert*-Butyl-3-chloro-2,2-dimethylpropionamide**[4c] was isolated from the dibenzoyl peroxide (1.74 mol %) initiated decomposition of 1.02 g (5.32 mmol) of *N*-chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide (**4a**) in 10 ml of benzene at 80% (dark). The solution was saturated with prepurified nitrogen for 30 min before heating and a positive pressure of nitrogen was maintained during the 3.5 hr of heating. Analysis by GLC (column C, 120°) indicated two major peaks at 3.5 and 9.4 min (ratio 1:1.4), the first corresponding to *N*-*tert*-butyl-2,2-dimethylpropionamide. Attempts to separate the components by crystallization (hexane) were unsuccessful. The second peak was collected by GLC: mp 76.0–77.5°; ir (CCl_4) 3450 (sh, NH), 1675 (s, C=O), and 1505 cm^{-1} (s, –NHC=O); NMR (CCl_4) δ 1.20 [s, 6 H, $-(CH_3)_2$], 1.32 [s, 9 H, $C(CH_3)_3$], 3.54 (s, 2 H, CH_2Cl), 5.34 (s, 1 H, NH); mass spectrum (70 eV) *m/e* (rel intensity) 191 (3), 178 (3), 176 (9), 155 (5), 138 (5), 136 (16), 121 (3), 119 (8), 100 (5), 93 (10), 91 (28), 58 (25), 57 (100), 56 (86), 55 (21), 42 (11), 41 (31).[28]

Analysis by GLC of the products of the dibenzoyl peroxide initiated decomposition of *N*-chloro-*N*-*tert*-butyl-2,2-dimethylpropionamide in 2,3-dimethylbutane and cyclohexane in 5 mm degassed, sealed tubes indicated a ca. 95% yield of one component with the same retention time and virtually identical NMR (of the gross reaction mixture after removing volatile components) as those of the chloro amide described above.

***N*-(1,1-Dimethyl-4-chloropentyl)acetamide.** A 0.5 *M* solution of *N*-chloro-*N*-(1,1-dimethylpentyl)acetamide in cyclohexane (degassed) was irradiated (at 0°). Replacement of the cyclohexane by hexane and cooling at −22° for several days afforded crystals. Two recrystallizations from hexane yielded colorless needles: mp 31–34°; ir (CCl_4) 3430 (sh, NH), 3310 (br, NH), 1685 (s, C=O), 1540 (s, –NHC=O), 1387 and 1367 cm^{-1} [m, $-C(CH_3)_2$]; NMR (CCl_4) δ 1.27 [s, 6 H, $-C(CH_3)_2$], 1.47 (d, 3 H, J = 6 Hz, $-CHClCH_3$), 1.85 (s, 3 H, CH_3CO-), 1.6–1.9 (m, 4 H, $-CH_2CH_2CHCl-$), 3.86 (m, 1 H, J = 6 Hz, –CHCl–), and 7.15 (s, 1 H, NH).

Anal. Calcd for $C_9H_{18}NOCl$: C, 56.39; H, 9.46; N, 7.31. Found: C, 56.67; H, 9.53; N, 7.32. An authentic sample, prepared by the Ritter reaction of 5-chloro-2-methyl-2-hexanol[21,29] with acetonitrile, had identical melting point, ir and NMR spectra, and GLC retention time.

1-Acetyl-2,2,5-trimethylpyrrolidine. A 1.689-g sample of 62% NaH oil dispersion (0.043 mol) was washed with three 20-ml portions of cyclohexane and transferred by use of 25 ml of cyclohexane to a solution of 7.06 g (0.037 mol) of *N*-(1,1-dimethyl-4-chloropentyl)acetamide (obtained from the photolysis reaction) in 25 ml of cyclohexane. The mixture was brought to reflux and a few drops of *tert*-butyl alcohol were added. After 19 hr the reaction mixture was cooled, washed with two 25-ml portions of water and 15 ml of saturated $(NH_4)_2SO_4$ solution, and dried ($MgSO_4$). The solvent was removed, leaving 5.29 g of colorless oil (97%). Vacuum distillation produced 2.77 g: bp 33.0–35.0° (0.07 mm); $n^{21.0}D$ 1.4650; ir (CCl_4) 1645 cm^{-1} (s, C=O); NMR (CCl_4) δ 1.19 (d, 3 H, J = 6.5 Hz, $-NCHCH_3$), 1.32 (s, 3 H, CCH_3), 1.48 (s, 3 H, CCH_3), 1.6–2.2 (m, 4 H, $-CH_2CH_2-$), 1.93 (s, 3 H, CH_3CO), 3.95 ppm (m, 1 H, J = 6.5 Hz, CH_2CHCH_3; mass spectrum (80 eV) m/e (rel intensity) 155 (13), 140 (23), 99 (9), 98 (100), 81 (10), 55 (6), 44 (5), 43 (14), 42 (10), 41 (7).

Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.52; H, 11.20; N, 9.16.

***N*-Chloro-*N*-(1,1-dimethyl-4-chloropentyl)acetamide** was prepared by treating *N*-(1,1-dimethyl-4-chloropentyl)acetamide with *tert*-butyl hypochlorite in methyl alcohol in the manner previously described: 75% yield; bp 65–67° (0.25 mm); $n^{25.0}D$ 1.4780; ir (CCl_4) 1680 (s, C=O), 1290 cm^{-1} (s); NMR (CCl_4) δ 1.40 [s, 9 H, $(CH_3)_2C$], 1.48 (d, 3 H, J = 6 Hz, $-CHClCH_3$), 1.67–2.0 (m, 4 H, $-CH_2CH_2-$), 1.28 (s, 3 H, CH_3CO), and 3.86 ppm (m, 1 H, J = 6 Hz, $-CH_2CHClCH_3$).

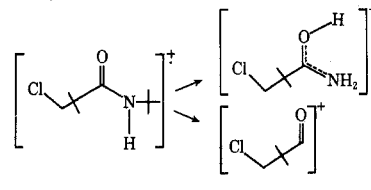
***N*-(1,1-Dimethyl-4,4-dichloropentyl)acetamide.** A solution of 1.40 g (0.00892 mol) of *N*-(1,1-dimethylpentyl)acetamide and 2.8 g (0.026 mol) of *tert*-butyl hypochlorite in 5 ml of methyl alcohol was stirred for 1 hr. The solvent and volatile components were removed on a rotoevaporator. A cyclohexane solution (10 mol) of the residual *N*-chloro amide was degassed and sealed in a Pyrex test tube and irradiated for 12 hr at 0°. On removal of the cyclohexane, the solid residue was again chlorinated and irradiated by repeating the above procedure, yielding 1.77 g of white solid, mp 66.5–68.0°. Three recrystallizations (hexane) afforded 0.87 g of white needles: mp 71.0–73.0°; ir (CCl_4) 3340 (sh, NH), 3320 (br NH), 1682 (s, C=O), and 1500 cm^{-1} (m, NHC=O); GLC analysis indicated ca. 90% dichloro amide and 10% monochloro amide; NMR (of dichloro amide) (CCl_4) δ 1.32 [s, 6 H, $-C(CH_3)_2$], 1.90 (s, 3 H, CH_3CO), 2.13 (s, 7 H, $-CH_2CH_2CClCH_3$), and 7.2 (s, 1 H, NH); NMR (C_6H_6) δ 1.18 [s, 6 H, $-C(CH_3)_2$], 1.68 (s, 3 H, $-CCl_2CH_3$), 1.92 (s, 3 H, CH_3CO-), and 2.13 ppm (s, 4 H, $-CH_2CCl_2-$).

A solution of 0.681 g (0.0030 mol, 0.30 *M*) of *N*-chloro-(1,1-dimethyl-4-chloropentyl)acetamide in cyclohexane was degassed and irradiated for 8 hr; GLC analysis (column temperature 124°) indicated peaks at 1.4 and 2.6 min with relative areas (in percent) of 15 and 85%, corresponding in retention time with the mono- and dichloro amides.

Registry No.—**1a,** 5014-39-1; **1b,** 79-16-3; **2a,** 10271-73-5; **2b,** 762-84-5; **3a,** 55281-79-3; **3b,** 5531-33-9; **3c,** 55281-80-6; **3e,** 55281-81-7; **4a,** 55281-82-8; **4b,** 686-96-4; **4c,** 55281-83-9; **5a,** 55281-84-0; **5b,** 55281-85-1; **5c,** 55281-86-2; **5d,** 55281-87-3; **6a,** 55319-71-6; **6b,** 55281-88-4; *tert*-butyl hypochlorite, 507-40-4; α,α-dimethyl-β-phenethylamine, 122-09-8; acetic anhydride, 108-24-7; *tert*-butylamine, 75-64-9; 2,2-dimethylpropionyl chloride, 3282-30-2; chlorine monoxide, 14989-30-1; *N*-(1,1-dimethyl-2-hydroxy-2-phenylethyl)acetamide, 55281-89-5; 1-phenyl-2-amino-2-methyl-1-propanol, 34405-42-0; TMP, 108-75-8.

References and Notes

(1) (a) Supported in part by the National Science Foundation. (b) Predoctoral Fellow of the National Institutes of Health, 1967–1970.
(2) R. S. Neale, *Synthesis*, **1**, 1 (1971).
(3) (a) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963); (b) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960); (c) R. S. Neale and M. R. Walsh, *ibid.*, **87**, 1255 (1965).
(4) R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Am. Chem. Soc.*, **88**, 3051 (1966).
(5) (a) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965); (b) A. L. J. Beckwith and J. E. Goodrich, *Aust. J. Chem.*, **18**, 747 (1965); (c) R. C. Petterson and A. Wambsgan, *J. Am. Chem. Soc.*, **86**, 1648 (1964).
(6) (a) M. Okahara, T. Ohashi, and S. Komori, *J. Org. Chem.*, **33**, 3066 (1968); (b) R. S. Neale and N. L. Marcus, *ibid.*, **34**, 1808 (1969); (c) T. Ohashi, M. Sugic, M. Okahara, and S. Komori, *Tetrahedron*, **25**, 5349 (1969).
(7) Y. L. Chow and T. C. Joseph, *Chem. Commun.*, 490 (1969).
(8) (a) L. P. Kuhn, G. G. Kleinspehn, and A. C. Duckworth, *J. Am. Chem. Soc.*, **89**, 3858 (1967); (b) Y. L. Chow and A. C. H. Lee, *Chem. Ind. (London)*, 827 (1967); (c) Y. L. Chow, N. S. Tam, and A. C. H. Lee, *Can. J. Chem.*, **47**, 2441 (1969).
(9) Following paper in this issue: R. A. Johnson and F. D. Greene, *J. Org. Chem.*, in press.
(10) (a) J. C. Stowell, Ph.D. Thesis, Massachusetts Institute of Technology, 1964; (b) H. Zimmer and L. F. Audrieth, *J. Am. Chem. Soc.*, **76**, 3856 (1954).
(11) P. Allen, Jr., and J. Ginos, *J. Org. Chem.*, **28**, 2759 (1963).
(12) For other examples of systems subject to competing chain processes, see J. G. Traynham and Y.-S. Lee, *J. Am. Chem. Soc.*, **96**, 3590 (1974); C. Walling and R. T. Clark, *ibid.*, **96**, 4530 (1974); and references cited therein.
(13) (a) J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature (London)*, **171**, 704 (1953); *Bull. Soc. Chem. Belg.*, **65**, 533 (1956); (b) W. A. Thaler, *Methods Free-Radical Chem.*, **2**, 1 (1969).
(14) The effect of TMP on the selectivity of solvent chlorination is discussed in Part II (ref 9). Apparently amidyl radicals, like chlorine atoms, are more reactive toward alkyl H than toward benzyl H, accounting for the lack of attack on the benzylic hydrogens of 2,4,6-trimethylpyridine.
(15) H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863 (1959).
(16) W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, **94**, 6853 (1972); see also W. C. Danen, C. T. West, and T. T. Kensler, *ibid.*, **95**, 5716 (1973); F. R. Stermitz and D. W. Neiswander, *ibid.*, **95**, 2630 (1973); T. Koenig, J. A. Houbler, C. E. Klopfenstein, G. Hedden, F. Sunderman, and B. R. Russell, *ibid.*, **96**, 4573 (1974).
(17) Amminium radicals (ref 18) and chlorine atoms (ref 19) show very low reactivity toward hydrogen on the same carbon with chlorine.
(18) F. Minisci, G. P. Gardini, and F. Bertini, *Can. J. Chem.*, **48**, 544 (1970), and references cited therein.
(19) M. L. Poutsma, *Methods Free-Radical Chem.*, **1**, 79 (1969).
(20) (a) R. H. Hesse, *Adv. Free-Radical Chem.*, **3**, 83 (1969); (b) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 729 (1972), and references cited therein; (c) L. R. C. Barclay, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 3011 (1974).
(21) F. D. Greene, M. L. Savitz, F. D. Osterholts, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).
(22) Y. L. Chow and J. N. S. Tam, *J. Chem. Soc. C*, 1138 (1970).
(23) (a) J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948); (b) L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 213 (1969).
(24) N. K. Kochetkov, A. Ya. Khorlin, L. A. Vorotnikova, and K. I. Lopatina, *Zh. Obshch. Khim.*, **29**, 3616 (1959); *Chem. Abstr.*, **54**, 19467a (1960).
(25) J. J. Ritter and F. X. Murphy, *J. Am. Chem. Soc.*, **74**, 763 (1952).
(26) J. M. Kornprobst, A. Laurent, and E. Laurent-Dieuzeide, *Bull. Soc. Chim. Fr.*, 3657 (1968).
(27) G. H. Cody, *Inorg. Synth.*, **5**, 156 (1957).
(28) The fragments at *m/e* 136, 138, 121, and 119 place the chlorine on the acyl portion of the amide. The *m/e* 136 and 138 fragments are derived from a McLafferty rearrangement splitting off an allylic radical: F. W. McLafferty, "Interpretation of Mass Spectra", W. A. Benjamin, New York, N.Y., 1966, p 138.



m/e	Rel intensity	
138	5.3	(4)
136	16.0	
121	2.0	(5)
119	8.0	

(29) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963).

Chlorination with *N*-Chloro Amides. II.[1a] Selectivity of Hydrogen Abstraction by Amidyl Radicals[1b]

Richard A. Johnson[1c] and Frederick D. Greene*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received January 15, 1975

Selectivity in chlorinations of alkanes with *N*-chloro amides has been examined, providing evidence for several different hydrogen-abstracting species as a function of reaction conditions; e.g., for *N*-chloro-*N*-*tert*-butylacetamide (**2a**) with 2,3-dimethylbutane the relative reactivity of the tertiary hydrogen compared with the primary hydrogen, k_t/k_p, is 19 ($h\nu$, degassed), 4.8 ($h\nu$, oxygen present), 1.6 ($h\nu$, with 2,4,6-trimethylpyridine present, or benzoyl peroxide, 80°). In the presence of oxygen (and absence of base) the principal chain-carrying species are chlorine atoms; in the presence of the base (or under initiation by benzoyl peroxide, 80°) the principal chain-carrying species are considered to be amidyl radicals. Selectivity in amidyl radical, CH_3CONR, is markedly dependent on R; e.g., with 2,3-dimethylbutane $k_t/k_p \simeq 95$ for R = methyl, 1.6 for R = *tert*-butyl. Decomposition of **2a** by photochemical initiation in the absence of oxygen or trimethylpyridine proceeds more rapidly and shows higher selectivities than in the presence of either of these additives; the abstracting species under these conditions is not known. Steric effects in hydrogen abstraction reactions are briefly discussed.

In Part I,[1a] the decomposition of a series of *N*-chloro amides in alkane solvents was examined. The compounds decompose by free-radical chain reactions of long chain length and afford products of intermolecular and intramolecular chlorination. Rates and products showed marked dependence on the *N*-chloro amide, on oxygen, on 2,4,6-trimethylpyridine (TMP), and on mode of initiation ($h\nu$, 25° or dibenzoyl peroxide, 80°). The results were suggestive of the occurrence of two principal chain mechanisms: amidyl radical paths and chlorine atom–HCl paths. The amidyl