ether. The combined ethereal extract was washed twice with 25 ml. of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the ether followed by short-path distillation under reduced pressure gave 13.663 g. (69%) of **25** as a light yellow liquid: b.p. 90–92° (0.04–0.05 mm.); $\nu_{max}^{CHCl_3}$ 1710 (s), 1650 (m), and 1640 cm.$^{-1}$ (sh); $\lambda_{max}^{heptane}$ 205 mμ (ε 16,200). The n.m.r. spectrum of **25** in chloroform-*d* showed absorption at δ 0.98 (6H, triplet, J = 7 c.p.s.), 1.5–2.3 (4H, broad multiplet), 2.4–2.8 (5H, quartet, J = 7 c.p.s.), 3.4–3.7 (1H, broad multiplet), 3.75 (3H, singlet), 5.6–6.0 (2H, multiplet), 5.93 (1H, quartet, J = 16 and 1.5 c.p.s.), and 7.32 (1H, quartet, J = 16 and 9 c.p.s.).

Anal. Calcd. for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 71.04; H, 9.95; N, 6.19.

The picrate had m.p. 163.0–163.5°; recrystallization from methanol gave m.p. 163.5–164.0°.

Anal. Calcd. for $C_{20}H_{26}N_4O_9$: C, 51.50; H, 5.62; N, 12.01. Found: C, 51.51, 51.69; H, 5.61, 5.79; N, 11.83, 11.83.

Hydrocinnamic Acid from 25.—Adduct **25** (1.450 g., 0.00611 mole) and 15 ml. of concentrated hydrochloric acid (37%) were refluxed for 15 hr. in a 50-ml. round-bottomed flask equipped with heating mantle, magnetic stirrer, and reflux condenser. The mixture was extracted three times with 10 ml. of ether and the combined ether solution was extracted three times with 10 ml. of aqueous 5% sodium bicarbonate. After acidification with concentrated hydrochloric acid, the mixture was extracted twice with 10 ml. of ether and the combined extract was washed with 5 ml. of saturated sodium chloride solution and finally dried over anhydrous magnesium sulfate. Removal of the ether afforded 0.470 g. (51%) of hydrocinnamic acid as a light brown oil which crystallized upon addition of a seed crystal. Molecular distillation under reduced pressure (60–80° at 0.04 mm.) afforded 0.334 g. (36%) of the acid as a white solid, m.p. 46.5–48.0; a mixture melting point showed no depression and the infrared spectrum was identical with that of authentic hydrocinnamic acid (m.p. 49.0–49.5°).

The Influence of Solvent and Chloramine Structure on the Free-Radical Rearrangement Products of N-Chlorodialkylamines

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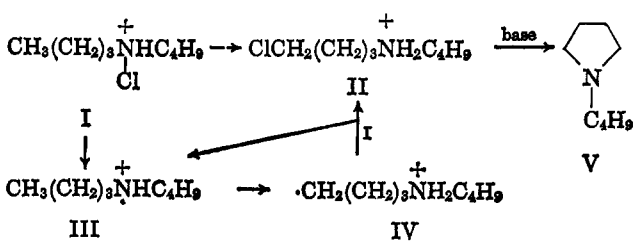
The influence of certain acidic solvents and chloramine structure on the photolytic Hofmann–Loeffler reaction has been studied. The δ-chloramine from N-chlorodi-*n*-butylamine was formed in 71% or better yield in the solvents 3.9 *M* sulfuric acid in acetic acid, nitromethane, or acetonitrile and in trifluoroacetic acid. The conversion of some δ-chloramines to the corresponding δ-hydroxyamines was demonstrated. In the aminium radical derived from N-chloro-N-methyl-5-phenylbutylamine only 62% of intramolecular hydrogen abstraction occurred at C-4 of the 5-phenylbutyl chain; 38% occurred at C-5 in the largest deviation from the usually high selectivity towards the C-4 position yet observed for an aminium radical. N-*t*-Butylchloramines were photolytically rearranged in acetic acid in order to observe any effect on the reaction efficiency and the selectivity due to the bulky N-alkyl group; the expected pyrrolidines were obtained in acceptable yields, and attack of the aminium radical occurred almost exclusively at C-4.

We wish to report some illustrations of the influence of solvent and of chloramine structure on the products obtained from photolytic rearrangements of N-chloramines (the Hofmann–Loeffler reaction[1]); the data should be useful in the further application of this reaction to organic synthesis.

Dependence on Solvent.—The literature does not reveal which of a variety of potential acidic solvents (Table I) are useful for effecting the desired rearrangement I → II or, perhaps, related reactions involving intermediate aminium radicals $R_2\overset{+}{N}H$, such as the addition of chloramines to unsaturated hydrocarbons.[2,3] We have studied mainly the rearrangement of N-chlorodi-*n*-butylamine, since we have already described in detail its reactions under varying conditions in sulfuric acid–acetic acid media.[4]



Our observations are summarized in Table II; entries 2–4 recall certain of our earlier results in sulfuric acid–acetic acid[4] for comparison with the new results, which follow. Thus, 83–88% yields of the pyrrolidine V are realized under several conditions of the photolytic reaction in acetic acid; in this solvent, the photolysis must be followed by basification to convert the primary product II to the isolable base V.

One useful alternative to sulfuric acid in acetic acid is trifluoroacetic acid (TFA, entries 7 and 8), claimed to be generally the solvent of choice for the chloramine rearrangement.[1] However, neither Wawzonek[5] nor we have found TFA to be superior, in terms of product yield, to sulfuric acid systems; for example, compare entries 2 and 7 in Table II and 1–3 in Table III. TFA may excell for steroidal chloramines[6] because it increases substrate solubility or decreases ionic side reactions involving other functional groups present in the steroid, such as C=C and C=O.

However, TFA does offer distinct advantages, as pointed out earlier[1,6]; principally, it allows simple isolation of the salt II. When II is isolated, derivatives other than V may then be obtained, such as the corresponding alcohol. Example 8 of Table II illustrates such a process; a primary chlorine atom was

(1) Reviewed by M. E. Wolff, *Chem. Rev.* **63**, 55 (1963).
(2) R. S. Neale, *J. Am. Chem. Soc.*, **86**, 5340 (1964).
(3) R. S. Neale and R. L. Hinman, *ibid.*, **85**, 2666 (1963).
(4) R. S. Neale and M. R. Walsh, *ibid.*, **87**, 1255 (1965).
(5) S. Wawzonek and T. P. Culbertson, *ibid.*, **81**, 3367 (1959).
(6) J. F. Kerwin, M. E. Wolff, F. F. Owings, B. B. Lewis, B. Blank, A. Magnani, C. Karash, and V. Georgian, *J. Org. Chem.*, **27**, 3628 (1962).

TABLE I
RELATIVE ACIDITIES OF PROTONATING MEDIA

Medium	$-H_0$	Ref.
Sulfuric Acid Systems		
1.0 *M* H_2SO_4 in HOAc with 30 vol. % Ac_2O	>12	*a*
100% H_2SO_4	11.1	*b*
1.87 *M* H_2SO_4 in TFA	8.07	*b*
3.52 *M* H_2SO_4 in 99% HOAc	4.10	*c*
8 *M* aq. H_2SO_4	4.0	*c*
0.03 *M* H_2SO_4 in CH_3NO_2	3.5	*d*
3.6 *M* H_2SO_4 in 85% HOAc	3.03	*e*
0.041 *M* H_2SO_4 in 99% HOAc	1.1	*c*
	(pK_{HA} = 7.25)	*f*
H_2SO_4 in CH_3CN	(pK_{HA} = 7.25)	*f*
Other Acidic Systems		
HF (<0.01 *M* H_2O)	9.97	*b*
22.5 wt. % HF in TFA	8.40	*b*
92 wt. % HF in H_2O	8.0	*b*
CH_3SO_3H	7.86	*g*
TFA	3.03	*b*
7.0 *M* H_3PO_4 in 99% HOAc	1.60	*e*
13.8 *M* H_3PO_3 in H_2O	1.34	*g*
4 *M* CH_3SO_3H in CH_3OH	~1.2	*h*
3.5 *M* H_3PO_4 in 99% HOAc	0.41	*c*

[a] The value pH(HOAc) = 12.86 is reported for this system by J. Russell and A. E. Cameron [*J. Am. Chem. Soc.*, **60**, 1345 (1938)]; since H_0 = pH(HOAc) + 0.41 for 1 *M* H_2SO_4 in HOAc (in the absence of Ac_2O; see ref. *e* for H_0 value), the value of H_0 in 30% Ac_2O may not differ greatly from pH(HOAc). However, there is a remarkable and uncommon enhancement of acidity on the addition of up to 15% Ac_2O to H_2SO_4–HOAc,[8] which renders questionable a comparison between $-H_0$ and pH(HOAc); the large initial increase in $-H_0$ due to added Ac_2O may be the result of its facilitating the complete ionization of the strong acid.[8] [b] H. H. Hyman and R. A. Garber, *ibid.*, **81**, 1847 (1959). [c] N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940); values for 100% H_2SO_4 were little different from those for 99% HOAc in ref. *e*. [d] L. C. Smith and L. P. Hammett, *ibid.*, **67**, 23 (1945). [e] J. Rocek, *Chem. Listy*, **50**, 726 (1956). [f] Dissociation of H_2SO_4 in acetonitrile, as in poor hydrogen-bonding solvents in general, is limited and proceeds according to $2HA \rightleftharpoons H^+ + AHA^-$; the dissociation in acetic acid is limited by the low dielectric constant of the solvent [I. M. Kolthoff, S. Bruchenstein, and N. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961)]. [g] K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959). [h] C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, *ibid.*, 2327 (1957).

replaced by a hydroxyl group on boiling the δ-chloramine salt in an acid solution containing bromide ion (eq. 1). The replacement of chlorine was not efficient,

$$CH_3(CH_2)_3NC_4H_9 \xrightarrow[h\nu]{\text{TFA}} \xrightarrow[\text{2. }\Delta,\ HBr,\ NaBr]{\text{1. evaporate}} \underset{76\%}{HOCH_2(CH_2)_3NHC_4H_9} \quad (1)$$
Cl

however, when the salt of rearranged N-chlorodi-*n*-pentylamine was boiled in acetic acid (Table III, entry 3). In the latter case, the amount of sodium chloride liberated far exceeded the amount of acetate produced; cyclization of the δ-chloramine must have occurred in preference to solvolysis.

In certain cases, partial hydrolysis of salts of type II occurs spontaneously. N-Chloro-N-methyl-4-phenylbutylamine was rearranged in acetic acid, but some hydrolysis to the benzyl alcoholic amine occurred on work-up; the hydrolysis could be nearly completed by brief warming of the diluted acidic reaction mixture (Table III, entry 4). When such a facile hydrolysis is not desired, one must use an alternative solvent, such as TFA or some other nonaqueous system described below.

Sulfuric acid in nitromethane (Table II, entries 9 and 10) was a surprisingly efficient medium for the rearrangement I → II, especially since light catalysis was neither required nor effective. Thus, when a polar but nonhydroxylic solvent is desired, nitromethane (dielectric constant[7] 35.9) may prove useful. However, it is not evident that all chloramines can be efficiently rearranged in nitromethane, since one in which the carbon radical analogous to IV was benzylic (Table III, entry 5) failed to give a good yield of products. Responsible for this failure may be sulfonation of the benzene ring, or a more nebulous effect such as the disruption of the chain reaction due to the participation of side products formed from the phenyl-substituted chloramine.

Sulfuric acid in acetonitrile (Table II, entry 11) also supported a useful, spontaneous rearrangement of I. Much of the product was isolated as the hydrochloride of II, and the total yield of rearrangement products was similar to that from TFA. Although the work-up required by the water miscibility of acetonitrile is a bit tedious, this solvent could prove useful when a nonhydroxylic medium of good solvating power is desired.

Other acidic media were less useful. In the mixture methanesulfonic acid–acetonitrile (Table II, entry 12), I rearranged very inefficiently, and no rearrangement product was obtained from methanesulfonic acid in methanol (entry 13) or sulfuric acid in acetic anhydride (entry 6); these failures may be attributable to lower acidities in the methanesulfonic acid systems (Table I) and the formation of reactive acetylium ions[8] from acetic anhydride.

The foregoing results show that the presence of strong acid is surely necessary but obviously is not sufficient for chloramine rearrangements; this is made further evident by the failure to obtain the photolytic rearrangement product of I in acetic acid alone[9] or in carbon tetrachloride[10] or of N-chloro-N-methyl-4-phenylbutylamine in benzene. Chemical initiation of rearrangements of I in carbon tetrachloride was also unsuccessful (entries 16 and 17).

Although we did not identify the products from the extremely slow photolysis of I in carbon tetrachloride (entry 14), Wawzonek and Nordstrom[10] carried it to completion and isolated the products dibutylamine hydrochloride (up to 56% yield) and butylamine (after hydrolysis of the presumed imine intermediates). The suggested mechanism[10] (eq. 2–5) clearly

$$Bu_2NCl \xrightarrow[\text{or R}\cdot]{h\nu} Bu_2N\cdot + Cl\cdot \text{ or } RCl \quad (2)$$

$$2Bu_2N\cdot \longrightarrow Bu_2NH + BuN{=}CHC_3H_7 \quad (3)$$

$$Cl\cdot + RH \longrightarrow HCl + R\cdot \quad (4)$$

$$Bu_2NH + HCl \longrightarrow Bu_2NH\cdot HCl \quad (5)$$

requires that *di*butylamine result from a disproportionation of neutral dibutylamino radicals and that the

(7) "Handbook of Chemistry and Physics," 45th Ed., The Chemical Rubber Co., Cleveland, Ohio, 1964, p. E31.
(8) H. A. E. Mackenzie and E. R. S. Winter, *Trans. Faraday Soc.*, **44**, 159 (1948).
(9) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).
(10) S. Wawzonek and J. D. Nordstrom, *J. Org. Chem.*, **27**, 3726 (1962).

TABLE II

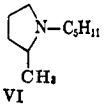
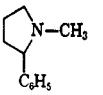
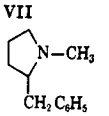
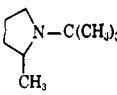
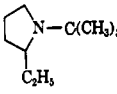
THE HOFMANN–LOEFFLER REACTION OF N-CHLORODI-*n*-BUTYLAMINE IN PYREX

Entry	Solvent	Chloramine *M*	Chloramine Purity[a]	Light[b]	Temp., °C.	Rate,[c] mmole/min.	% yield[d] NBP	% yield[d] DBA	% reaction
1	3.9 *M* H_2SO_4–1.5 *M* H_2O in HOAc	0.42	U	Dark	22	0.008	88	0	70
2	3.9 *M* H_2SO_4–1.5 *M* H_2O in HOAc[e]	0.46	U	A	20	0.37	88	0	98
3	1.9 *M* H_2SO_4–1.5 *M* H_2O in HOAc[e]	0.45	U	B	20	3.27	83	2	98
4	1.9 *M* H_2SO_4–1.5 *M* H_2O in HOAc[e]	0.46	D	A	20	0.43	87	1	98
5	3.9 *M* H_2SO_4 in 30/70 (v./v.) Ac_2O–HOAc	0.50	U	*f*	20	2.66	65	5	95
6	3.9 *M* H_2SO_4 in Ac_2O	0.50	U	Dark	20–33	>2.2	0	75	88[g]
7	TFA	0.80	U	A[h]	5	1.00	79	...	95
8	TFA	0.74	U	B	−4 to +10	7.1	76[i]	...	100
9	3.9 *M* H_2SO_4 in nitromethane	0.45	D	Dark	24	0.49	85	...	95
10	1.9 *M* H_2SO_4 in nitromethane	0.46	D	Dark[j]	33–47	0.16	70	...	95
11	3.9 *M* H_2SO_4 in acetonitrile	0.30	U	Dark[j]	25	1.30	71[k]	...	95
12	4 *M* CH_3SO_3H in acetonitrile	0.50	U	B	20	2.19[l]	~10	~56	100
13	4 *M* CH_3SO_3H in methanol	0.48	U	B	20	1.43	0	81	95
14	CCl_4[m]	0.35	D	B	24	0.02	...	...	39
15	2 *M* TFA in CCl_4	0.29	D	B	22	...	53	13	95
16	CCl_4–$CHCl_3$ (4:1) + 0.05 *M* Bz_2O_2	0.11	D	B	60	0.03	0	46	87
17	CCl_4 + 0.04 *M* AIBN[n]	0.40	D	None	77	≥0.025	0	78[o]	22

[a] D, distilled; U, undistilled, used as obtained crude from N-chlorosuccinimide in ether. [b] A, Hanovia 100-w. lamp at 6 in., with filter to transmit 300–420 mμ; B, unfiltered Hanovia lamp. [c] Loss of positive chlorine between 0–80% reaction. [d] NBP, N-*n*-butylpyrrolidine; DBA, di-*n*-butylamine; yields based on reacted chloramine. [e] Data taken from ref. 4. [f] G.E. RS Sunlamp at 34 in.; first 12% of reaction was spontaneous, irradiation was then required. [g] Irradiation failed to complete the reaction. [h] Strongly fluorescent during reaction. [i] Product was $HO(CH_2)_4NHC_4H_9$ (see Experimental Section). [j] Irradiation did not increase reaction rate. [k] Includes 20% NBP plus 51% $Cl(CH_2)_4NHC_4H_9 \cdot HCl$. [l] Rate given for reaction at 20° (to 20% reaction). [m] In quartz; decomposition of reaction mixture with HCl gave only dibutylamine hydrochloride. [n] AIBN, azobisisobutyronitrile. [o] Based on chloramine consumed, which equalled the number of equivalents of AIBN employed.

TABLE III

REARRANGEMENTS OF N-CHLORAMINES IN ACIDIC SOLVENTS

Entry	Chloramine Structure	Chloramine Purity[a]	Chloramine M	Solvent	Light[b]	Temp., °C.	Rate[c]	% reaction	Products	% yield
1	$(n\text{-}C_5H_{11})_2NCl$	D	0.46	3.9 *M* H_2SO_4–1.3 *M* H_2O in HOAc	Dark[d] A	20	0.725 1.10	52 99	 (VI)	60
2		D	0.80	TFA	B	2	3.06	95	VI $CH_3CH(CH_2)_3NHC_5H_{11}$ OAc	60 7[e]
3		U	0.60	TFA	B	0–15	4.0	100	VI $CH_3CH(CH_2)_3NHC_5H_{11}$ OH	24 17[f]
4	$C_6H_5(CH_2)_4NCl$ CH_3	U	0.45	3.6 *M* H_2SO_4–1.5 *M* H_2O in HOAc	Dark[d] A	15–20	0.81	31	$C_6H_5CH(CH_2)_3NHCH_3$ (VII) OH	57[g]
									 (VIII)	4
5		U	0.30	4 *M* H_2SO_4 in CH_3NO_2	Dark	20	2.1	100	VIII VII	10 5
6	$C_6H_5(CH_3)_2NCl$ CH_3	U	0.40	3.9 *M* H_2SO_4–1.5 *M* H_2O in HOAc	B	7–12	2.0	100	 $C_6H_5CH(CH_2)_4NHCH_3$ OH	43 26
7	$CH_3(CH_2)_4NC(CH_3)_2$ Cl	U	0.66	4 *M* H_2SO_4–0.9 *M* H_2O in HOAc	B[h]	25	>6.6	100		44[i]
8	$CH_3(CH_2)_2NC(CH_3)_2$ Cl	U	0.49	4 *M* H_2SO_4–0.9 *M* H_2O in HOAc	B[h]	27–31	9.8	100		68

[a] Footnote *a*, Table II. [b] Footnote *b*, Table II; Pyrex reaction vessel. [c] Loss of positive chlorine in millimoles per minute over stated per cent reaction. [d] When spontaneous reaction ceased, irradiation was begun. [e] Concentrated reaction mixture was boiled 6 hr. in HOAc–NaOAc; basification and distillation afforded both products. [f] Concentrated reaction mixture was boiled 5 hr. in 5 *N* aqueous H_2SO_4; structure of alcohol was assumed from its conversion to VI with $SOCl_2$–$CMCl_3$. [g] Diluted reaction mixture was warmed 2 hr. before basification. [h] Vicor flask. [i] Crude yield 84%, see Experimental Section.

hydrogen chloride formed react only in the sense of precipitating the amine. Unfortunately, the facile reaction sure to occur[11] between the chloramine and hydrogen chloride was ignored; this reaction instantaneously gives dibutylamine and chlorine (eq. 6) (the latter may be detected by the appearance of its color and ultraviolet spectrum). We therefore believe that dibutylamine results mainly from processes 6 and 7 and, possibly, also *via random* hydrogen abstraction reactions of $Bu_2N\cdot$, a radical whose presence in the system remains to be demonstrated.

$$Bu_2NCl + HCl \longrightarrow Bu_2NH + Cl_2 \quad (6)$$

$$Cl_2 \xrightarrow{h\nu} Cl\cdot \xrightarrow{RH} HCl + R\cdot \quad (7)$$

On the basis of our present results, it appears that a useful solvent must be highly acidic (see Table I) but should not produce species other than solvated ions of its strong-acid component. The reversible protonation of acetonitrile by sulfuric acid, which no doubt occurs to a slight extent, may be a special case; although no further product results from it during the chloramine rearrangement, the protonated acetonitrile may lead to the observed traces of acetamide when the reaction mixture is diluted with water. A solvent having a high radical chain-transfer constant in polymerization reactions, such as a mercaptan, would of course be unsuitable for use in chloramine rearrangements.

Acids useful in the rearrangement I → II are indeed candidates for use in other chloramine reactions. Thus, sulfuric acid in acetic acid has proved to be generally useful,[2,3] and TFA, in addition to supporting the addition of N-chlorodiethylamine to butadiene,[3] promotes more efficient chloramine additions to terminal alkyl olefins than does sulfuric acid–acetic acid. This development will be illustrated in a forthcoming paper; the low dielectric constant (8.2 at 25°)[12] of TFA may retard the ionic chlorination process which competes with the desired radical addition.

Dependence on Chloramine Structure.—Control of selectivity in the Hofmann–Loeffler reaction with respect to reaction of an aminium radical at C-5 rather than at C-4, the usual position of attack,[9] has not been explored, the few available data showing only that the nature of the nonreacting N-alkyl group may be important: the photolysis of N-chloromethylhexylamine gave the pyrrolidine (from attack at C-4) and the piperidine (from attack at C-5) in ratios of 8.5 to 1 in concentrated sulfuric acid near 0°[9] but only 4 to 1 in 85% acid at room temperature[13] (eq. 8, R = CH_3), whereas N-chlorodi-*n*-hexylamine in 85% acid gave a

$$CH_3CH_2CH_2(CH_2)_3\overset{+}{N}(Cl)HR \xrightarrow[\text{room temp.}]{85\%,\ H_2SO_4} CH_3\underset{Cl}{C}HCH_2(CH_2)_3\overset{+}{N}H_2R + CH_3CH_2\underset{Cl}{C}H(CH_2)_3\overset{+}{N}H_2R \quad (8)$$

R	% product composition	
CH_3	20	80
n-C_6H_{13}	4.4	95.6

pyrrolidine/piperidine ratio of 21.7 to 1 (eq. 8, R = n-C_6H_{13}).[13]

To probe this point briefly, we photolyzed N-chloro-N-methyl-5-phenylpentylamine in acetic acid with the intent to maximize attack at the now benzylic position C-5. When first the diluted acid solution was warmed to hydrolyze the benzylic chloride (C-5 attack), then the basified mixture was warmed to cyclize the δ-chloramine remaining (C-4 attack), products were obtained (Table III, entry 6) whose yields (eq. 9) indicate the ratio of C-4/C-5 attack was 1.6 to 1, lower than that from any previous example. In contrast, activation of C-5 in tertiary alkoxyl radicals by phenyl or methyl (eq. 10 and 11)[14] is not as great as in dialkylaminium radicals.

$$C_6H_5\overset{5}{C}H_2\overset{4}{C}H_2(CH_2)_3\overset{+}{N}HCH_3 \longrightarrow$$

26% C-5 product + 43% C-4 product (9)

$$C_6H_5\overset{5}{C}H_2\overset{4}{C}H_2(CH_2)_2\underset{CH_3}{\overset{CH_3}{C}}-O\cdot \xrightarrow[CCl_4]{0^\circ}$$

7.7% C-5 product + 73.3% C-4 product (10)

$$CH_3CH_2CH_2(CH_2)_2\underset{CH_3}{\overset{CH_3}{C}}-O\cdot \xrightarrow[CCl_4]{0^\circ}$$

5.5% C-5 product + 80.5% C-4 product (11)

Although both aminium and alkoxy radicals can undergo intramolecular rearrangement efficiently and usually selectively, they differ greatly in that addition of aminium radicals to unsaturated hydrocarbons of several types[2,3] is not observed of alkoxy radicals, which in the presence of olefins[15a] or acetylenes[15b] are consumed by hydrogen abstraction or β cleavage. Addition of both aminium[3] and alkoxy[16] radicals to 1,3-dienes, however, appears to occur with ease.

Finally, the rearrangements of two N-*t*-butylchloramines were studied to discover any unusual consequences of the bulky group attached to the reacting aminium radical. In the case of N-chloro-N-*t*-butylpentylamine, the rearrangement under optimum conditions in acetic acid[4] proceeded as expected to afford the corresponding pyrrolidine (Table III, entry 7). The preference for intramolecular hydrogen atom abstraction at C-4 analogous to III → IV persisted in the rearrangement of N-chloro-N-*t*-butylhexylamine (Table III, entry 8); little if any of the piperidine, produced by attack at C-5, could be detected as an ultimate reaction product. Thus, when viewed with the cases reported by Wawzonek and Culbertson (eq. 8), this result suggests that a large N-alkyl group in a chloramine undergoing rearrangement in a sulfuric acid medium renders the process exceptionally selective for attack at C-4, *i.e.*, *via* the usual six-atom cyclic transition state. An interesting experiment in this connection would be to rearrange N-

(11) G. H. Coleman and W. A. Noyes, *J. Am. Chem. Soc.*, **43**, 2211 (1921); G. H. Coleman and H. P. Howells, *ibid.*, **45**, 3084 (1923).
(12) W. Dannhauser and R. H. Cole, *ibid.*, **74**, 6105 (1952).
(13) S. Wawzonek and T. P. Culbertson, *ibid.*, **82**, 441 (1960).
(14) C. Walling and A. Padwa, *ibid.*, **85**, 1597 (1963).
(15) (a) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961); C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963); J. K. Kochi, *ibid.*, **84**, 1572 (1962); F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. M. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling, L. Heaton, and D. D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965).
(16) F. Minisci and R. Galli, *Tetrahedron Letters*, **12**, 533 (1962); J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 2785, 3271 (1962).

chloro-N-*t*-butyl-5-phenylpentylamine and compare the result with that from the N-methyl compound (Table III, entry 6).

Experimental Section

Rearrangements in Acetic Acid.—The apparatus and procedure followed were those previously described.[4] The chloramines prepared in purified form were N-chlorodi-*n*-butylamine, b.p. 59° (5 mm.), $n^{24}D$ 1.4359 [lit.[17] b.p. 64–64.8° (10 mm.)]; N-chlorodi-*n*-pentylamine, b.p. 69–72° (2 mm.), $n^{25}D$ 1.4421 (*Anal.* Calcd. for $C_{10}H_{22}ClN$: Cl, 18.50. Found: Cl, 18.36.); and N-chloro-N-methyl-4-phenylbutylamine, b.p. 68° (0.001 mm.), $n^{25}D$ 1.5162 (*Anal.* Calcd. for $C_{11}H_{16}ClN$: Cl, 17.9. Found: Cl, 16.9.). As indicated in the tables, the chloramines were usually used as obtained in crude form from the reaction between N-chlorosuccinimide (10% excess) and the appropriate amine stirred in ether[9] for 1 hr.

Rearrangement of N-Chlorodi-*n*-pentylamine.—A 150-ml. portion of the solution described in Table III, entry 1, spontaneously lost titratable chlorine until 52% had disappeared; the reaction was completed by irradiation as indicated. The acid solution was then poured into 150 g. of ice and 400 ml. of water, the diluted solution was extracted with pentane and ether, the aqueous phase was basified with 12 *N* sodium hydroxide, and the liberated oil was extracted into pentane after standing 12 hr. over the basic solution. The residue from the pentane (10.9 g.) was steam distilled from 2.4 *N* sodium hydroxide to give 7.2 g. of crude product, which contained 84% of **N-*n*-pentyl-2-methylpyrrolidine** by g.l.p.c. analysis (Perkin-Elmer column W), along with two minor lower boiling components. Analysis by picrate formation similarly indicated the crude product to contain 85% of the pyrrolidine (60% yield). The pyrrolidine had b.p. 101.5° (50 mm.), $n^{24}D$ 1.4401, picrate m.p. 111.0–111.5°; lit.[18] b.p. 96–97° (41 mm.), $n^{25}D$ 1.4385, picrate m.p. 114–115°.

Anal. Calcd. for $C_{16}H_{23}N_4O_7$: C, 50.12; H, 6.05; N, 14.62. Found: C, 50.05; H, 6.28; N, 14.45.

4-Phenylbutylamine.—In a 3-l. flask under nitrogen were heated for 4 hr. under reflux 28.8 g. (0.76 mole) of lithium aluminum hydride and 100 g. (0.69 mole) of Eastman 4-phenylbutyronitrile in 1740 ml. of ether. The cooled solution was cautiously decomposed by the dropwise addition over 2.5 hr. first of 30 ml. of water, then 23 ml. of 20% sodium hydroxide solution, then 100 ml. of water. The ether solution of amine and ether washings of the precipitated salts afforded 91% of 4-phenylbutylamine: b.p. 100° (4.5 mm.), $n^{24}D$ 1.5180, hydrochloride m.p. 164.5–165.0° (recrystallized from nitromethane); lit.[19] b.p. 118° (17 mm.), hydrochloride m.p. 161°.

N-Methyl-4-phenylbutylamine.—A mixture of 38.5 g. (0.258 mole) of 4-phenylbutylamine and 119 g. of 98% formic acid (2.58 moles) was heated until 75 ml. of the theoretical 82 ml. of excess formic acid and water had been distilled from a 2 ft. × 8 mm. column containing a spiral of tantalum wire, b.p. 101–104.5°. The residue (45.7 g.) of crude formamide was heated under reflux for 6 hr. in 1200 ml. of ether with 19.2 g. (0.516 mole) of lithium aluminum hydride and worked up with 20 ml. of water, 16 ml. of 20% sodium hydroxide, and 68 ml. of water. The crude product was distilled to afford 34.4 g. (82%) of N-methyl-4-phenylbutylamine: b.p. 84–85° (2.2 mm.), $n^{23}D$ 1.5061, hydrochloride (from acetone) m.p. 125.5–127°; lit.[20] b.p. 95.0–95.4° (5 mm.), $n^{25}D$ 1.5035, hydrochloride m.p. 126.2–126.8°.

Purification of the intermediate **4-phenylbutylformamide** gave a pale yellow oil, b.p. 129° (0.02 mm.), $n^{24}D$ 1.5310.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.29; H, 8.32; N, 7.99.

Rearrangement of N-Chloro-N-methyl-4-phenylbutylamine.—The chloramine could not be purified for use owing to extensive decomposition on attempted distillation. The solution (120 ml.) described in Table III, entry 4, was worked up following the dark and irradiated periods of reaction by basifying the diluted mixture with 150 ml. of 12 *N* sodium hydroxide and then stirring the mixture at 50–60° for 3 hr. The products were extracted into ether and distilled to afford 0.36 g. (4%) of **N-methyl-2-phenylpyrrolidine,** identical with a sample prepared earlier, which had b.p. 83° (5 mm.), $n^{24}D$ 1.5203, picrate (*Anal.* Calcd. for $C_{17}H_{18}N_4O_7$: C, 52.30; H, 4.65; N, 14.36. Found: C, 52.02; H, 4.65; N, 14.41.) m.p. 147–148° [lit.[21] b.p. 96° (11 mm.), picrate m.p. 145°]; also distilled was 5.5 g. (57%) of **N-methyl-4-hydroxy-4-phenylamine** (*Anal.* Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.82. Found: C, 73.28; H, 9.08; N, 7.89.), b.p. 100–103.5° (0.05 mm.), $n^{23}D$ 1.5274, m.p. 53–63°.

The hydroxyamine (2.0 g., 0.011 mole) was converted to the pyrrolidine by heating in 75 ml. of chloroform with 2.65 g. (0.023 mole) of thionyl chloride. The resulting solution was evaporated and the residue was steam distilled from 150 ml. of 1.6 *N* sodium hydroxide; the product was then treated with 60 ml. of ethanolic picric acid solution to afford 3.22 g. (73%) of N-methyl-2-phenylpyrrolidine picrate, m.p. 146–147°.

N-Methyl-5-phenylpentylamine.—The crude acid chloride from 100 g. (0.84 mole) of thionyl chloride and 100 g. (0.56 mole) of Aldrich 5-phenylvaleric acid was added to 500 g. of 40% aqueous methylamine at 10°. After 1 hr. the resulting amide was extracted into ether. The dried ether solution (1700 ml.) and 42.6 g. (1.12 moles) of lithium aluminum hydride were then heated under reflux for 2.5 hr.; after standing overnight at 24°, the salts were precipitated by dropwise addition of 44 ml. of water, 34 ml. of 20% sodium hydroxide, and 150 ml. of water in order. Distillation afforded 86.6 g. (88%) of N-methyl-5-phenylpentylamine, b.p. 98° (1.9 mm.), $n^{24}D$ 1.5028.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.50; H, 10.53; N, 8.19.

Rearrangement of N-Chloro-N-methyl-5-phenylpentylamine.—The photolysis of 100 ml. of the solution described in Table III, entry 6, was carried out as indicated, and the reaction mixture was then poured into 150 g. of ice and 300 ml. of water. The resulting solution was extracted with pentane, stirred at 25° for 3 hr., and finally basified. The basic mixture was stirred at 50–60° for 1.5 hr., cooled, and extracted with ether. Distillation of the products gave 2.9 g. (43%) of **N-methyl-2-phenylmethylpyrrolidine:** b.p. 63° (0.35 mm.), $n^{23}D$ 1.5196, picrate m.p. 143.5–144.5°; lit.[22] b.p. 69–70° (0.3 mm.), $n^{25}D$ 1.5186, picrate m.p. 144–145°. The higher boiling product was 1.9 g. (26%) of **N-methyl-5-hydroxy-5-phenylpentylamine,** b.p. 113° (0.06 mm.), $n^{23}D$ 1.5270. A correct analysis could not be obtained for this hydroxyamine, but the n.m.r. spectrum showed the proper features, including only one benzylic hydrogen. The hydroxyamine was converted to N-methyl-2-phenylpiperidine in 75% yield on heating with excess thionyl chloride in chloroform followed by steam distillation from 1.5 *N* base, picrate m.p. 171–172° (lit.[23] m.p. 174–174.5°). The g.l.p.c. spectrum of the piperidine showed only a trace of the isomeric pyrrolidine to be present (Carbowax 20M–KOH on Fluoropak).

***t*-Butylpentylamine.**—The requisite precursor amide, m.p. 48–50°, was prepared in 96% yield from valeryl chloride and *t*-butylamine in benzene at 5°. A recrystallized sample of N-*t*-butylvaleramide had m.p. 48.8–49.8°; the n.m.r. spectrum was as expected.

Anal. Calcd. for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.80; H, 12.16; N, 8.44.

The desired amine resulted on heating 12.4 g. (0.08 mole) of the amide with 150 ml. of 1 *M* borane in THF (0.14 mole) followed by the recommended work-up.[24] Distillation afforded 10.5 g. (95%) of *t*-butylpentylamine, b.p. 76–78° (56 mm.), $n^{23}D$ 1.4146, whose structure was assured by its n.m.r. spectrum.

Anal. Calcd. for $C_9H_{21}N$: C, 75.43; H, 14.78; N, 9.78. Found: C, 74.95; H, 15.44; N, 9.77.

Rearrangement of N-Chloro-*t*-butylpentylamine.—The photolysis of the solution described by Table III, entry 7, was accomplished in 10 min. The usual work-up was followed by stirring the liberated base with the basic aqueous phase at 60° for 2.5 hr.; this yielded 8.2 g. (84%) of the crude pyrrolidine. Distillation from powdered potassium hydroxide, however, afforded only 4.5 g. (44%) of **N-*t*-butyl-2-methylpyrrolidine,** b.p. 45–46° (10 mm.), $n^{23}D$ 1.4407, picrate m.p. 237–238°. The structure was assumed on the basis of adequate analogy[1] and the n.m.r. spectrum (CCl_4) which showed three N–C–H hydrogens to be present in a cyclic structure along with the >$CHCH_3$ group (doublet CH_3 peak).

(17) G. S. Myers and G. F Wright, *Can. J. Res.*, **B26**, 257 (1948).

(18) R. M. Hill and H. Adkins, *J. Am. Chem. Soc.*, **60**, 1033 (1938).

(19) M. Métayer, *Ann. chim.* (Paris), [12] **4**, 196 (1949); *Chem. Abstr.*, **44**, 3922 (1949).

(20) A. C. Cope and S. M. McElvain, *J. Am. Chem. Soc.*, **53**, 1587 (1931).

(21) R. Lukeš, *Chem. Listy*, **27**, 392, 409 (1933); *Chem. Abstr.*, **29**, 1720 (1935).

(22) J. H. Burckhalter and J. H. Short, *J. Org. Chem.*, **23**, 1281 (1958).

(23) R. Lukeš and M. Černý, *Collection Czech. Chem. Commun.*, **24**, 1287 (1959); *Chem. Abstr.*, **53**, 15075 (1959).

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

Anal. Calcd. for $C_{15}H_{22}N_4O_7$: C, 48.64; H, 5.99; N, 15.13. Found: C, 48.63; H, 6.07; N, 15.00.

Preparation and Rearrangement of N-Chloro-*t*-butylhexylamine.—The distilled amide, b.p. 81–82° (0.5 mm.), $n^{23}D$ 1.4424, prepared from hexanoyl chloride and *t*-butylamine in benzene at 5°, was reduced with diborane in THF[24] to afford ***t*-butylhexylamine** in 90% yield, b.p. 96–98° (63 mm.), $n^{24}D$ 1.4244.

Anal. Calcd. for $C_{10}H_{23}N$: C, 76.34; H, 14.75; N, 8.90. Found: C, 76.13; H, 15.05; N, 8.83.

The crude chloramine in 100 ml. of solution was rearranged on irradiation for 5 min., as summarized in Table III, entry 8. The diluted and basified reaction mixture was stirred at 60° for 3 hr., but cyclization was not completed by this treatment in contrast to the previous experiment, since distillation of the product from potassium hydroxide afforded 2.75 g. of **N-*t*-butyl-2-ethylpyrrolidine** (*Anal.* Calcd. for $C_{10}H_{21}N$: C, 77.35; H, 13.63; N, 9.02. Found: C, 77.02; H, 13.98; N, 9.19.), b.p. 68° (5 mm.), $n^{23}D$ 1.4449, picrate (*Anal.* Calcd. for $C_{16}H_{24}N_4O_7$: C, 49.99; H, 6.29; N, 14.58. Found: C, 50.01; H, 6.27; N, 14.57.) m.p. 168–169°, along with 2.87 g. of a material which liberated chloride ion on standing, b.p. to 80° (5 mm.). The latter material was cyclized on boiling for 6 hr. in 25 ml. of 25% sodium hydroxide. The total yield of the pyrrolidine was 5.2 g. (67%); the material appeared free of isomers on g.l.p.c. analysis (Wilkens SF96 on HMDS–Chromosorb W) with the possible exception of a shoulder estimated to comprise <2% of the sample. The shoulder, which could not be resolved from the main peak, no doubt represented the isomeric piperidine derivative. The structure of the pyrrolidine was confirmed by its n.m.r. spectrum, which showed the proper area ratios including three N–C–H hydrogens in carbon tetrachloride; the triplet due to the $-CH_2CH_3$ hydrogens could be observed only in trifluoroacetic acid. The doublet due to the $>CHCH_3$ group of the piperidine was not observed in either solvent.

Reactions of N-Chlorodi-*n*-butylamine in Acids Other than Acetic. Trifluoroacetic Acid.—The reaction summarized by entry 8 of Table II was carried out in 35 min. with 29 g. of the chloramine in 240 ml. of TFA. Excess acid was then removed under vacuum and the 69 g. of residue was boiled for 4.5 hr. in 750 ml. of water containing 80 g. of sodium bromide and 50 ml. of concentrated hydrobromic acid. A small amount of insoluble material was removed by filtration with carbon; the solution was then made basic with 100 ml. of 12 *N* sodium hydroxide, saturated with sodium chloride, and extracted with ether to afford 21.5 g. of a residue after drying over potassium hydroxide, $n^{23}D$ 1.4506. Distillation gave 19.4 g. (76%) of **N-(4-hydroxybutyl)butylamine**, b.p. 70–72° (0.4 mm.), $n^{24}D$ 1.4508. The structure was defined by the n.m.r. spectrum and conversion of the material to N-*n*-butylpyrrolidine (NBP) on treatment with thionyl chlororide in chloroform followed by cyclization in base.

Sulfuric Acid–Nitromethane (Table II, Entry 9).—To 200 ml. of a solution containing 44 ml. of concentrated sulfuric acid and 156 ml. of nitromethane was added 14.6 g. of the chloramine, whereupon a bright yellow color formed instantly and active chlorine was lost during 252 min. in the dark. The resulting solution was poured over 150 g. of ice, nitromethane was removed by extraction with ether, and 9.7 g. of NBP was obtained on basification and warming of the aqueous phase.

Sulfuric Acid–Acetonitrile (Table II, Entry 11).—The rate of loss of active chlorine in the dark (200 ml. of solution) increased on irradiation; the reaction mixture was poured into 192 ml. of saturated aqueous sodium chloride and 96 ml. of water and was extracted with methylene chloride, acetonitrile–methylene chloride (1:1), and again methylene chloride. The combined organic extracts were extracted with 2% hydrochloric acid–saturated sodium chloride, then with sodium chloride solution alone. The dried organic phase gave 4.5 g. (38%) of N-(4-chlorobutyl)-butylamine hydrochloride, m.p. 210–213°, and 1.0 g. of a lachrymatory liquid (ν 1740 cm.$^{-1}$) which was not identified. The acidic extracts of the organic phases were evaporated, and the residue was extracted with hot acetonitrile to give, after one recrystallization, a further 1.5 g. (13%) of the amine salt, m.p. 207–215°. The recrystallized salt (acetonitrile) had m.p. 217–218° (lit.[5] m.p. 211–212°) and yielded NBP on basification.

The remaining rearrangement product was recovered on basification and extraction of the aqueous phase from the original reaction mixture; this gave 1.5 g. (20%) of NBP.

Methanesulfonic Acid–Acetonitrile (Table II, Entry 12).—Active chlorine was lost from 200 ml. of this solution at the indicated rate at 20° in the dark; at 6° the loss continued at about one-fourth this rate, and irradiation at 10° had no effect. The reaction was completed by warming the solution to 41°, whereupon basification and ether extraction of one-half of the solution gave 4.0 g. of di-*n*-butylamine (DBA) and NBP in the indicated amounts (by g.l.p.c.). A sample of the reaction mixture gave suddenly a highly insoluble 2,4-dinitrohydrazone (2,4-DNP) derivative in ethanol following a 15-sec. induction period; the part soluble in hot acetonitrile had m.p. 212–215° and was, no doubt, a 2,4-dinitrophenylosazone derived from an imine precursor such as detected previously as side products in the Hofmann–Loeffler reaction.[4,25]

Methanesulfonic Acid–Methanol (Table II, Entry 13).—The chloramine titer was initially stable in the dark at 20° but continued to decrease slowly when irradiation was interrupted midway in the reaction. The 200 ml. of solution was poured into 250 g. of ice, and the resulting solution was extracted with ether. The basified aqueous phase gave 10.0 g. of DBA shown to be free of NBP by g.l.p.c.

Carbon Tetrachloride (Table II, Entry 17).—A mixture of 5.0 g. (0.03 mole) of the chloramine and 0.5 g. (0.003 mole, 20 equiv. %) of azobisisobutyronitrile (AIBN) in 75 ml. of carbon tetrachloride was heated at 79° for 3 hr. Only 19% of the active chlorine had been lost at this point. The solution was extracted with two 20-ml. portions of 5 *N* sulfuric acid and 0.6 g. of DBA was liberated from the acid on basification (78% based on chloramine reacted). The dried organic phase still contained 76% of the original active chlorine.

(25) G. F Wright, *J. Am. Chem. Soc.*, **70**, 1958 (1948).