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.

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

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Chlorination with *N*-Chloro Amides. II.[1a] Selectivity of Hydrogen Abstraction by Amidyl Radicals[1b]
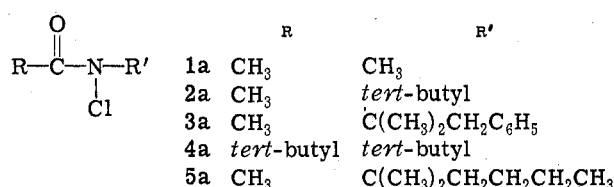
Richard A. Johnson[1c] and Frederick D. Greene*

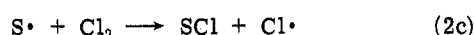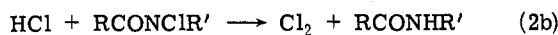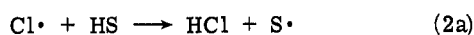*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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

$$R-\underset{\underset{Cl}{|}}{\overset{\overset{O}{||}}{C}}-N-R'$$

		R	R'
1a	CH$_3$	CH$_3$	
2a	CH$_3$	*tert*-butyl	
3a	CH$_3$	C(CH$_3$)$_2$CH$_2$C$_6$H$_5$	
4a	*tert*-butyl	*tert*-butyl	
5a	CH$_3$	C(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$CH$_3$	

radical path appeared to be operative in two situations: (a) initiation by light in the presence of 2,4,6-trimethylpyridine and (b) decomposition (in the absence of oxygen) of an N-chloro amide in which the resulting amidyl radical had the opportunity for intramolecular 1,5 hydrogen abstraction by the nitrogen atom. The chlorine atom–HCl

$$RCO\overset{\cdot}{N}R' + HS \longrightarrow RCONHR' + S\cdot \qquad (1a)$$

$$S\cdot + RCONClR' \longrightarrow SCl + RCO\overset{\cdot}{N}R' \qquad (1b)$$

$$Cl\cdot + HS \longrightarrow HCl + S\cdot \qquad (2a)$$

$$HCl + RCONClR' \longrightarrow Cl_2 + RCONHR' \qquad (2b)$$

$$S\cdot + Cl_2 \longrightarrow SCl + Cl\cdot \qquad (2c)$$

path appeared to be operative in the decompositions in the absence of trimethylpyridine and to be of increased importance in decompositions in the presence of molecular oxygen. In order to provide further evidence on these points and to learn about the selectivity of amidyl radicals, decompositions of the N-chloro amides have been carried out in a series of hydrocarbons (n-hexane, cyclohexane, 2,3-dimethylbutane,[2] 2,2-dimethylbutane, and adamantane), analyzing for the chloroalkanes.[3] Selectivity in hydrogen abstraction was observed to depend markedly on reaction conditions. Various additives were examined as possible scavengers for chlorine atoms or HCl. Trichloroethylene, which has proved useful with alkyl hypochlorites,[4] had some effect. Much more effective was the hindered base 2,4,6-trimethylpyridine. Most of the work has been done with N-chloro-N-*tert*-butylacetamide (2a). The results are presented in Tables I–V. A summary of the selectivities in chlorinations with 2a, relative to the primary hydrogen of n-hexane, is shown in Table VI.

Discussion

The principal findings regarding the selectivity of hydrogen abstraction for decomposition of N-chloro amide 2a in alkane solvent are: (a) selectivity is markedly dependent on reaction conditions (e.g., k_t/k_p for 2,3-dimethylbutane: $h\nu$, degassed, 19; $h\nu$, undegassed, 4.8; $h\nu$, trimethylpyridine,

1.6); (b) in the presence of oxygen the selectivity is approximately the same as for Cl$_2$, $h\nu$ (Table VI, 4 vs. 5); (c) selectivity is increased severalfold by removal of oxygen (Table VI, 1 vs. 4); (d) selectivity is altered by the addition of 2,4,6-trimethylpyridine[5] (Table VI, 1 vs. 2) and is *not* the same as for Cl$_2$, $h\nu$ (Table VI, 2 vs. 5); (e) selectivity is approximately the same for initiation by $h\nu$, 25° in the presence of trimethylpyridine as for initiation by dibenzoyl peroxide, 80% (Table VI, 2 vs. 3).

Nature of the Reaction and Assessment of the Hydrogen-Abstracting Species. The results of this study of chlorinations with N-chloro amides provide evidence for three different hydrogen-abstracting species as a function of reaction conditions.[6]

A. RCON(Cl)R', $h\nu$, 25°, Undegassed (Table VI, Line 4).

Assignment. Chlorine atom–HCl chains.

Basis. (a) The selectivities are approximately the same as for Cl$_2$, $h\nu$ (for some comments on how oxygen may increase the importance of the chlorine atom–HCl chains, see Part I[1a]); (b) the inhibition in rate and changes in selectivity observed upon the addition of trimethylpyridine are most simply ascribed to the scavenging of HCl by the base;

Table I
Light-Initiated Chlorination of 2,3-Dimethylbutane with 0.038 M N-Chloro-N-*tert*-butylacetamide (2a) at 25°

Scavenger[a] (M)	k_t/k_p per H	% yield[b]
None	14.5	97
None	15.5	100
Oxygen[a]	4.4	84
TCE (0.10)	16.0	93
TCE (0.50)	13.5	93
TCE (1.00)	11.0	84
TMP (0.05)	1.9	89
TMP (0.10)	1.9	74
TMP (0.50)	2.8	58
TMP (0.50), C$_6$H$_6$ (2.8)[c]	5.0	
C$_6$H$_6$ (4.0)[c]	25 (34)[d]	
C$_6$H$_6$ (4.0), Cl$_2$	20[d]	
Cl$_2$[e]	3.9[e]	

[a] Ox ≡ sample was not degassed; TCE, trichloroethylene; TMP, 2,4,6-trimethylpyridine; C$_6$H$_6$, benzene. [b] Percent yield of 1- and 2-chloro-2,3-dimethylbutanes based on N-chloro amide. [c] 2a, 0.054 M. [d] Reference 2. [e] Photochlorination with Cl$_2$ at 25°, ref 3.

Table II
Chlorination of 2,3-Dimethylbutane and Cyclohexane with N-Chloro-N-*tert*-butylacetamide (2a)

[2a], M	Conditions[a]	DMB/C$_6$H$_{12}$ (mol ratio)	k_t/k_p	k_c/k_p	% yield[b]
0.18	$h\nu$, 25°	1.37	19	11	
0.08	$h\nu$, 21°, N$_2$[c]	2.34	7.7	3.7	
0.08	$h\nu$, 21°, Ox[d]	2.34	4.8	3.1	
0.12	$h\nu$, 25°, 0.11 M TMP	0.87	1.8	10.5	97
0.12	$h\nu$, 25°, 0.11 M TMP	2.81	1.6	9.8	91
0.06	$h\nu$, 25°, C$_6$H$_{12}$[e]				97
0.06	$h\nu$, 25°, C$_6$H$_{12}$, 0.19 M TMP[f]				89
0.12	80°, dark, 9 mol % DBPO		1.5		100
0.14	80°, dark, 5 mol % DBPO	1.57	1.6	9.5	98
0.12	80°, dark		5.3		93[g]
	Cl$_2$, $h\nu$, 40°[h]		3.9	2.7	

[a] TMP, 2,4,6-trimethylpyridine; DBPO, dibenzoyl peroxide. [b] Percent yield of all chloroalkanes. [c] Degassed by bubbling nitrogen through the solution for 10 min before irradiation. [d] Oxygen bubbled into the solution for 1 min before irradiation. [e] $t_{1/2}$ of 3 min. [f] $t_{1/2}$ of 125 min. [g] Approximately 55% of the N-chloro amide remained after 21 days at 80°. [h] Photochlorination with Cl$_2$, ref 3.

Table III
Chlorination of *n*-Hexane and Cyclohexane with 0.10 *M* N-Chloro-N-*tert*-butylacetamide (2a)

| | Relative reactivity[a] per H | |
Conditions[b]	k_s/k_p	k_c/k_p
$h\nu$, 25° [c]	7.3	
$h\nu$, 25° [d]	7.5	7.6
$h\nu$, 25°, not degassed	2.7	
$h\nu$, 25°, not degassed[d]	2.8	2.8
$h\nu$, 25°, TMP (0.05 M)[c]	4.5	
$h\nu$, 25°, TMP (0.05 M)[d]	4.4	4.2
Dark, 80°, DBPO (2.5 mol %)[c]	4.1	
Dark, 80°, DBPO (2.5 mol %)[d]	3.8	3.8
$h\nu$, 25°, Cl$_2$	2.8	

[a] k_s ≡ rel $k_{secondary}$ for C-2 and C-3 together; k_p ≡ rel $k_{primary}$ for C-1; k_c ≡ rel $k_{cyclohexyl}$. [b] TMP, DBPO: see Table II, footnote a. [c] Chloroalkane yield determined, quantitative. [d] The mole ratio of *n*-hexane/cyclohexane was 1.65.

Table IV
Chlorination of 2,2-Dimethylbutane and Cyclohexane with 0.10 *M* N-Chloro-N-*tert*-butylacetamide (2a)

| | Relative reactivity per H[a] | | |
Conditions[b]	k_{p1}/k_{p4}	k_s/k_{p4}	k_c/k_{p4}
$h\nu$, 25° [c]	0.84	8.0	
$h\nu$, 25° [d]	0.85	8.5	8.0
$h\nu$, 25°, not degassed	0.89	2.9	
$h\nu$, 25°, not degassed[d]	0.90	3.0	2.8
$h\nu$, 25°, TMP (0.06 M)[e]	0.11	0.45	
$h\nu$, 25°, TMP (0.05 M)[d]	0.10	0.38	4.7
80° dark, DBPO (2.5 mol %)[c]	0.10	0.52	
80° dark, DBPO (2.5 mol %)[d]	0.09	0.44	4.2
25°, $h\nu$, Cl$_2$	0.77	3.3	

[a] k_{p1} ≡ $k_{primary}$ at C-1; k_{p4} ≡ $k_{primary}$ at C-4; k_s ≡ $k_{secondary}$ at C-3; k_c ≡ $k_{cyclohexyl}$. [b] TMP, DBPO: See Table II, footnote a. [c] Chloroalkane yield determined, quantitative. [d] The mole ratio of 2,2-dimethylbutane/cyclohexane was 6.55. [e] Chloroalkane yield determined, 72%.
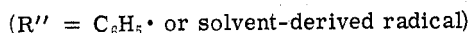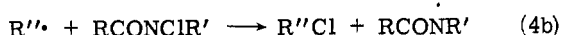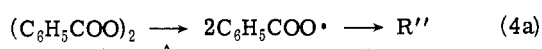
(c) the changes in intra- vs. intermolecular reaction discussed in Part I[1a] are most easily understood on the basis of this assignment.

B. RCON(Cl)R′, $h\nu$, 25°, 2,4,6-Trimethylpyridine, Degassed (Table VI, Line 2).

C. RCON(Cl)R′, Dibenzoyl Peroxide, 80°, Dark (Table VI, Line 3).

Assignment for B and C. Amidyl radical chains.

Basis. The selectivities observed under these two conditions are approximately the same. A feature that these two reaction conditions have in common is the absence of chlorine atom chains; toward some substrates selectivity in hydrogen abstraction is *lower* than for chlorine atom, toward others the selectivity is *higher* than for chlorine atom. The light-initiated reaction, B, would generate both amidyl radicals and chlorine atoms (eq 3), but the chlorine atom–HCl

$$RCONClR' \xrightarrow{h\nu} RCONR' + Cl\cdot \quad (3)$$

$$(C_6H_5COO)_2 \xrightarrow{\Delta} 2C_6H_5COO\cdot \longrightarrow R'' \quad (4a)$$

$$R''\cdot + RCONClR' \longrightarrow R''Cl + RCONR' \quad (4b)$$

$$(R'' = C_6H_5\cdot \text{ or solvent-derived radical})$$

chain sequence (eq 2a–c) could be eliminated by the acid-scavenging action of the trimethylpyridine. (The lack of attack on the benzylic hydrogens of the trimethylpyridine is suggestive that amidyl radicals, like chlorine atoms,[3a] are more reactive toward alkyl H than toward benzyl H). Under initiation by dibenzoyl peroxide, reaction would proceed as shown in eq 4a,b with no path for initiation of chlorine atom chains. On these grounds, the principal hydrogen-abstracting species under conditions B and C is considered to be amidyl radicals. This conclusion is also consistent with the changes in intra- and intermolecular reactions as a function of reaction conditions discussed in Part I,[1a] and with the specific hydrogen atom selectivities observed, detailed examination of which is taken up after the fourth major reaction condition, D.

D. RCON(Cl)R′, $h\nu$, 25°, Degassed (Table VI, Line 1). Decomposition of 2a under these conditions proceeds more rapidly and shows higher selectivities than decomposition in the presence of trimethylpyridine or oxygen (Table VI, 1 vs. 2 and 4). The abstracting species under these conditions is not known. Hydrogen chloride probably is involved in some way, since the addition of trimethylpyridine strongly inhibits the rate (e.g., Table II, line 6 vs. 7) and changes the

Table V
Relative Reactivities in the Light-Initiated Chlorination of Adamantane and 2,3-Dimethylbutane with 0.3 *M* N-Chloro-N-*tert*-butylacetamide (2a) at 16°

| | Relative reactivity per H[c] | | | | Percent yield[d] |
Conditions[a,b]	k_t/k_p	k_{At}/k_{As}	k_{At}/k_p	k_{As}/k_p	
a	25.	5.1	42.	8.2	100
a	25.	5.5	40.	7.9	100
Ox	12.	2.9	14.	4.9	88
Ox	15.	3.7	21.	5.6	89
TMP (0.1 M)	1.7	35.	15.	0.44	76
TMP (0.2 M)	1.8	18.	14.	0.79	61
TMP (0.1 M), Ox	1.6	23.	18.	0.82	71
TMP (0.2 M), Ox	1.8	21.	20.	0.92	57
Cl$_2$, CCl$_4$, $h\nu$, 25° [e]		1.9			

[a] Ratio of 2,3-dimethylbutane to adamantane ~30. [b] Ox ≡ not degassed; TMP, 2,4,6-trimethylpyridine. [c] k_t/k_p ≡ $k_{tertiary}/k_{primary}$ for 2,3-DMB;[1] k_{At}/k_{As} ≡ k_{tert} for adamantane/k_{sec} for adamantane. [d] Percent yield of chloroalkanes. [e] Reference 7.

selectivity. Some suggestions on the nature of the abstracting species under these conditions are taken up at the end of this paper.

Selectivity in Hydrogen Abstraction by the *N-tert*-Butylacetamidyl Radical. Conditions for amidyl radical chains: $h\nu$, 25°, trimethylpyridine, B, or dibenzoyl peroxide, 80°, C.

The selectivities in Tables I–VI show some striking changes from usual expectations. (a) The selectivity toward tertiary hydrogen of 2,3-dimethylbutane is low (k_t/k_p = 1.6), even lower than that of chlorine atom (k_t/k_p = 3.9). (b) The selectivity for cyclohexyl hydrogen vs. the primary hydrogen of 2,3-dimethylbutane is higher (k_c/k_p = 10.5) than that for chlorine atom (k_c/k_p = 2.7). (c) Selectivity for the secondary hydrogens of 2,2-dimethylbutane is very low, even less than for the primary hydrogens at C-4 of this molecule (k_s/k_{p4} = 0.38). (d) Selectivity for the primary hydrogens at C-1 of 2,2-dimethylbutane is much below that for the primary hydrogens at C-4 (k_{p1}/k_{p4} = 0.1). (e) Discrimination between the tertiary and secondary positions of adamantane is high (k_{At}/k_{As} = 35), much above that for chlorine atom (k_{At}/k_{As} = 1.9).[7]

Steric hindrance appears to be an important factor in the selectivity of the *N-tert*-butylacetamidyl radical. The biggest reductions in rate are associated with abstraction of

Table VI
Summary of Reactivities in Chlorinations with N-Chloro-N-tert-butylacetamide Relative to the Primary Hydrogens of n-Hexane

| Conditions^a	n-Hexane		C₇--- hexane	2,3-DMB^a		2,2-DMB^a			Adamantane	
	k_p	k_s	k_c	k_p	k_t	k_{p1}	k_{p4}	k_s	k_{As}	k_{At}
1 $h\nu$, 25°	1.0	7.5	7.6	0.69	13.	0.81	0.95	8.1	5.5	28.
2 $h\nu$, TMP, 25°	1.0	4.4	4.2	0.43	0.69	0.09	0.90	0.34	0.17	6.5
3 DBPO, 80°	1.0	3.8	3.8	0.39	0.62	0.09	0.90	0.40		
4 $h\nu$, Ox, 25°	1.0	2.8	2.8	0.90	4.2	0.90	1.0	3.0		
5 $h\nu$, Cl₂, 25°^b	1.0	~2.8	~2.7	1	3.9	.8	1	3.3	(1/1.9)^c	

^a 2,3-DMB, 2,3-dimethylbutane; 2,2-DMB, 2,2-dimethylbutane; TMP, 2,4,6-trimethylpyridine; DBPO, dibenzoyl peroxide; Ox ≡ samples not degassed. ^b Reference 3. ^c Reference 7.

hydrogen from the tertiary position of 2,3-dimethylbutane and from hindered secondary positions (2,2-dimethylbutane and adamantane). One also notes a reduction in reactivity of primary hydrogen in the following series.[8]

	CH_3CH_2—	CH_3—C(—CH_3)(—H)—	CH_3—C(—CH_3)(—CH_3)—
relative reactivity per primary H	1	0.4	0.1
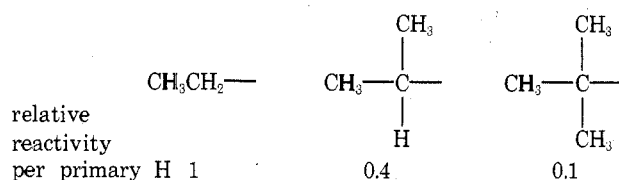
To test the importance of steric hindrance, some studies have also been carried out on a less hindered system, N-chloro-N-methylacetamide (1a), and on a more hindered one, N-chloro-N-tert-butyl-2,2-dimethylpropionamide (4a). The results of light-initiated chlorination of 2,3-dimethylbutane and cyclohexane with 1a are summarized in Table VII. The degree of inhibition in the presence of trimethylpyridine was similar to that observed for 2a. The selectivities in hydrogen abstraction with 1a are high and, in contrast with 2a, are largely unaffected by the presence of trimethylpyridine. A sample which was not degassed had a much lower selectivity. The high reactivity toward tertiary hydrogen in chlorination of 2,3-dimethylbutane with 1a is consistent with hydrogen abstraction by a selective N-methylacetamidyl radical which lacks the steric hindrance of the N-tert-butylacetamidyl radical.

With the highly hindered N-chloro amide 4a, efforts to effect chlorination of hydrocarbons under amidyl radical chain conditions resulted mainly (>95%) in conversion of 4a into N-tert-butyl-2,2-dimethyl-3-chloropropionamide (eq 5).[1a] The yields of chlorinated solvent were too low to

4a → (N·) → (C·) ... 4a + N·   (5)
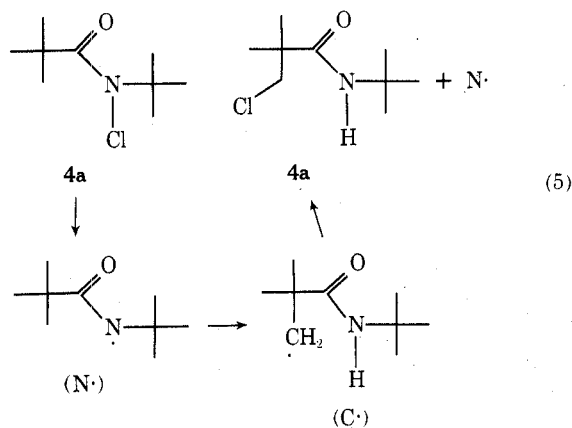
determine the selectivity for the intermolecular portion of the reaction.

The finding of a steric effect in the hydrogen abstraction step by CH_3CON-tert-butyl is of interest and may be of

Table VII
Light-Initiated Chlorination of 2,3-Dimethylbutane and Cyclohexane with N-Chloro-N-methylacetamide (1a)^a at 25°

Additive (M)^b	Relative reactivity		
	k_t/k_p	k_c/k_p	% yield^c
	86		97
	81	24^d	
Ox	14		77
TMP (0.036)	96	29^d	
TMP (0.20)	94	29^d	94
e	f		
TMP (0.22)^e	g		
C_6H_6 (4.0)	65^h		

^a 1a ~0.2 M. ^b Ox ≡ sample was not degassed; TMP, 2,4,6-trimethylpyridine. ^c Percent yield of all chloroalkanes based on initial N-chloro amide. ^d The mole ratio of 2,3-dimethylbutane/cyclohexane is 1.44. ^e Cyclohexane solvent, 1a 0.15 M. ^f Time for 50% consumption of 1a, 10 min. ^g Time for 50% consumption of 1a, 320 min. ^h Reference 2.

use in directing attack at unhindered positions in other chlorinations. Other examples also have been reported. In the chlorination of 3,3-diethylpentane by $C_6H_5SO_2NCl$-t-Bu, $k_s/k_p = 0.6$.[8,9] More recently, large variations in selectivity in chlorinations by R_2NCl, H_2SO_4, $h\nu$ as a function of the size of R have been reported and attributed to steric effects.[10] In contrast, an example of steric acceleration in a free-radical bromination reaction has also been reported.[11]

Mechanism of Light-Initiated Chlorination with N-Chloro Amides in the Absence of Trimethylpyridine and Oxygen, D. As indicated above, chlorinations with 2a under these conditions are faster and generally severalfold more selective than in the presence of oxygen (chlorine atom chains) or in the presence of the base (amidyl radical chains). Chlorination of 2,3-dimethylbutane by the unhindered N-chloro amide 1a under these conditions is also faster than in the presence of the base; in this case the selectivity in hydrogen abstraction is high and is largely unaltered by the presence of the base.[12] Chlorination of 2,3-dimethylbutane with the highly hindered N-chloro amide 4a under these conditions (degassed, no trimethylpyridine) afforded a 50% yield of the chloroalkanes with $k_t/k_p = 30$ even though decomposition of 4a under conditions B or C went largely via intramolecular 1,4-hydrogen transfer (eq 5) rather than attack on solvent. High selectivity (k_t/k_p for 2,3-dimethylbutane ≃ 20) was also observed under conditions D with 3a. These results require a hydrogen-abstracting species more selective than chlorine atom and not subject to the steric effect shown by the amidyl radical derived from 2a. One possibility considered was chlorine

atom complexed to an amide. However, chlorination of 2,3-dimethylbutane by Cl_2, $h\nu$ in the presence and absence of N-(1,1-dimethylpentyl)acetamide (0.09 M) showed no change in selectivity (k_t/k_p = 3.96 ± 0.08 vs. 3.92 ± 0.08). Other possibilities for species of the composition amidyl radical–HCl can be formulated. In the absence of additional evidence, further discussion is not warranted. It is worth stressing, however, that the selectivity with 2a in hydrogen abstraction is considerably greater, and the rate of decomposition is faster, under these conditions ($h\nu$, degassed) than in the presence of oxygen or trimethylpyridine. Some high selectivities observed in chlorinations with N-chlorosuccinimide[13] may also be associated with complexities of the type described here.

Experimental Section

The preparation and characterization of the N-chloro amides and their amide products have been described, as have procedures for decomposition and columns for GLC analysis.[1a] The reaction solutions were directly analyzed by GLC after complete disappearance of the N-chloro amide. Typical retention times (in minutes) using column C^{1a} (column temperature 60°, flow rate 60 ml/min) follow: 2-chloro-2,3-dimethylbutane (4.3), 1-chloro-2,3-dimethylbutane (5.9), chlorobenzene (7.7), chlorocyclohexane (10.3), N-tert-butylacetamide (14.7), and 2,4,6-trimethylpyridine (21.5). The products were stable to reaction and GLC analysis conditions, and were identified by comparison with authentic samples.

The chlorination products of n-hexane were analyzed on column D.[1a] The 2- and 3-chlorohexanes were not separable and formed a single symmetrical peak. The products were identified by comparison with authentic samples.

The chlorination products of 2,2-dimethylbutane were identified by comparison with authentic samples obtained from the photochlorination with Cl_2. The alkyl chlorides were collected by preparative GLC and structural assignments were made from the NMR spectra. A commercial sample of 4-chloro-2,2-dimethylbutane (Eastman) was also available. 1-Chloro-2,2-dimethylbutane: δ 0.83 (m, 3 H, CH_2CH_3), 0.93 [s, 6 H, $(CH_3)_2C–$], 1.29 (m, 2 H, CH_2CH_3), and 3.25 ppm (s, 2 H, $–CH_2Cl$). 3-Chloro-2,2-dimethylbutane: δ 1.00 [s, 9 H, $(CH_3)_3C–$], 1.40 (d, J = 7 Hz, 3 H, –CHClCH_3), and 3.80 ppm (q, J = 7 Hz, 1 H, $–CHClCH_3$). 4-Chloro-2,2-dimethylbutane: δ 0.93 [s, 9 H, $(CH_3)_3C–$], 1.70 (m, 2 H, $–CH_2CH_2Cl$), and 3.47 ppm (m, 2 H, $–CH_2CH_2Cl$).

Products from the chlorination of adamantane in 2,3-dimethylbutane were analyzed with column C.[1a] An authentic sample was used to identify 1-chloroadamantane, which had a shorter retention time than 2-chloroadamantane, as reported.[7]

The conditions and results are summarized in Tables I–VII.

References and Notes

(1) (a) Part I: R. A. Johnson and F. D. Greene, preceding paper in this issue. (b) Supported in part by the National Science Foundation. (c) Predoctoral Fellow of the National Institutes of Health, 1967–1970.
(2) Chlorination of this substrate by 1a and 2a in 4 M benzene has been reported: R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Am. Chem. Soc.*, **88**, 3051 (1966).
(3) For reviews on chlorination, see (a) M. L. Poutsma, *Methods Free-Radical Chem.*, **1**, 79 (1969); (b) "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 159.
(4) C. Walling and J. A. McGuinnes, *J. Am. Chem. Soc.*, **91**, 2053 (1969).
(5) Trichloroethylene (ref 4) has a much smaller effect on reactivity (see Table I).
(6) For evidence on changes in the chain-carrying species in N-bromosuccinimide brominations as a function of conditions, see J. G. Traynham and Y. Lee, *J. Am. Chem. Soc.*, **96**, 3590 (1974); J. C. Day, M. L. Lindstrom, and P. S. Skell, *ibid.*, **96**, 5616 (1974).
(7) (a) G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961). (b) High discrimination between the tertiary and secondary positions of adamantane has also been observed with $Cl_3C·$ [I. Tabushi, Y. Aoyama, S. Kojo, J. Hamuro, and Z. Yoshida, *J. Am. Chem. Soc.*, **94**, 1177 (1972)] and with photoexcited biacetyl [I. Tabushi, S. Kojo, and Z. Yoshida, *Tetrahedron Lett.*, 2329 (1973)] and attributed, in part, to steric effects.
(8) A trend in the same direction has also been seen in chlorinations with sulfonamide radicals: A. E. Fuller and W. J. Hickinbottom, *J. Chem. Soc.*, 3228 (1965), Table 5.
(9) For chlorination of 3,3-diethylpentane by Cl_2, $h\nu k_s/k_p$ = 1.4: M. Kosugi, K. Takeuchi, and T. Migita, *Bull. Chem. Soc. Jpn.*, **42**, 3354 (1969).
(10) N. C. Deno, R. Fishbein, and J. C. Wyckoff, *J. Am. Chem. Soc.*, **93**, 2065 (1971). See also R. Bernardi, R. Galli, and F. Minisci, *J. Chem. Soc. B*, 324 (1968).
(11) S. J. Cristol and H. W. Mueller, *J. Am. Chem. Soc.*, **95**, 8489 (1973).
(12) The similarity in selectivity with 1a in the presence and absence of the base may be fortuitous; the hydrogen-abstracting species need not be the same under the two conditions.
(13) J. H. Markgraf, *J. Chem. Educ.*, **46**, 610 (1969); O. Cerny and J. Hajek, *Collect. Czech. Chem. Commun.*, **26**, 2624 (1961).

$2H$-Cyclopenta[d]pyridazines. Electrophilic Halogenation[1,2]

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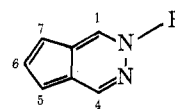
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2-Methyl- and 2-phenyl-2H-cyclopenta[d]pyridazine (1 and 2) and the parent system (3) undergo electrophilic halogenation with N-halosuccinimides. The 5-, 7-, 5,7-, and 5,6,7-chloro and bromo derivatives, the 5,7-iodo derivative, and the 5-trifluoroacetyl-7-bromo and 5-bromo-7-trifluoroacetyl derivatives of 1 were prepared. Based on product yields, the relative position reactivities are 7 > 5 ≫ 6. Dipyridineiodonium nitrate was used to prepare the 5,6,7-triiodo derivative of 1. The 5-, 7-, 5,7-, and 5,6,7-chloro derivatives of 2 and the 7-chloro and 5,7-dichloro derivatives of 3 were also obtained. The substituent long-wavelength spectral shifts for halogen and trifluoroacetyl were found to be qualitatively additive.

The preceding papers established the positions of protonation[6] and acylation[7] on the 2H-cyclopenta[d]pyridazine system for mono- and disubstitution. In the present study, electrophilic mono-, di-, and trihalogenation are reported for this heteroanalog of azulene containing both π-excessive and π-equivalent ring nitrogens.

Chlorination of 1. As with azulene and cyclopenta-

1, R = CH_3
2, R = C_6H_5
3, R = H