The Chemistry of Nitrogen Radicals. IV. The Rearrangement of N-Halamides and the Synthesis of Iminolactones[1]

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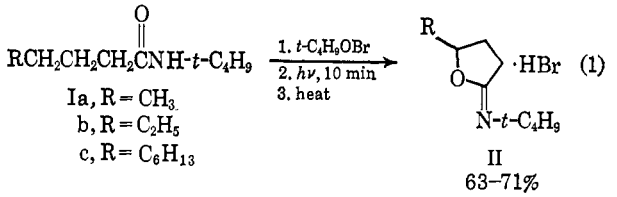
Abstract: The photolytic rearrangement of aliphatic N-bromamides to the isomeric 4-bromamides, which is most efficient with the N-*t*-butyl derivatives, occurs rapidly in benzene or carbon tetrachloride; the products are cyclized by brief heating to readily isolable iminolactone hydrobromides (II) in 63–71% yields based on the parent amides. Analogous rearrangements of N-chloramides can also be carried out, but they are efficient only in benzene or pyridine, and the isolation of cyclic products now requires hydrolytic or reductive procedures. The marked solvent effect in the latter reactions is discussed.

The free-radical rearrangements of N-iodamides[2] and N-chlorimides[3] to the corresponding 4-halacyl isomers and the hydrolysis of these primary reaction products to γ-lactones were described recently. We have studied concurrently the rearrangements of some aliphatic N-bromamides and N-chloramides and found that certain of their features differ markedly from those of the work cited. The present results therefore provide new insight into both the mechanistic and synthetic aspects of free-radical N-halamide reactions.

N-Bromamides. Treatment of a benzene or carbon tetrachloride solution of N-*t*-butylamides with a 10% excess of *t*-butyl hypobromite in carbon tetrachloride at room temperature produced solutions of the corresponding N-bromamides. On subsequent irradiation these solutions lost their electropositive halogen within 10 min, and the infrared spectra of the residues obtained after removal of solvent still showed strong absorption characteristic of secondary amides. Brief heating effected ring closure of these 4-bromamides to the insoluble iminolactone hydrobromides II, which could be isolated very simply by filtering the liquid–solid mixture after dilution with anhydrous ether; the yields were 63–71% after one recrystallization (eq 1). The structures of the salts II were readily established (see the Experimental Section) from their spectral properties and their conversion to γ-lactones or the free iminolactones.



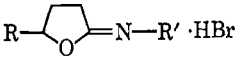
Ia, R = CH_3
b, R = C_2H_5
c, R = C_6H_{13}

II
63–71%

(1)

Reaction 1 is unique both in the product produced and in its requirement of an N-*t*-buyl group to promote the rearrangement most effectively. In contrast, only unsubstituted N-iodamides could be photolytically rearranged,[2] and the procedure was incompatible with the isolation of iminolactones, although iodine monochloride complexes of two N-iodiminolactones were successfully isolated. However, the N-hydro derivatives of II may also be generally accessible by the present method, although at a reduced efficiency compared to the N-*t*-butyl compounds, since the rearrangement of N-bromopentanoamide yielded 37% of the corresponding unsubstituted iminolactone hydrobromide (Table I). N-Methylbromamides failed to rearrange, as did an N-methyliodamide,[2] but this was apparently due to the heightened reactivity of the α hydrogens N–C–H (see discussion of N-chloramide reactions below). We therefore attempted to utilize N-trityl and N-phenyl derivatives of pentanoamide, which in common with the N-*t*-butylamides lack α hydrogens, but these amides failed to yield a product analogous to II.

Table I. Synthesis of Iminolactone Hydrobromides from Amides $R(CH_2)_3CONHR'$



R	R′	Solvent	Temp, °C	Reaction time, min	Yield, % (% crude)
CH_3	H	Benzene	24	120	37
CH_3	*t*-C_4H_9	Benzene	26	10	71 (82)
		CCl_4	26	10	(79)
C_2H_5	*t*-C_4H_9	Benzene	26	10	(64)
		CCl_4	26	6	71 (75)
n-C_6H_{13}	*t*-C_4H_9	Benzene	0	10	63 (66)
		CCl_4	26	10	61 (65)
CH_3	$C(C_6H_5)_3$	Benzene	25	10	None[a]
CH_3	C_6H_5	Benzene	25	120	None[b]
CH_3	CH_3	Benzene	25	150	None[c]
		CCl_4	25	150	None[d]

[a] Only product was original amide. [b] Nuclear bromination was suggested by the infrared spectrum of the product. [c] 48% of active bromine remained. [d] 31% of active bromine remained.

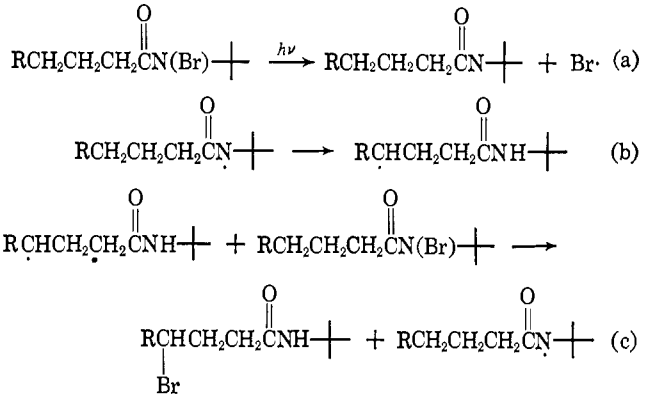
The N-bromamide and N-iodamide[2] work also differs in two other aspects. Our reaction times are short (Table I), in contrast with the 5–7-hr reactions characteristic of Barton's procedure (comparable light sources). Furthermore, the nonisolable 4-iodamides spontaneously cyclize to iminolactones and thereby liberate a mole of HI, which then degrades 1 mole of N-iodamide to the parent amide as 1 mole of iodine is produced; this reduces the theoretical yield of rearrangement product, based on a stoichiometric mixture of the reagents, to 50%. To overcome this restriction, an excess of oxidizing agent was employed,[2] but this

(1) Part III: R. S. Neale, *Tetrahedron Letters*, 483 (1966).
(2) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965).
(3) R. C. Petterson and A. Wambsgans, *J. Am. Chem. Soc.*, 86, 1648 (1964).

can limit the iodination procedure to the use of amides which do not bear groups reactive toward long exposure to light and/or an oxidizing medium. The use of N-bromamides should mitigate this synthetic limitation in many cases.

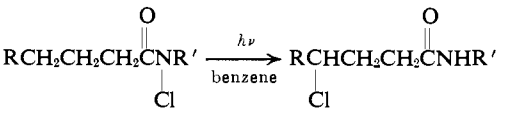
The simple procedure summarized by eq 1 illustrates the facile conversion of straight-chain amides to members of a heterocyclic system not otherwise accessible for saturated, unsubstituted precursors.[4] This short series of operations, which is carried out in a single flask, is yet another example of a free-radical synthesis that would be difficult or even impossible to accomplish by a nonradical approach, and it further spotlights the increasing usefulness of nitrogen radicals in organic synthesis.[1,5,6a]

Reaction 1 and the analogous N-chloramide rearrangements discussed below are no doubt free-radical chain processes, since the bromamides and chloramides both rearrange rapidly but only upon weak irradiation. Furthermore, the loss of active chlorine, which ceased abruptly when chloramide reaction mixtures were shielded from the light, resumed when the light was restored, and the rearrangements were greatly slowed (although not completely inhibited) when air was bubbled through the solutions. The high selectivity for halogenation of C-4 in the acyl chain requires the chain reactions to include an intramolecular hydrogen shift involving a six-atom transition state analogous to that characteristic of intramolecular hydrogen abstraction by protonated nitrogen radicals,[6,7] and we assume the sequence of events is the following.



N-Chloramides. The N-chloramides are inferior to their N-bromo counterparts as starting materials for halamide rearrangements to immediately isolable derivatives. However, their reactions are of considerable mechanistic interest in regard to the production and reactivity of N-acylamino radicals.

There is no report in the literature of the rearrangement of chlorine from nitrogen into the acyl chain of an N-chloramide, although rearrangement into the N-alkyl group has been observed.[6a] Petterson and Wambsgans,[3] who recently reported the moderately efficient rearrangement of N-chlor*imides* to the 4-chloracyl isomers, showed that a primary N-chlor*amide* on irradiation in fluorotrichloromethane gave only random chlorination products typical of chlorine atom chains. However, we have successfully rearranged the N-alkyl-N-chloramides III to the 4-chloracyl isomers IV by irradiation in benzene (eq 2). We have determined the influence of chloramide structure and solvent on the efficiency of the process, and the rather surprising results are described below.

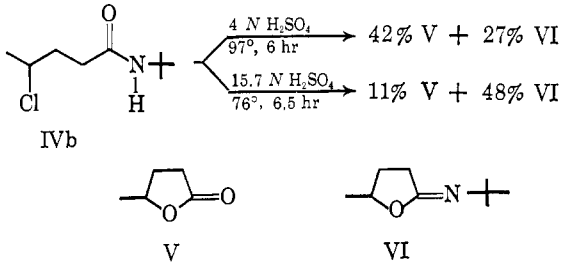


IIIa, R = R′ = CH_3
b, R = CH_3; R′ = t-C_4H_9
c, R = C_2H_5; R′ = t-C_4H_9

IV

In contrast to the bromamide rearrangements already described, the N-chloro derivatives of both N-methyl- and N-t-butylpentanoamide were successfully rearranged in benzene to the 4-chloro isomers, but the process was more efficient in the case of the N-t-butyl compound (Table II); also in contrast to the bromamide series, the N-hydro compound N-chloropentanoamide was now quite unreactive. N-Trityl- or -phenylamides again failed as substitutes for the N-t-butyl compounds, since N-chloro-N-phenylpentanoamide failed to undergo any reaction on irradiation and N-tritylpentanoamide failed even to form the N-chloro derivative.

The rearrangement products of the N-methyl- or t-butylchloramides IIIa,b hydrolyzed in aqueous acid without difficulty to 4-hydroxypentanoic acid γ-lactone (V), a measure of the desired rearrangement of chlorine to C-4, and to the parent acid, a measure of the amide product bearing no substituents in the acyl chain. Although V was the only derivative isolated from the N-methyl compound IVa, varying amounts of both V and 2-t-butylimino-5-methyltetrahydrofuran (VI) were obtained on hydrolysis of the t-butyl compound IVb (eq 3). Whether the analogous N-methyliminolactone



IVb

V VI

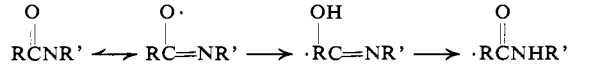
formed transiently in the hydrolysis of IVa was not investigated. Since simply heating the 4-chloramides effected no change in the compounds, the unexpected ring closure to the iminolactone VI in hot aqueous acid may occur *via* ionization of chlorine followed by or

(4) C. J. M. Stirling, *J. Chem. Soc.*, 255 (1960), described similar ring closures starting with δ-bromamides prepared in another way and surveyed the few preparations of iminolactones previously described in the literature.

(5) (a) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 2666 (1963); (b) R. S. Neale, *ibid.*, **86**, 5340 (1964); (c) R. S. Neale, M. R. Walsh, and N. L. Marcus, *J. Org. Chem.*, **30**, 3683 (1965); (d) F. Minisci, R. Galli, and G. Pollina, *Chim. Ind.* (Milan), **47**, 736 (1965); (e) C. J. Aloisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, 81, 1489 (1959).

(6) (a) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963); (b) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).

(7) Although we assume throughout our discussion that amide radicals exist with the carbonyl group intact, we cannot rule out the possibility in any of the known N-halamide rearrangements that intramolecular H abstraction is performed by amide oxygen rather than nitrogen, followed by tautomeric regeneration of the normal amide group.



This would result in the same size cyclic transition state as that preferred by ordinary alkoxy radicals: see C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963).

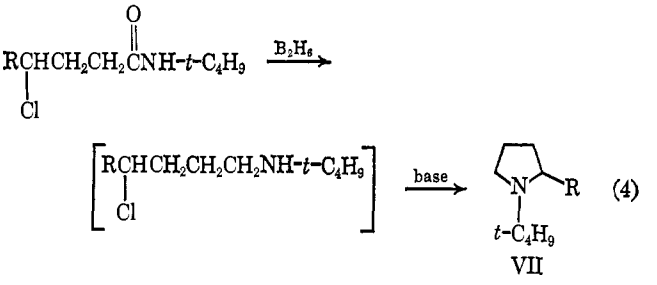
Table II. Rearrangement of N-Chloramides[a]

R	R′	M	Solvent	Flask, temp (°C)	Time, min	Product amides[b] Rearranged	Unsubstd	Type of work-up[c]
n-C_4H_9	CH_3	0.3[d]	Benzene	P, 30	20	43	42	A
		0.3	Benzene	P, 10	240	40	50	A
		0.3	CH_3CN	P, 30	410	17	79	A
		0.3	Pyridine	V, 26	195	21	72	A
		0.3	$CHCl_3$	V, 26	260	27	59	A
		0.3	CH_3NO_2	V, 29	>420	...	...	...
		0.15	CS_2	V, 26	230	...	...	...
		0.6	1.2 M H_2SO_4 in TFA[e]	V, 5	75	35	42	B
i-C_5H_{11}	CH_3	0.36	Benzene	V, 30	20	49	23	A
		0.30	Benzene	P, 30	15	49	23	A
		0.29	CCl_4	P, 26	120	Trace	30	A
		0.47	0.94 M H_2SO_4 in TFA	V, 5	115	45	28	A
n-C_4H_9	t-C_4H_9	0.40	Benzene	V, 5	45	69	15	B
		0.45	Benzene	P, 30	40	...	...	...
		0.25	Benzene	V, 5	30	57	8	C
		0.15	Benzene[f]	V, 5	8	...	...	...
		0.25	Benzene	V, 23	25	53	...	C
		0.25	CS_2	V, 23	390	0	...	C
		0.25	Pyridine	V, 23	25	60	...	C
		0.15	Pyridine	V, 28	5	...	...	...
		0.25	CH_3CN	V, 23	25	17	38	C
		0.15	CH_3CN	V, 28	15	...	...	...
		0.25	CCl_4	V, 23	55	0	44	C
		0.15	CCl_4	V, 28	25	...	...	...
		0.20	$(CH_3)_3SiCH{=}CH_2$	V, 23	15	16	16	C
		0.40	4 M H_2SO_4–HOAc	V, 23	245	0	23	C
n-C_5H_{11}	t-C_4H_9	0.40	Benzene	V, 26	15	52	0	C
n-C_3H_7	t-C_4H_9	0.50	Benzene	V, 23	35	10	...	C
CH_3	t-C_4H_9	0.45	Benzene	V, 23	270	37[g]	48	D
		0.26	Benzene	V, 23	85	...	...	...

[a] Under N_2 in Pyrex or Vycor flask; irradiation at 12 in. [b] As determined from the derivative actually isolated; rearranged amides are the 4-chloro compounds except when R = CH_3, and "unsubstituted" refers to the acyl group in the amides. [c] Method A: hydrolysis in 10 N H_2SO_4 for 5 hr and glpc analysis of the γ-lactone and unsubstituted acid. Method B: specific hydrolysis conditions, see the Experimental Section. Method C: reduction with B_2H_6–THF to the 4-chloramine, cyclization to the pyrolidine, and analysis therefor by picrate formation and glpc. Method D: direct conversion to the oxazoline on glpc analysis of the reaction mixture. [d] All reaction mixtures from this amide except those obtained in benzene were yellow after irradiation. [e] Trifluoroacetic acid. [f] Reaction time ten times longer under air; product an oil instead of the usual solid. Irradiation of a 2 M solution of chloramide gave only 80% loss of active chlorine in 145 min. [g] Product was N-(1,1-dimethyl-2-chloroethyl)acetamide.

along with internal solvation of the resulting carbonium ion by the carbonyl oxygen. Alternatively, a facile ring closure might follow the prior formation of the 4-hydroxyamide.[8] The unexpected stability of VI must depend in part on the presence of the N-t-butyl substituent, which should hinder attack of water at the imino group.

The hydrolytic conversion of 4-chloro-N-t-butylhexanoamide (IVc) to the γ-lactone was unsuccessful, although this might have been anticipated from the unusually low rate of cyclization shown previously[5c] by the corresponding 4-chloramine. In order to establish the extent to which IVc was formed, and to show that the γ-lactones isolated from the successful hydrolyses truly represented amides chlorinated at C-4 and not at C-3 or C-5, the rearrangement products IVb and IVc were reduced to the 4-chloramines (eq 4). These were isolated as the corresponding pyrolidines VII in 57 and 52% yields over-all, which confirmed that chlorination did occur mainly at C-4. We should also note that this rearrangement–reduction procedure illustrates a method of preparing certain pyrolidines from saturated linear compounds in the absence of the acidic medium required for the Hofmann–Loeffler chloramine rearrangement.[5c,6,9]



(4)

VII

Perhaps most remarkable of all the chloramide rearrangements were the reactions of IIIa and IIIb carried out to determine the influence of the solvent on the rearrangement. For both N-methyl- and t-butylchloramides, benzene was easily the solvent of choice in respect to both the extent of rearrangement and the reaction time; furthermore, the yield of the N-t-butyl rearrangement product IVb was also high (at least 60%) in pyridine. In contrast, none of IVb was obtained in

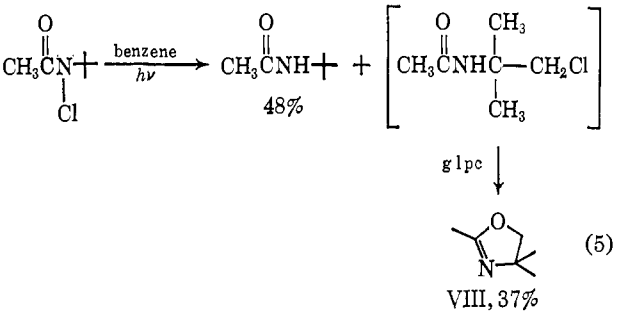
(8) L. Zurn, *Ann.*, **631**, 56 (1960), demonstrated a 50-fold rate enhancement in the hydrolysis of γ- or δ-hydroxyamides over the unsubstituted compounds.

(9) R. S. Neale and M. R. Walsh, *J. Am. Chem. Soc.*, **87**, 1255 (1965).

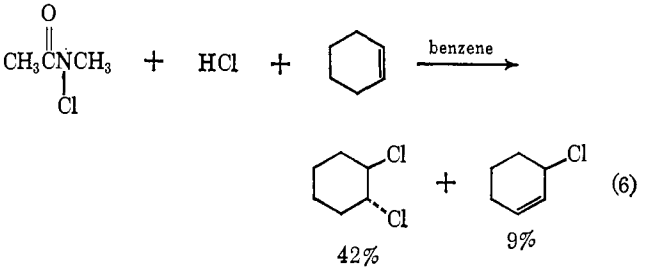
carbon tetrachloride or carbon disulfide. Such an effect was not at all in evidence during the corresponding N-bromamide reactions.

It was noted above that even in benzene the rearrangements of N-methylchloramides were far less efficient than those of the N-*t*-butyl compounds. The cause of this difference is probably the dehydrohalogenation reaction possible only with the N-methylchloramides: $RCONClCH_3 \rightarrow RCON{=}CH_2 + HCl$. Thus, the yield of γ-valerolactone (V) from the N-methyl compound IIIa was lower than that from the N-*t*-butyl compound IIIb, but the yield of the unsubstituted acid was higher. Furthermore, far more polymeric material was observed in the reaction products from all the N-methyl compounds than from the N-*t*-butyl derivatives. Side reactions involving the N-alkyl group rather than the acyl group were therefore indicated; the polymeric products could be of the type $(-OCR{=}NCH_2-)_x$, which on hydrolysis should yield the acid with the R group intact. Since it only occurs during irradiation of the chloramides, the side reaction is no doubt a free-radical process.

Further evidence of dehydrohalogenation reactions resulted from the irradiation of first N-chloro-N-methylacetamide, then N-*t*-butyl-N-chloroacetamide. The N-methyl compound reacted completely within 30 min to give a gummy product, and N-chloropyrrolidone behaved similarly; however, the N-*t*-butylchloramide with no α hydrogens N–C–H was unreactive for 180 min under identical conditions (benzene, Pyrex), although N-*t*-butylchloramides with long acyl chains reacted rapidly. In a Vycor vessel, N-*t*-butyl-N-chloroacetamide slowly decomposed to a mixture of the parent amide and a β-chloramide, which cyclized to the oxazoline VIII on glpc analysis of the reaction products (eq 5). Thus, hydrogens of type $N–CH_3$ appear to be far more reactive than those of type $N–C–CH_3$, and both are more labile than those of the acetyl methyl group.[10]



The solvent dependency of the chloramide reactions prompted us to probe the nature of side reactions other than dehydrohalogenation, since it seemed possible that the useful, aromatic solvents either inhibited certain of these side reactions or somehow specifically accelerated the rearrangements. The most obvious side reaction possible with all the chloramides was random, intermolecular chlorination by chlorine atom, the amide radical, or both. This was suggested by the presence of some unsubstituted amide in every reaction product of N-*t*-butylchloramides. These amides were either isolated (eq 5) or inferred to be present by the absence of the characteristic CH_2Cl singlet in the nmr spectra of crude reaction products; this showed that no significant chlorination of the *t*-butyl group had occurred in the amides whose unsubstituted acyl moiety was later isolated as the parent acid by hydrolysis. The unsubstituted amides could have been products of either intermolecular hydrogen abstraction by amide radicals or of reactions of the chloramides with the HCl produced from hydrogen abstraction by chlorine atoms. The latter process, which must yield chlorine as well as the parent amides, was demonstrated to occur readily by deliberately treating a chloramide with HCl and trapping the chlorine as it formed with cyclohexene (eq 6). Whatever process leads to the formation of the unsubstituted amides should also produce randomly mono- or dichlorinated amides, and the hydrolysis of these can account for the miscellaneous minor products that were always detected in glpc spectra of the crude lactones.



Further experiments showed that the alkyl radical forming step of intermolecular chlorination reactions must be attributable in part to hydrogen abstraction by amide radicals. Thus, we determined roughly the reactivity ratios per hydrogen of the tertiary and primary hydrogens of 2,3-dimethylbutane toward chlorine and toward two chloramides that were incapable of facile rearrangement (Table III). The ratios show that the selectivity in the chloramide reactions was greater than that in the chlorine reaction, indicating that chlorination of the hydrocarbon by chloramide radicals occurred to a significant extent. This result is similar to those reported recently for sulfonamide radicals.[11]

Table III. Chlorination of 2,3-Dimethylbutane in 4 *M* Benzene

	Reagent				
	Cl_2[a]	Cl_2 obsd	*t*-C_4H_9-OCl[b]	CH_3-CON-$ClCH_3$	CH_3-CONCl-*t*-C_4H_9
Tertiary/primary	20	16	69.9	65	34
Temp, °C	25	25–40	25	20–23	20–25

[a] See ref 13. [b] C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(10) The enhanced reactivity of hydrogens α or attached to amine nitrogen is of interest in the present situation involving amide nitrogen, for which there are no pertinent data. In essence, it is not clear either from gas phase or solution reactions whether the N–H or the α hydrogen N–C–H is the more labile (toward carbon radicals), although the heightened reactivity of one or both of these positions over ordinary CH_3 hydrogens is obvious: P. J. Kozak and H. Gesser, *J. Chem. Soc.*, 448 (1960); R. K. Brinton, *Can. J. Chem.*, **38**, 1339 (1960); A. E. Fuller and W. J. Hickenbottom, *Proc. Chem. Soc.*, 147 (1963); G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 188 (1952); W. H. Urry and O. O. Juveland, *J. Am. Chem. Soc.*, 80, 3322 (1958). Similarly relevant is the high reactivity of tri-*n*-butylamine *vs.* cumene toward *t*-butoxy radical: J. H. Raley, F. F. Rust, and W. E. Vaughan, *ibid.*, 70, 1336 (1948). Nevertheless, it is evident from the work of Kozak and Gesser that primary α hydrogens N–C–H are considerably less reactive than secondary ones in the gas phase; the enhanced reactivity of the primary hydrogens $N–CH_3$ in the N-methylchloramides (presumably toward chlorine atom) was therefore somewhat unexpected.

(11) A. E. Fuller and W. J. Hickinbottom, *J. Chem. Soc.*, 3228 (1965).

Intermolecular hydrogen abstraction by amide radicals thus appears to be a reaction competitive with the rearrangement of N-*t*-butylchloramides. Since only the aromatic solvents were beneficial (or at least not detrimental) to the rearrangement,[12] the question arises whether this reflects a favorable effect on the competition between intra- and intermolecular hydrogen abstraction or some other influence of the solvent. The latter possibility seems the more probable to us, since the N-bromamide rearrangements are not subject to the same solvent effect as those of the chloramides. This suggests that the solvent may influence the reactivity of the N-halo group or the free halogen atom, but not that of the free acylamino radical, which is formed from either halamide. A solvent effect involving the N-chloro group is possible, for example, if we assume that the chloramide rearrangements are *initiated* by a photolytic cleavage of N-chlorine bonds, but that the efficiency of this cleavage (and hence of the over-all rearrangement) is affected by the ability of the ground or excited state of the chloramide to form a charge-transfer complex with the solvent. We have not, however, detected any evidence of a ground-state complex of IIIa or IIIb with benzene. Any such solvent effect should not be as important in the case of bromamide reactions, since the N-bromine bond should be weaker and more photolabile than an N-chlorine bond. Of course, the possible involvement of a chloramide–solvent complex in the initiation step does not imply that such a complex must also influence the course of the chain reaction that follows.

Another possible explanation of the efficacy of aromatic solvents is that complexing[13] of undesirably reactive chlorine atoms, but not of less reactive bromine atoms, by such solvents is required to partially inhibit random chain halogenation reactions and thereby enhance the desired rearrangement. However, this rationale apparently cannot account for the observed results, since the rearrangement of either IIIa or IIIb in carbon disulfide, an even better moderator of chlorine atom reactivity than benzene,[13] failed to occur. Of course, the lack of an efficient rearrangement in carbon disulfide would have no significance if acylamino radicals were found to react with this solvent.

Because the halamide rearrangements resemble so closely the Hofmann–Loeffler rearrangement of N-chloramines,[6] the possible addition of chloramides to unsaturated hydrocarbons in a manner analogous to the additions of chloramines[5a,b,d] was investigated. However, N-*t*-butyl-N-chloracetamide failed to add to 1-hexene, 1-hexyne, 1,3-cyclooctadiene, or trimethylvinylsilane; in the presence of these substrates, no more than 20% of the chloramide was decomposed in benzene either photolytically at 25° or with AIBN at 80°, even after several hours. Furthermore, 1-hexene and 1-hexyne also inhibited the rate of photolytic decomposition of N-chloro-N-methylacetamide in benzene by a factor of 10 or more. Butadiene completely inhibited the decomposition of N-chloro-N-methylpentanoamide (IIIa), although the recovered IIIa rearranged normally in the absence of butadiene.

Curiously, AIBN did not initiate the rearrangement of N-*t*-butyl-N-chloropentanoamide (IIIb) in hot benzene, even though the normally rapid photolytic reaction is probably due to a facile light-initiated radical-chain process. In contrast to the acetamide derivative, IIIb did react rapidly in benzene in the presence of 1-hexene, 1-hexyne, 1,3-cyclooctadiene, or trimethylvinylsilane, but no addition products could be detected; the last reaction produced considerably less of the normal rearrangement product than that obtained in benzene alone (Table II).

The failure of amide radicals to add to olefins may be of particular significance. Thus the present results reinforce our current hypothesis that neutral amino, alkylamino, or acylamino radicals may be expected to abstract hydrogen from olefins in preference to adding to the double bond,[14] whereas protonated[1,5a,b] amino radicals, or those produced in metal oxidation–reduction systems[5d,e] (in which the amino radicals can be either protonated or coordinated to a metal ion), prefer to add to a double bond. The recent addition of N-nitrosamines to olefins[15] requires an acidic medium and may involve a protonated amino radical intermediate; if it does, this reaction is also consistent with the above hypothesis.

Experimental Section

Infrared spectra, either from KBr disks or liquid films, were recorded on a Beckman IR5A instrument, and nmr spectra were obtained in CCl_4 solution. Glpc spectra were obtained using SF96 liquid phase on HMDS-treated Chromsorb W or Carbowax 20M on Fluoropak in 0.25-in. columns supplied by the Wilkens Instrument Co. The ultraviolet source was an Hanovia Model 30600 100-wt medium-pressure mercury arc lamp equipped with a Vycor heat filter. Titrations for positive halogen were conducted by thiosulfate assay of iodine liberated from 20% aqueous KI acidified with 40% acetic acid. Melting and boiling points are uncorrected.

2-*t*-Butylimino-5-methyltetrahydrofuran Hydrobromide (IIa). A 0.4 *M* solution of *t*-butyl hypobromite in CCl_4 was prepared[16] as follows. To 85 g of sodium bromide and 57 ml of *t*-butyl alcohol in 1.5 l. of 5% aqueous sodium hypochlorite at 5° was added 66 ml of glacial acetic acid over 45 min. The liberated hypobromite was extracted into 200 ml of CCl_4 and the resulting solution was washed with two 100-ml portions of water, 100 ml of saturated $NaHCO_3$ solution, and again with water, and was dried over Na_2SO_4. Less washing of the hypobromite did not dramatically improve the yield (11–13%). Acetic acid was thoroughly removed by the base washes, undoubtedly at the expense of the hypobromite,[17] in order to facilitate isolation of nonsolvated iminolactone salts.

The N-bromo derivative of N-*t*-butylpentanoamide[5c] was then prepared in a 300-ml Vycor flask outfitted as described earlier[9] by treating 1.41 g (0.009 mole) of the amide in 10 ml of benzene with 25 ml of 0.4 *M* *t*-butyl hypobromite in CCl_4 in the dark for 1 hr at room temperature. The N–H band of the amide was now no longer present in the infrared spectrum of an evaporated aliquot of this solution. The bromamide was further diluted by addition of

(12) R. C. Petterson, A. Wambsgans, and R. S. George have recently observed a similar preference for aromatic solvents in the photolytic rearrangement of N-chlorimides but have found that benzene does not photosensitize the reaction: 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, see Paper No. 53, section K of Abstracts.

(13) G. A. Russell, *J. Am. Chem. Soc.*, 80, 4987 (1958).

(14) Unfortunately, there is a paucity of data relevant to the reactions of neutral amino radicals with olefins. The most significant study in this area appears to be that made by B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961), who failed to observe the addition of dimethylamino radicals from the thermal decomposition of tetramethyltetrazene (TMTZ) to 1-octene but did obtain "addition" products from α-methylstyrene. However, a further study of the latter system is required to determine how much of the adduct amines resulted from (a) dimethylamino radical addition to the double bond and (b) allylic hydrogen abstraction from the olefin followed either by coupling of the resulting radical with an amino radical or reaction of the allylic radical with TMTZ.

(15) Y. L. Chow, *J. Am. Chem. Soc.*, 87, 4642 (1965).

(16) C. Walling, personal communication.

(17) C. Walling and A. Padwa, *J. Org. Chem.*, 27, 2976 (1962).

85 ml of benzene and the solution was purged for 15 min with a stream of nitrogen. On irradiation at 6 in. the titration for electropositive halogen had dropped to nearly zero after 10 min and was not changing further. The solution was then evaporated at 15 mm in a warm water bath and then reevaporated twice with 50 ml of benzene in order to remove traces of elemental bromine. The infrared spectrum of the residue was nearly identical with that of the starting amide; thus, little of the ring-closed product was present at this point. On heating the residue for 2–5 min on the steam bath, crystallization of the product began. The white solid was filtered from the cooled residue after dilution with ether. The ether was evaporated and the residue was reheated to precipitate more of the hydrobromide salt. After a final repetition of this process, there was obtained a total 1.74 g of precipitate, mp 184–186°, which was recrystallized from acetone to afford 1.52 g (71%) of IIa, mp 190.5–191.5°.

Compound IIa was identified by comparison of the free iminolactone, obtained from the salt and aqueous base, with a known sample provided by the corresponding chloramide rearrangement (see below), and by conversion of the latter iminolactone to a hydrobromide identical with that isolated from the present reaction. The characteristic C=N infrared band of the iminolactone hydrobromide[18] appeared at 1690 cm^{-1}.

Anal. Calcd for $C_9H_{18}BrNO$: C, 45.77; H, 7.68; Br, 33.84; N, 5.93. Found: C, 45.50; H, 7.72; Br, 34.00; N, 5.82.

2-*t*-Butylimino-5-ethyltetrahydrofuran Hydrobromide (IIb). The procedure of the preceding example was followed in the conversion of 0.009 mole of N-*t*-butylhexanoamide[5c] to the N-bromo derivative; the solution this time was diluted with CCl_4, and a rapid rearrangement (10 min) ensued on irradiation. The product amides now required 5–10-min heating periods on the steam bath to afford the iminolactone salt, ultimately a total 1.60 g after recrystallization from acetone, mp 163–164.5°. Characteristic infrared bands appeared at 1600 and 686 cm^{-1}. The free iminolactone was identical with that isolated from the N-chloramide rearrangement, for which satisfactory analyses could not be obtained.

Anal. Calcd for $C_{10}H_{20}BrNO$: C, 48.01; H, 8.06; Br, 31.94; N, 5.60. Found: C, 47.95; H, 8.18; Br, 32.64; N, 5.62.

2-*t*-Butylimino-5-*n*-hexyltetrahydrofuran Hydrobromide (IIc). The parent amide was prepared from *t*-butylamine and Matheson decanoyl chloride and used without special purification (mp 30–32°). The bromamide was prepared as in the first example and diluted with CCl_4 or benzene, then irradiated at either 24 or 0° to afford the iminolactone hydrobromide in 66–76% crude yield, mp 90–92.5°, and 61–63% after recrystallization from acetone, mp 92–94° (extremely hygroscopic).

The structure was confirmed by boiling IIc for 2 hr in 3 *N* HCl; the glpc spectrum of the product extracted from the cooled solution disclosed the presence of a single compound. The infrared spectrum of a sample purified by glpc, $n^{25}D$ 1.4476 (lit.[19] $n^{20}D$ 1.4497) was identical with that of the expected 4-hydroxydecanoic acid γ-lactone (Sadtler spectrum no. 20026). In addition, the spectrum of the iminolactone salt exhibited bands at 1690 and 692 cm^{-1} in the infrared, in agreement with its lower homologs. The nmr spectrum showed bands too diffuse to be definitive.

Anal. Calcd for $C_{14}H_{28}BrNO \cdot 0.5H_2O$: C, 53.33; H, 9.27; Br, 25.35; N, 4.44. Found: C, 53.13; H, 8.94; Br, 26.64; N, 4.56.

2-Imino-5-methyltetrahydrofuran Hydrobromide. The mono-N-bromamide was presumably formed on mixing pentanoamide and *t*-butyl hypobromite according to the preceding examples. Irradiation of the solution after dilution with benzene led to consumption of active bromine only after 140 min, but work-up as usual gave the iminolactone salt, mp 132.5–134°, in 37% yield following one recrystallization from acetone–ether; a sample recrystallized for analysis had mp 135–137°. The C=N band now appeared at 1720 cm^{-1} in the infrared. The salt on treatment with aqueous acid afforded γ-valerolactone, whose infrared and glpc spectra were identical with those of the known compound.

Anal. Calcd for $C_5H_{10}BrNO$: C, 33.35; H, 5.60; Br, 44.38; N, 7.78. Found: C, 32.65; H, 5.68; Br, 44.59; N, 7.78.

Preparation and Rearrangement of N-*t*-Butyl-N-chloropentanoamide (IIIb). A mixture of 19.6 g (0.125 mole) of N-*t*-butylpentanoamide and 14.9 g (0.15 mole) of *t*-butyl hypochlorite (Frinton Laboratories) in 200 ml of CCl_4 was heated at 76° for 2 hr in the presence of 0.2 g of $K_2CO_3 \cdot 0.5H_2O$. The solution was evaporated and the residue was distilled to afford 80% of the chloramide, bp 48–49° (0.25 mm), $n^{23}D$ 1.4525, $\lambda_{max}^{isooctane}$ 256 mμ (ϵ_{max} 470).

Anal. Calcd for $C_9H_{18}ClNO$: active Cl, 18.47. Found: active Cl, 18.39.

The rearrangement of 0.12 mole of the chloramide was carried out on a preparative scale in 600 ml of benzene in a Pyrex flask. Nitrogen was passed through the rapidly stirred solution for 30 min, the temperature was lowered to 10°, and irradiation by two preheated lamps located 6 in. from the reaction flask was begun. Titratable chlorine was completely lost in 10 min. Evaporation of the solution left 23 g (100%) of crude amides; analysis of the nmr peak intensities of the mixture suggested that ~75% of the product contained the >CHCl group.

2-*t*-Butylimino-5-methyltetrahydrofuran (VI). The conversion of the 4-chloramide IVb to the iminolactone was best effected as follows. A mixture of 23 g (0.12 mole) of the crude, rearranged chloramide and 200 ml of 15.7 *N* H_2SO_4 was stirred at 76° for 6 hr. The cooled mixture was extracted with ether, and the ether solution was washed with aqueous sodium bicarbonate and then dried. Evaporation gave 2.9 g of a mixture of amides. The bicarbonate wash yielded 1.0 g of pentanoic acid on acidification. The original acid reaction mixture was diluted with 400 ml of water and basified with 150 ml of 12 *N* NaOH as the temperature was maintained at <20°. The liberated base was extracted into ether, dried over Na_2SO_4 and then $CaSO_4$, and obtained still slightly wet (12.9 g) on evaporation of the ether. The material was then distilled with 15 ml of benzene to afford after a forerun of wet benzene 10.0 g of the iminolactone VI, bp 69° (6 mm), $n^{23}D$ 1.4438. The product was found by glpc to consist of 97% VI (52% yield based on the N-chloramide) and 3% of the lactone V (2% yield).

The proof of structure of VI followed from several observations: the presence of chlorine predominantly at C-4 in the rearranged chloramide (see below); hydrolysis of VI to the known lactone V; the strongly basic nature of VI; and the iminolactone C=N band[18] at 1715 cm^{-1}. These data require VI to be either the iminolactone or the isomeric lactam, which would have to possess an unusually high basicity. The nmr spectrum of VI was definitive, however, as it contained both the multiplicity of sharp bands at τ 7.4–8.5 also observed of the lactone V and a multiplet centered at τ 5.55 due to the tertiary hydrogen $-CH(CH_3)O-$. This multiplet was strikingly similar in pattern as well as chemical shift to the analogous absorption in the lactone V (τ 5.40). These features of the nmr spectrum and the high basicity of VI rule out the alternative lactam structure. In addition, the nmr spectrum of VI contained the expected methyl group doublet (τ 8.70) also found in the spectrum of V (τ 8.65), and the integrated peak intensities observed were 0.93:3.92:3.16:8.96 (calcd 1:4:3:9). The hydrochloride had mp 123–124°; the hydrobromide IIa was described above.

Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.82; H, 11.15; N, 8.71. Calcd for $C_9H_{18}ClNO$: C, 56.39; H, 9.46; Cl, 18.49; N, 7.31. Found: C, 56.16; H, 9.58; Cl, 18.66; N, 7.51.

Other Rearrangements of N-*t*-Butyl-N-chloropentanoamide. The rearrangement of the chloramide IIIb was also carried out in 100 ml of each of several solvents as recorded in Table II. The product obtained from a 0.4 *M* solution of IIIb at 5° in benzene was hydrolyzed in two ways. The first, similar to that used in the preparative reaction just described, gave 48% of VI and 11% of V; the second, 4 *N* H_2SO_4 at 97° for 6 hr, gave 27% of VI, 42% of V, and 15% of pentanoic acid. The latter result is given in Table II and both are summarized in eq 3.

A reductive work-up employing diborane (eq 4) was used to establish the efficiency of several other reactions listed in Table II. An illustrative procedure, which established the major point of chlorine substitution in the product obtained from rearrangement of IIIb in benzene at 5°, involved reduction of 8.2 g (0.043 mole) of the amide mixture with 0.05 mole of B_2H_6 in 140 ml of THF under nitrogen.[20] The resulting mixture was heated under reflux for 3 hr and worked up to give after steam distillation 5.9 g of a mixture of bases. Analysis of the mixture by formation of N-*t*-butyl-2-methylpyrrolidine picrate[5c] showed the 4-chloramide to have been present in the chloramide rearrangement products in 57% yield (or more, if the reduction was less than 100% efficient), and glpc estimation of the yield of N-*t*-butylpentylamine showed at least 8% of the unsubstituted amide to have resulted from the rearrangement. A similar work-up of a pyridine and of another benzene reaction mixture inexplicably failed to yield the pyrolidine

(18) H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *J. Org. Chem.*, **28**, 1795 (1963).

(19) G. T. Muys, B. van der Ven, and A. P. de Jonge, *Appl. Microbiol.*, **11**, 389 (1963); *Chem. Abstr.*, **59**, 9110 (1963).

(20) H. C. Brown and P. Heim, *J. Am. Chem. Soc.*, **86**, 3566 (1964).

following steam distillations from base; now, the amine–δ-chloramine mixtures had to be heated for 3 hr in 1.5 *N* NaOH in 50% aqueous ethanol to effect the cyclizations.

Preparation and Rearrangement of N-*t*-Butyl-N-chlorohexanoamide (IIIc). The chloramide was prepared in 75% yield in the manner described in the previous example, bp 68–70° (0.4 mm), n^{24}D 1.4544.

Anal. Calcd for $C_{10}H_{20}ClNO$: active Cl, 17.29. Found: active Cl, 17.08.

The rearrangement was carried out on a preparative scale exactly as described in the preceding example; the time required for complete reaction was 25 min. Hydrolysis of the crude 4-chloramide under either the strong or dilute acid conditions of the preceding example or under other conditions of temperature or reaction time failed to yield products in reasonable amounts. From the reaction in 15.7 *N* H_2SO_4 at 76° for 6 hr was isolated by glpc a sample of **2-*t*-butylimino-5-ethyltetrahydrofuran,** formed in 9% yield, whose infrared spectrum contained characteristic bands at 1710 and 689 cm^{-1}, and whose nmr spectrum supported the assigned structure by its integrated peak intensities and by its similarity to that of the lower homolog. Thus, the >CH–O multiplet appeared at τ 5.75, the methyl absorption appeared as a triplet typical of the group CH_2CH_3, and the methine–methylene–methyl group absorption intensities were in the ratio 0.9:6.2:11.9 (theoretical 1:6:12). Satisfactory elemental analyses could not be obtained for this extremely hygroscopic compound, whose hydrobromide salt was described above. The iminolactone hydrolyzed in water to a neutral carbonyl compound, infrared 1770 cm^{-1}, presumably γ-caprolactone; the nmr spectrum of this product contained peaks due to low-field–high-field hydrogens in the expected ratio 1:9.

The diborane reduction of another rearrangement product of IIIc (Table II) yielded a largely uncyclized material after rapid steam distillation from aqueous base; cyclization was completed by heating the organic distillate in pyridine under reflux for 3 hr. The pyridine solution was then diluted with 10 volumes of water, extracted with pentane, and basified to liberate the pyrrolidine, bp 87–88° (45 mm), $n^{23.5}$D 1.4468. A sample free of the traces of pyridine accompanying this distillate was collected by glpc using a column containing Apiezon L on HMDS-treated Chromosorb W; this sample was identical with the known N-*t*-butyl-2-ethylpyrrolidine.[5c] The minimum yield of the 4-chloramide IVc produced in the N-chloramide rearrangement was calculated from picrate analysis of the pyrrolidine to be 52%, again assuming 100% efficiencies of the reduction and cyclization.

Preparation and Rearrangement of N-Chloro-N-methylpentanoamide (IIIa). N-Methylpentanoamide was prepared from methylamine and the acid chloride, bp 122–123° (10 mm), $n^{25.5}$D 1.4397 (lit.[21] bp 169° (90 mm), n^{20}D 1.4401). The chloramide was prepared in 61% yield in slightly impure form in the manner described above, bp 71° (10 mm), n^{24}D 1.4551.

Anal. Calcd for $C_6H_{12}ClNO$: active Cl, 23.68. Found: active Cl, 22.85.

The photolytic decomposition of the chloramide was carried out in several neutral solvents (Table II); products were obtained from each in the following manner. Irradiation of 5 g (0.03 mole) of the chloramide in 100 ml of solvent was begun after the solution had been flushed with nitrogen for 15 min. A residue was obtained on evaporation of the solution after the reaction had been completed; the exceedingly diffuse nmr and infrared spectral bands pointed to the presence of considerable amounts of polymeric material in each residue. The residues were boiled with 50 ml of 10 *N* H_2SO_4 for 5 hr, and the yields of the resulting γ-lactone V and pentanoic acid were determined by glpc analysis on the Carbowax column.

The rearrangement was also carried out in an acidic medium in analogy with N-chloramine rearrangements. Following irradiation under the conditions given in Table II, the reaction mixture was poured into 400 ml of water and boiled for 2 hr; the resulting mixture was then extracted with ether, the ether was distilled along with some TFA, and the residue was diluted with CH_2Cl_2 for glpc assay of the lactone and acid. In another experiment, the TFA was removed from the reaction mixture under vacuum and the residue was poured over ice. The amides were extracted into CH_2Cl_2, the solution was washed with aqueous $NaHCO_3$ and evaporated, and the residue was distilled to afford 21% of **N-methyl-4-chloropentanoamide,** bp 101° (0.7 mm), $n^{23.5}$D 1.4724, which was identified from its nmr spectrum (doublet methyl group due to CH_3CHCl) and elemental analysis.

Anal. Calcd for $C_6H_{12}ClNO$: C, 48.17; H, 8.08; Cl, 23.70; N, 9.36. Found: C, 48.31; H, 7.82; Cl, 23.89; N, 9.61.

Preparation and Rearrangement of N-Chloro-N,4-dimethylpentanoamide. Eastman White Label 4-methylpentanoyl chloride was converted to the N-methylamide, bp 102° (1.8 mm), n^{24}D 1.4427, and this was converted to the N-chloramide in the usual way in 70% over-all yield, bp 59° (2.5 mm), n^{24}D 1.4551. Although the active chlorine content was correct, later work showed that the original acid chloride and derived N-methylamide contained about 20% of the 3-methyl isomer. The product yields (Table II) have therefore been corrected to allow for the 20% impurity in the chloramide.

Anal. Calcd for $C_7H_{14}ClNO$: active Cl, 21.67. Found: active Cl, 21.59.

The rearrangements in neutral solution were carried out and the products were isolated as described in the preceding example. The γ-lactone of 4-hydroxy-4-methylpentanoic acid was collected by glpc, n^{23}D 1.4320 (lit.[22] n^{20}D 1.4352), and identified from its nmr spectrum, which showed only a 6-H singlet at τ 8.60 and a 4-H multiplet between 7.2 and 8.2. The 4-methylpentanoic acid was also collected and identified as the indicated isomer from its nmr spectrum, which contained the doublet methyl peak.

The reaction in H_2SO_4–TFA was worked up by removing TFA under vacuum, dissolving the residue in ether, and washing the ether solution with water and aqueous $NaHCO_3$. The residue obtained from the ether on evaporation was then hydrolyzed in the usual way (Table II).

Reaction of N-Chloro-N-methyl-4-phenylbutanoamide. The chloramide, prepared from the amide, bp 125° (0.05 mm), n^{24}D 1.5295, mp 41–44°, could not be distilled without decomposition; the crude material, which contained 91% of the theoretical active chlorine, was irradiated in benzene to determine whether a benzylic 4 position in the acyl chain would greatly enhance rearrangement of chlorine to that carbon. However, only traces of a neutral carbonyl-containing compound that was not an amide could be detected following the usual work-up. Irradiation of the chloramide in H_2SO_4–TFA led only to a ring-chlorinated 4-phenylbutanoic acid which was not identified further.

N-Chloro-N-methylacetamide was prepared in the usual way in 65% yield, bp 42° (24 mm), $n^{23.5}$D 1.4583 (lit.[23] bp 40.5° (24.5 mm), n^{16}D 1.4615).

Anal. Calcd for C_3H_6ClNO: active Cl, 32.97. Found: active Cl, 32.73.

When 75 ml of a 0.3 *M* benzene solution of the chloramide was irradiated in Vycor, a transient yellow color (Cl_2?) appeared following some initial fuming (HCl?). After 20 min at 20° the decomposition was complete, and 2.2 g of insoluble polymer had formed.

When 0.02 mole of the chloramide was irradiated in a 4 *M* solution of benzene in 2,3-dimethylbutane at 20° (Table III), a precipitate formed as the active chlorine titer fell to zero in 45 min. The yellow filtrate was analyzed by glpc with the aid of a known mixture of the tertiary- and primary-chlorinated hydrocarbons.

N-*t*-Butyl-N-chloracetamide was obtained in the usual way in 61% yield, bp 44° (9 mm), n^{23}D 1.4510, $\lambda_{max}^{isooctane}$ 256 mμ (ϵ_{max} 410).

Anal. Calcd for $C_6H_{12}ClNO$: active Cl, 23.75. Found: active Cl, 23.64.

The photolytic rearrangement of this compound (Table II) gave products best assayed by direct glpc analysis of the residue obtained on removal of the solvent. The SF96 column was used at 112° with the injector at 220°. Under these conditions were collected samples of N-*t*-butylacetamide and 2,4,4-trimethyloxazoline (VIII) for identification and to permit analysis for VIII in the crude photolysis product. The hygroscopic oxazoline, $n^{23.5}$D 1.4200, was identified by its infrared band at 1680 cm^{-1} (lit.[24] 1678 cm^{-1}) and its nmr spectrum, which contained singlets at τ 6.22, 8.17, and 8.84 (lit.[25] τ 6.232, 8.162, and 8.825).

In contrast to the lengthy reaction time in the absence of a substrate or in the presence of unsaturated substrates, the chloramide required only 25 min to react completely in the presence of 2,3-

(21) G. F. D'Alelio and E. E. Reid, *J. Am. Chem. Soc.*, **59**, 109 (1937).

(22) R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *ibid.*, 70, 1379 (1948).

(23) R. Hügel and A. Pasetti, Italian Patent 579,122 (July 8, 1958); *Chem. Abstr.*, **54**, 1310 (1960).

(24) P. Bassignana, C. Cogrossi, and M. Gandino, *Spectrochim. Acta*, **19**, 1885 (1963).

(25) M. A. Weinberger and R. Greenhalgh, *Can. J. Chem.*, **41**, 1038 (1963).

dimethylbutane,; the tertiary:primary hydrogen reactivity ratio was then determined by glpc analysis of the colorless solution which resulted (Table III).

N-Tritylpentanoamide. The procedure used is related to that for the synthesis of tritylamides.[26] A mixture of 8.3 g (0.1 mole) of Eastman valeronitrile, 12.0 g (0.046 mole) of Matheson triphenylcarbinol, 4.9 g (0.05 mole) of concentrated H_2SO_4, and 15 ml of dioxane was heated at 60° for 3 hr, cooled, and poured into 300 ml of ice-cold water. The precipitated solid was collected, boiled with hexane, and recrystallized twice from ethanol–water to give 5.4 g (32%) of N-tritylpentanoamide, mp 184.5–185.5°. The yield was even less when acetic acid or dibutyl ether was used as solvent.

Anal. Calcd for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08. Found: C, 83.64; H, 7.33; N, 4.25.

(26) J. A. Sanguigni and R. Levine, *J. Med. Chem.*, 7, 573 (1964).

The Spectral Properties of Alkoxymethyl Cations[1]

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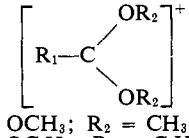
Abstract: The results of the first detailed nmr, infrared, and ultraviolet spectroscopic investigations of alkoxymethyl cations (alkoxycarbonium ions) are reported. These ions were studied as Meerwein fluoroborate salts or as generated in acid solutions from corresponding ortho esters or ketals. All of the results are consistent with near-coplanar structures for $(CH_3O)_3C^+$ (C_{3h} point group indicated), $(CH_3O)_2CCH_3^+$, and $(CH_3O)_2CH^+$, which may be regarded as resonance hybrids ($C^+—OCH_3 \leftrightarrow >C{=}O^+CH_3$). The $COCH_3$ bond is estimated to have 0.2–0.3 π bond order. An energy of activation for restricted rotation about this bond of 11 ± 4 kcal/mole has been obtained for $(CH_3O)_2CCH_3^+$. The proton nmr shielding of OCH_3 is shifted to lower fields by about 1.8 ppm on formation of the methoxymethyl cation from ortho ester or ketal. The precise value of this shift depends upon solvent and upon R_1 and R_2 of $CH_3OCR_1R_2^+$, as expected by considerations of delocalization of positive charge to oxygen. This investigation accords with earlier mass spectroscopic appearance potential studies and the results of Meerwein's alkoxy exchange reactions which indicate very large stabilization energies for alkoxymethyl cations. In spite of this high thermodynamic stability it has been noted that alkoxymethyl cations may be rapidly discharged by the following two general reactions: (a) $ROCR_1R_2^+ + H_2O \rightarrow O{=}CR_1R_2 + ROH + H^+$ and (b) $ROCR_1R_2^+ + N^\nu \rightarrow O{=}CR_1R_2 + RN^{\nu+1}$ (where N is a nucleophile of charge ν).

Alkoxymethyl cations have recently been found to possess large gaseous stabilization energies relative to the methyl cation.[3,4] For example, the stabilization energy of $CH_3OCH_2^+$ is 68 kcal compared to 35 kcal[3] for $CH_3CH_2^+$ and that for both $(CH_3O)_2CH^+$ and $(CH_3O)_3C^+$ is 92 kcal[4] compared to 74 kcal[5] for $(CH_3)_3C^+$.

The finding of large stabilization energy was in particular anticipated by the excellent investigations of Meerwein and his associates:[6] the fluoroborate salts of a number of alkoxymethyl cations were prepared and isolated; the transfer of OR between carbonium ions was established as a general reaction; the methoxy transfer reaction between equimolar methyl orthocarbonate and the trityl (triphenylmethyl) cation was shown to proceed with essentially complete formation of $^+C(OCH_3)_3$ ($(C_6H_5)_3C^+ + C(OCH_3)_4 \rightarrow C(OCH_3)_3^+ + (C_6H_5)_3COCH_3$), dramatically illustrating that the familiar trityl cation possesses less stabilization energy.

These facts based upon observations in both the vapor and condensed phases provide supporting explanation for the mechanistic evidence[7] that alkoxymethyl cations are formed as reaction intermediates in acid-catalyzed hydrolysis of acetals, ketals, and ortho esters without nucleophilic assistance. Supporting physical properties or structural evidence has been lacking for this interesting class of organic cation. In this study we have determined the ultraviolet, infrared, and nuclear magnetic resonance spectra for a representative series of alkoxymethyl cations. These spectral investigations have been made with the fluoroborate salts prepared by Meerwein's method *and* with the ions which we have found can be generated in H_2SO_4, 30% SO_3–H_2SO_4, and CF_3CO_2H solutions from corresponding ortho esters or ketals.



a, $R_1 = OCH_3$; $R_2 = CH_3$
b, $R_1 = OC_2H_5$; $R_2 = C_2H_5$
c, $R_1 = CH_3$; $R_2 = CH_3$
d, R_1 = *o*- and *p*-FC_6H_4; $R_2 = CH_3$
e, $R_1 = H$; $R_2 = CH_3$
f, $R_1 = H$; $R_2 = C_2H_5$

In the case of c, the nmr spectra provide an approximate value for the activation energy for rotation about the CH_3O–C bond.

Experimental Section

Preparation of Starting Materials. Methyl Orthocarbonate. Methyl orthocarbonate was prepared by the addition of 1 mole of chloropicrin in methanol to 3.5 moles of sodium methoxide in sufficient methanol to effect solution. It is important that the

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