

bonate solution, and filtration and acidification of the bicarbonate extract gave a yellow precipitate. Recrystallization from ethanol and from methyl ethyl ketone-hexane afforded 1.0 g. of yellow and red crystals of the presumed 2-anthrylglyoxylic acid, m.p. 240–284° dec., which was not purified further.

A solution of 0.5 g. of the glyoxylic acid in 0.5 ml. of N,N-dimethyl-*p*-toluidine was heated gently until decarboxylation commenced. The temperature was raised from 150 to 190° over 0.5 hr. until gas evolution ceased. Work-up as above yielded a product which was crystallized from ethanol to give 0.3 g. of yellow flakes, m.p. 208.5–211.5°. Several recrystallizations from absolute ethanol gave impure IVa as pale yellow flakes, m.p. 209–210.5°, lit.⁷ m.p. 203–204°. Combustion analysis indicated that this sample was contaminated with anthracene.

B. McFadyen-Stevens Method. Methyl 2-anthroate, m.p. 193.5–194° (lit. m.p. 128°⁴² and 192–193°⁴³), was prepared by esterification of the acid in dry methanol with hydrogen chloride. This ester (26 g., 0.11 mole) and 150 ml. of hydrazine hydrate (85%) were refluxed for 36 hr. To the cooled mixture 600 ml. of water was added. Filtration afforded 20 g. (77%) of yellow crystals, m.p. 245–248.5° dec. Four recrystallizations from pyridine produced an analytical sample of 2-anthroylhydrazine as long, flat, yellow plates, m.p. 241–244° dec., with subsequent resolidification.

Anal. Calcd. for C₁₅H₁₂N₂O: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.10; H, 5.04; N, 12.05.

To 20 g. (0.085 mole) of 2-anthroylhydrazine in 100

(42) K. Lauer, *Ber.*, **70B**, 1288 (1937).

(43) F. H. C. Stewart, *Australian J. Chem.*, **13**, 478 (1960).

ml. of pyridine at room temperature was added dropwise with stirring 15 g. (0.085 mole) of benzenesulfonyl chloride. After 15 min. a clear solution resulted, but stirring was continued for 3 hr. The solution was poured onto ice to give 28.8 g. (90%) of yellow solid, m.p. 250–255° dec. Five recrystallizations from acetic acid and one from pyridine-cyclohexane gave 2-anthroylbenzenesulfonylhydrazide as small, light yellow flakes, m.p. 237.5–239° dec.; mixture melting point with 2-anthroylhydrazine was 209–220° dec.

Anal. Calcd. for C₂₁H₁₆N₂O₃S: C, 67.01; H, 4.29; N, 7.44; S, 8.50. Found: C, 66.81; H, 4.32; N, 7.50; S, 8.35.

To a stirred mixture of 11.3 g. (0.0301 mole) of 2-anthroylbenzenesulfonylhydrazide and 200 ml. of ethylene glycol heated to 165°, 8 g. of sodium carbonate was added in one portion. After 1 or 2 min. the vigorous reaction had subsided. Water was added to the cooled mixture, and the gelatinous mass was filtered. The product was washed, dried, and extracted continuously with ether. The residue obtained on evaporation was recrystallized from benzene-ethanol to yield impure IVa, m.p. 199–206°. Sublimation gave 2.9 g. (45.3%) of yellow crystals, m.p. 199–203°. Five recrystallizations from ethyl acetate-ethanol produced an analytical sample of IVa, m.p. 201.5–202.9°, lit. m.p. 203–204°.⁷

Anal. Calcd. for C₁₅H₁₀O: C, 87.35; H, 4.89. Found: C, 87.15; H, 4.83.

Acknowledgment. We wish to thank the National Science Foundation and the University of Massachusetts Research Council for grants in support of this work.

New Aspects of the Hofmann-Loeffler N-Chloramine Rearrangement in Acetic Acid

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Received August 20, 1964

The photolytic rearrangement I → IV of N-chlorodi-n-butylamine (I) in acetic acid was carried out under several sets of reaction conditions in order to determine why the process requires an excess of sulfuric acid to occur in good yield. The optimum conditions for the synthetic utilization of the chloramine rearrangement in acetic acid were thereby defined. The enhancement in yield of the Hofmann-Loeffler end product V with increasing acidity³ was confirmed, but the over-all reaction rate was found to decrease with increasing acidity in contrast to an earlier report.³ Excess sulfuric acid reduces the rate of a nonradical disproportionation of I to N,N-dichloro-n-butylamine; in the absence of externally added impurities, the dichloramine is believed to be the primary initiator of the rearrangement I → IV. The yield of V falls rapidly under those conditions which facilitate the accumulation of small amounts of the dichloramine in the reaction mixture during photolysis.

There have been many reports in the recent literature of synthetic applications of the Hofmann-Loeffler N-chloramine rearrangement,¹ and through the efforts of two groups of investigators^{2,3} the mechanism of this free-radical chain process has been adequately defined with respect to the propagation sequence (II → IV);

this involves nitrogen cation radicals R₂NH⁺ (aminium radicals, II) as key intermediates. In order to define more precisely than previously³ the requirement of an excess of sulfuric acid in the Hofmann-Loeffler rearrangement, and in other reactions involving aminium radicals generated from N-chloramines,⁴ we have

(1) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

(2) S. Wawzonek and P. J. Thelen, *J. Am. Chem. Soc.*, **72**, 2118 (1950); S. Wawzonek and T. P. Culbertson, *ibid.*, **81**, 3367 (1959).

(3) E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

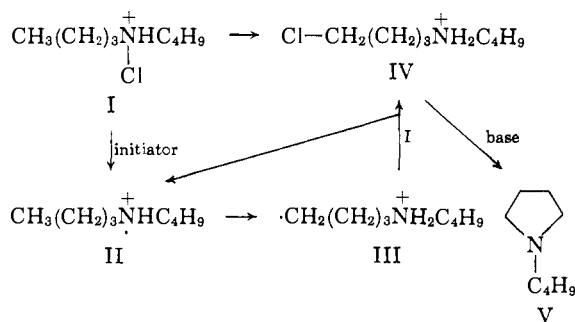
(4) (a) R. S. Neale and R. L. Hinman, *ibid.*, **85**, 2666 (1963); (b) R. S. Neale, *ibid.*, **86**, 5340 (1964).

Table I. Photolytic Rearrangement of N-Chlorodi-*n*-butylamine at 20° in 1.5 M Water–Acetic Acid

| Entry | Molarity | | Source | | Rate N ₂ sweep ^c | Rate ^d | Total time, min. ^e | % yield | |
|-----------------|--------------------------------|---------------------|----------------------------------|--------------------|--|-------------------|-------------------------------|------------------|------------------|
| | H ₂ SO ₄ | Bu ₂ NCl | Bu ₂ NCl ^a | Light ^b | | | | DBA ^f | NBP ^g |
| 1 | 0.49 | 0.45 | U-1 | A | S | 0.13 | >2 days | 65 | 2 |
| 2 | 0.97 | 0.48 | U-1 | A | S | 0.10 | >2 days | 47 | 17 |
| 3 | 0.99 | 0.26 | U-1 | A | S | 1.02 | 60 | 31 | 35 |
| 4 | 1.0 | 0.14 | U-1 | A | S | 0.35 | 110 | 17 | 51 |
| 5 | 1.5 | 0.44 | U-1 | A | F | 0.81 | 162 | ~1 | 75 |
| 6 | 1.5 | 0.46 | U-1 | A | S ^h | 0.98 | 106 | 18 | 50 |
| 7 | 1.5 | 0.46 | U-1 | A | S | 1.13 | 80 | 26 | 41 |
| 8 | 1.9 | 0.46 | U-1 | A | S | 0.96 | 110 | 19 | 56 |
| 9 | 3.9 | 0.46 | U-1 | A | S | 0.37 | 320 | 0 | 88 |
| 10 | 1.5 | 0.46 | U-2 | A | F | 0.70 | 236 | 4 | 79 |
| 11 ⁱ | 1.5 | 0.43 | U-2 | A | M | 0.82 | 126 | 6 | 82 |
| 12 ^B | | | | | | | | | |
| 12 | 1.5 | 0.46 | U-2 | A | S | 1.08 | 90 | .. | .. |
| 13 | 1.9 | 0.46 | U-2 | A | S | 0.98 | 143 | 16 | 65 |
| 14 | 3.9 | 0.46 | U-2 | A | S | 0.34 | 300 | .. | .. |
| 15 | 1.5 | 0.46 | U-2 | B | S | 3.65 | 30 | 20 | 55 |
| 16 | 1.9 | 0.45 | U-2 | B | S | 3.27 | 33 | 2 | 83 |
| 17 | 4.0 | 0.46 | U-2 | B | S | 2.40 | 44 | .. | .. |
| 18 | 1.5 | 0.46 | U-2 | C | S | 1.62 | 66 | 20 | 42 |
| 19 | 1.9 | 0.46 | U-2 | C | S | 0.85 | 142 | 7 | 72 |
| 20 ^j | 1.0 | 0.25 | U-1 | C | S | 0.22 | 124 | 10 | 60 |
| 21 ^j | 2.5 | 0.24 | U-1 | C | S | 0.14 | 400 est. | 6 | 75 |
| 22 | 1.0 | 0.46 | D | A | S | 0.05 | ^k | 34 | 49 |
| 23 | 1.9 | 0.46 | D | A | S | 0.43 | 260 | 1 | 87 |
| 24 | 3.9 | 0.46 | D | A | S | 0.24 | 480 | 0 | .. |
| 25 | 7.7 | 0.46 | D | A ^l | S | 0.16 | 1 | 0 | 95 |

^a Chloramine used as prepared from N-chlorosuccinimide (NCS) without purification (U-1); from recrystallized NCS (U-2); or after distillation (D). ^b Hanovia Model 30600 medium pressure mercury arc lamp: (A) with filter, transmission 300–410 mμ, maximum (50%) at 350–370 mμ, at 6 in. from reaction vessel; (B) without filter; (C) without filter at 24 in. ^c Slow (S), individual bubbles of nitrogen observable; moderate (M), solution opaque due to bubbles; fast (F), considerable frothing. ^d Rate given in mmoles of electropositive chlorine consumed per minute over 0–80% of the reaction (except entries 1 and 2: 0–30%; entry 10: 18–72%). ^e To 98% reaction. ^f Di-*n*-butylamine; yield determined by g.l.c. ^g *N-n*-Butylpyrrolidine; most yields checked also by picrate formation. ^h Reaction mixture swept unusually long and rapidly prior to photolysis. ⁱ First half of reaction mixture worked up at *t*_{1/2} (part A), remainder at end of reaction (part B); loss of positive chlorine ceased on interruption of irradiation. ^j Anhydrous. Experiment 21 completed with type B irradiation after 80% reaction. ^k To 65% reaction; filter then removed to complete reaction. ^l To 31% reaction (irradiation ineffective, spontaneous decomposition); reaction completed under irradiation B.

studied several aspects of the rearrangement of N-chlorodi-*n*-butylamine (I) in acetic acid.



Results

The variables considered in the rearrangement I → IV at 20° in acetic acid 1.5 M in water and of varied molarity in sulfuric acid were: (1) acidity, (2) the degree of purity of I, (3) the wave length and intensity of the applied ultraviolet radiation, and (4) the rate at which the reaction mixture was swept by nitrogen during the photolyses. The results are collected in Table I.

Acidity. The data of Table I confirm that the yield of *N-n*-butylpyrrolidine (NBP, V) increases with increasing acidity.³ However, in direct contrast to the previous results,³ the over-all rate of reaction (loss of electropositive chlorine with time) was found to decrease

with increasing acidity. These two trends remained consistent under these sets of conditions: at constant sulfuric acid concentration and decreasing chloramine concentration (entries 3 and 4), at constant chloramine concentration and increasing sulfuric acid concentration in the presence of water (entries 7–9, 12–14, 15–17, 18–19, and 23–24), and in the absence of water (entries 20 and 21, the conditions in ref. 3). However, the rate of rearrangement fell off sharply at acid/chloramine ratios of 1:1 or 2:1 (entries 1, 2, and 22), and low yields of NBP accompanied these very slow reactions. In anhydrous acetic acid (entries 20 and 21), the acidity was enough enhanced due to the absence of water⁵ that low acid/chloramine ratios did not result in low yields of NBP, despite the slow reaction rates.

Wave Length and Intensity of Irradiation. As expected, an increase in the intensity of the initiating ultraviolet light led to enhanced decomposition rates (entries 15 and 18, 16 and 19), and the rate was suppressed more by filtering out the low wave length portion than by decreasing the intensity of the light (compare entries 12, 15, and 18 and also 13, 16, and 19; the relative intensities of sources A/B/C were approximately 8:16:1). Unexpected, however, were the increased yields of NBP with increased radiation intensity and decreased wave length (entries 13 vs. 16 and 15 vs.

(5) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

18). Thus, at a given acidity the yields of NBP were dependent upon the rates at which the decompositions of undistilled chloramine were carried out. If the only effect of light on the process were to initiate chains, and the principal initiator were unprotonated chloramine present in very low concentration,³ a change in the light source should have changed the rate of reaction but *not* the yield of NBP. Light therefore has some more complex effect than simply the photolysis of neutral chloramine.

Chloramine Purity. The samples of I used for the experiments reported in Table I were of three degrees of purity. N-Chlorosuccinimide (NCS, Matheson Co., reagent grade) was mixed with di-*n*-butylamine in ether solution³ to give I which was lemon yellow; these samples were either used directly (designated U-1 in Table I) or were distilled (D) to afford a colorless product. Alternatively, recrystallization of the NCS from benzene prior to use led to undistilled samples of I (U-2) which possessed only a faintly yellow color. Samples of I, whose impurities were never identified, gave NBP in yields which increased with increasing chloramine purity (compare entries 2 and 22; 8, 13, and 23). However, the reaction rate fell as the chloramine purity was increased (entries 8, 13, and 23; 9, 14, and 24), the greatest difference appearing in the very slow reactions of distilled I (entries 23 and 24).

Rate of Nitrogen Sweep. In 1.5 *M* sulfuric acid, using poorest quality (U-1) chloramine and filtered irradiation (A), the yield of NBP was increased remarkably from 41 to 75% merely by increasing greatly the flow of nitrogen through the reaction mixture during photolysis (entries 5–7). On rapid sweeping, the same yield of NBP was produced from I of either U-1 or U-2 quality (entries 5 and 10). The effect of the nitrogen sweep rate was further reflected in the shape of the titration curves; positive chlorine disappeared linearly with time from the fast-sweep reaction mixtures, as it did also from other mixtures which reacted very rapidly. However, in slow-sweep reactions the titration curves were sigmoid without exception. These results, along with those described above, suggested the presence of volatile, reactive impurities in solutions of the chloramine which had far-reaching effects on the course of the rearrangement.

These results are summarized in Table II (columns

Table II. Influence of Reaction Variables on the N-Chloramine Rearrangement^a

| Increasing variable | Yield of NBP | Over-all reaction rate | Accumulation of BuNCl ₂ |
|---------------------|--------------|------------------------|------------------------------------|
| Acidity | I | D | D |
| Chloramine purity | I | D | N ^b |
| Light intensity | I | I | ... |
| Light wave length | D | D | ... |
| Nitrogen sweep rate | I | D | D |

^a Increases (I); decreases (D); no effect (N); not studied (...).

^b For dark reaction; photolysis accompanied by new reactions (see text).

1–3); they should be a useful guide for more effective synthetic applications of the Hofmann–Loeffler re-

action in acetic acid, because it should be possible to improve product yields by balancing reaction conditions along the lines indicated by Tables I and II. Since most chloramines are difficult to purify, the variables permitting the optimum utilization of unpurified chloramines become of prime importance.

Volatile Impurities. The formation of volatile compounds in our reaction solutions, suggested by the preceding results, was demonstrated as follows. Ultraviolet spectra were periodically recorded of samples of actual reaction mixtures during photolytic decompositions. One of three situations obtained in each case. (1) In excess strong acid the neutral chloramine (Figure 1, curve 1) became protonated (*e.g.*, Figure 1, curve 4) and no new absorption developed. (2) At low acidity, solutions of undistilled I swept slowly with nitrogen developed a new (variable) absorption in the region 312–320 $m\mu$ which grew to a maximum near 60–70% reaction and then disappeared as the active chlorine titer fell to zero (*e.g.*, Figure 2, curves 4–7); in anhydrous acetic acid a less pronounced maximum appeared in the region 320–340 $m\mu$. When distilled I was used, however, λ_{\max} remained constant at 306 $m\mu$, and the absorption of solutions of undistilled I also remained constant at 306 $m\mu$ when they were kept in the dark. (3) Reaction mixtures swept rapidly with nitrogen showed λ_{\max} 274 and 282 (sh) $m\mu$ (Figure 2, curves 8–9) which remained constant during most of the reaction and also appeared in pentane extracts of the reaction mixture and in the exit gas bubblers (acetic acid); at least partly responsible for this absorption was a carbonyl-containing material (1710 cm^{-1} , crude 2,4-DNP m.p. 148–149°, vinyl-H and CHCl by n.m.r.) which may be a precursor of ethylglyoxal, a product isolated as described below.

Thus, the build-up of new compounds absorbing >300 $m\mu$ occurred when the acidity was not high and when the nitrogen sweep was not rapid. The absorbing species which formed in the dark (λ_{\max} 306 $m\mu$) was then proved to be volatile by sweeping it in a nitrogen stream from a relatively weakly acidic solution of undistilled chloramine into an acetic acid trap. The compound still absorbed at 306 $m\mu$, and it was slowly destroyed by ultraviolet irradiation. Dilution of the reaction mixture with water followed by extraction gave a pentane solution of dibutylchloramine and the unknown (λ_{\max} 272 and 307 $m\mu$); the unknown was then distilled to give a pentane solution absorbing only at 307 $m\mu$ (Figure 1, curve 6). An apparent ϵ'_{\max} 160 was determined by iodometric titration, and treatment of the solution with gaseous hydrogen chloride liberated chlorine (λ_{\max} 332 $m\mu$ ⁶). The 307- $m\mu$ absorber was identified as *N,N*-dichloro-*n*-butylamine by comparison with a sample of the product formed from NCS and butylamine ($\lambda_{\max}^{\text{ether}}$ 307 $m\mu$ (ϵ_{\max} 330)) (Figure 1, curve 5). Similar absorption has been observed previously⁷ for the homologs *N,N*-dichloromethylamine and *N,N*-dichloroethylamine ($\lambda_{\max}^{\text{aq}}$ 303 $m\mu$ (ϵ_{\max} 260)).

Finally, we examined the rate of formation in the dark of the dichloramine in acetic acid–1.5 *M* water as a function of the ratio sulfuric acid/monochloramine. In excess acid (ratio 8:1) the dichloramine formed

(6) H. Martin and R. Gareis, *Z. Elektrochem.*, **60**, 959 (1956).

(7) W. S. Metcalf, *J. Chem. Soc.*, 148 (1942).

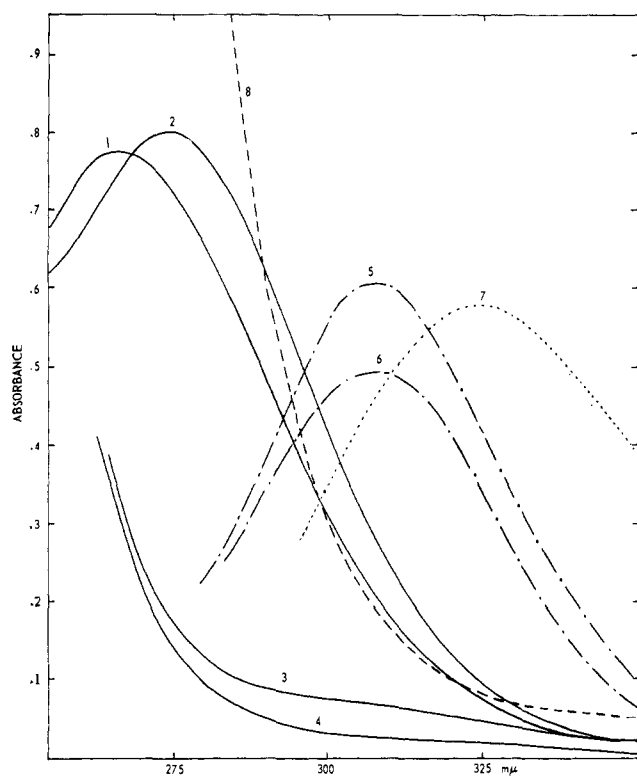


Figure 1. N-Chlorodi-*n*-butylamine: (1) $2.65 \times 10^{-3} M$ in HOAc, cell 1.0 cm.; (2) $1.98 \times 10^{-3} M$ in CCl_4 , cell 1.0 cm.; (3) $0.46 M$ in $1.0 M H_2SO_4-1.5 M H_2O-HOAc$, cell 0.105 cm.; and (4) $0.46 M$ in $1.5 M H_2SO_4-1.5 M HOAc$, cell 0.105 cm. N,N-Dichloro-*n*-butylamine: (5) $1.86 \times 10^{-3} M$ in ether, cell 1.0 cm., from NCS and butylamine; (6) $1.56 \times 10^{-3} M$ in pentane, cell 1.0, isolated from reaction mixture (see text); (7) Cl_2 in HOAc; (8) absorbance of 2-mm. thickness Pyrex glass, vs. air.

very slowly but in lesser amounts of acid more rapidly until 74% of the original monochloramine had been converted into the dichloramine in 49 min. at a monochloramine/acid ratio 1:2. The increase in dichloramine formation and the total photolytic decomposition rate with decreasing acidity is to be stressed. However, solutions of both undistilled and distilled chloramine showed the *same* rate of formation of the dichloramine with acidity over several hours in the dark, although photolytic decompositions of undistilled chloramine occurred far more rapidly than those of the distilled material at a given acidity. Certain of the foregoing results are summarized in the fourth column of Table II.

Other Side Products. Products present at the *conclusion* of the reactions, in addition to NBP and the major side product dibutylamine, were isolated. It was found that both the reaction mixtures and pentane-ether extracts of the diluted mixtures afforded precipitates with ethanolic 2,4-DNP reagent and that the amount obtained was greatest from solutions of low acidity; this result parallels the enhanced production of the dichloramine in solutions of low acidity. Purification of the crude products led in every case to a red material, m.p. 233–235°, whose elemental analysis was correct for the 2,4-dinitrophenylosazone of ethylglyoxal and which gave the intense violet color in cold alcoholic base expected⁸ of 2,4-dinitrophenylosazones. Other

(8) L. N. Owen, *J. Chem. Soc.*, 463 (1943).

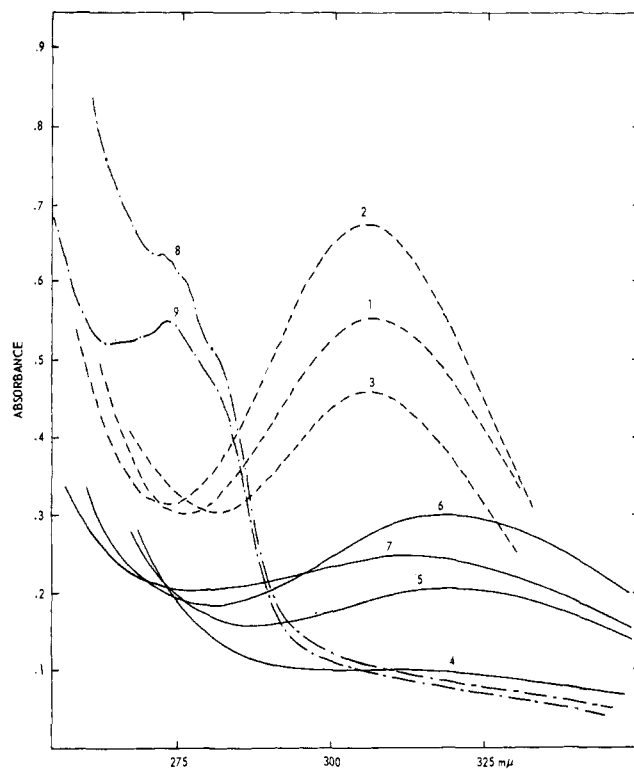


Figure 2. Absorption of acid solutions (Table 1) of $0.46 M$ N-chlorodi-*n*-butylamine in $1.5 M H_2O-HOAc$ during photolysis at various stages of positive chlorine loss (in parentheses); path length 0.105 cm. Entry 22: (1) 32%, (2) 66%, and (3) 73%. Entry 18: (4) 12%, (5) 39%, (6) 65%, and (7) 88%. Entry 5: (8) 27% and (9) 94%.

2,4-DNP derivatives were present in trace amounts in the crude precipitates, but were not identified; the isolated ethylglyoxal accounted for a maximum of only 17% of the starting material not ultimately observed as NBP or dibutylamine (acid/chloramine ratio 2:1).

The carbonyl-containing material detected during photolysis of mixtures swept rapidly with nitrogen was no doubt a precursor of ethylglyoxal, which is presumed to have formed from an α -chloro- or an α,α -dichloroaldehyde imine similar to that obtained by Wright⁹ from the thermal decomposition of N-chlorodi-*n*-butylamine, *i.e.*, $CH_3CH_2CH(Cl)CH=NR$. In the present case R is presumed not to be simply $n-C_4H_9$, since no trace of butylamine, the other hydrolysis product of the imine, could ever be detected by g.l.c. analysis of the products extracted from the basified reaction mixtures.

No trace of amides, such as N,N-di-*n*-butylacetamide obtained from the thermal decomposition of I in acetic acid,⁹ was ever detected, nor was ammonia a reaction product.

It is therefore qualitatively correct to state that increased amounts of carbonyl products produced during the photolytic decompositions, presumably *via* imines, accompanied the more rapid formation of N,N-dichlorobutylamine and the decrease in yield of the desired rearrangement product NBP. However, a quantitative correlation between total unrecovered nitrogen and the observable production of new compounds during the reactions was not apparent.

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

Discussion

The previous discussion³ on the requirement for excess strong acid in the Hofmann–Loeffler reaction was based on the then observed increase in reaction rate with increasing acidity, as well as on the increase in yield of NBP. It was concluded that the "acid catalysis" reflected a decreased rate of chain termination and/or an acceleration of the propagation steps, the former *via* reduced coupling of protonated nitrogen radicals relative to the neutral species. However, the rate–acidity profile must now be acknowledged to be an *inverse* relationship on the basis of the results of Table I, and we believe that the sulfuric acid required in excess of that for protonation of N-chlorodibutylamine need not *directly* alter the rate of any aspect of the rearrangement process. Thus, the excess acid indirectly influences the initiation and termination steps of the rearrangement by controlling metathetical side reactions whose products do become directly involved in the rearrangement. We present our reasons for this conclusion in the following sections.

Initiation. The protonated chloramine Bu_2NHCl^+ is not an initiator³ because its absorption in the Pyrex region (above 280 $m\mu$; Figure 1, curve 8) is minimal (Figure 1, curve 4), especially relative to the neutral species Bu_2NCl (ϵ 320; Figure 1, curve 1). However, neither is the neutral chloramine a probable initiator, as previously supposed,³ although our rate–acidity profile supports this view better than the earlier one. Thus, protonation of the monochloramine in all our reactions was >99%, which was evident both from $\text{p}K_a^{\text{H}_2\text{O}} \approx 0.4$ for Bu_2NHCl^+ (see Experimental section) and the ultraviolet spectra of the reaction mixtures, which would have disclosed >1% of the weakly absorbing unprotonated base ($\lambda_{\text{max}}^{\text{HOAc}}$ 267 $m\mu$ (ϵ_{max} 320)). To be an effective initiator, the traces of neutral chloramine present in the solutions studied would have to absorb light and dissociate very efficiently; however, irradiation of this compound in both acetic acid³ and in carbon tetrachloride¹⁰ does not appear to have given reactive radicals. Furthermore, no reaction took place in the latter solvent even in the presence of excess butadiene,^{4a} despite a recent claim that *neutral* radicals $\text{R}_2\text{N}\cdot$ generated from chloramines in acidic aqueous media by metal redox couples do add to the diene.¹¹ The apparent photolytic stability of the neutral chloramine, coupled with its low concentration and low extinction coefficient, therefore argues against its initiating a free-radical chain reaction by photostimulation.

On the other hand, we believe that initiation of the rearrangement of distilled chloramine depends upon the formation of dichlorobutylamine and its photolysis into initiating radicals, and that solutions of undistilled chloramine contain additional initiators. Thus, in solutions of distilled chloramine: (a) both the over-all rate of reaction and the rate of formation of the very weakly basic (unprotonated) dichlorobutylamine decreased as the acidity was increased and (b) the photolabile dichloramine has a constant absorption maxi-

mum and broad tailing within the range of the radiation actually incident on the reaction mixture. When the dichloramine does not accumulate due to its photolysis immediately on formation, differences in the over-all rates should depend mainly on the rate of initiation, and the over-all rate should decrease with increasing acidity, as observed. Although the rates of active chlorine loss in reactions of undistilled chloramine followed the same pattern as those of the distilled chloramine, they were faster. It is probable that the yellow, undistilled chloramine contained traces of a very photolabile material which, by photolyzing into initiating radicals or by undergoing initiator-forming reactions, enhanced the over-all reaction rates over those which depend solely upon prior formation and less efficient photolysis of the dichloramine.

Chain Termination and the Yield of NBP. Termination of the Hofmann–Loeffler rearrangement is best considered in terms of the impact of certain variables upon the yield of NBP. The relative chloramine purity certainly has an important influence on the rearrangement efficiency. Thus, there was a marked drop in yield of NBP with decreasing chloramine purity at constant acidities, which became more pronounced at each lower acidity level; the formation of carbonyl compounds was slower at a given acidity in solutions of distilled chloramine; and the absorption of acid solutions of undistilled chloramine was variable during photolysis (312–320 $m\mu$), although stable in the dark (306 $m\mu$), whereas the absorption of acid solutions of distilled chloramine both in the dark and during photolysis remained constant (306 $m\mu$). It therefore appears that a much greater variety of side reactions must take place during photolysis of solutions of undistilled than of distilled chloramine, and that these must somehow inhibit the rearrangement of I. The side reactions involving N-chloro groups are presumed to be of a radical type, since no loss of positive chlorine occurred on interruption of irradiation during a reaction.

Another noteworthy result was the large increase in the yields of NBP which resulted from the more rapid decompositions using more intense or lower wave length light. It seems reasonable to conclude that N-chlorinated side products were photolyzed on formation in these cases and therefore acted primarily as initiators of the desired chain rearrangement instead of accumulating to become reaction substrates. Rapid sweeping of reaction mixtures with nitrogen served the same purpose by removing the volatile impurities which otherwise would have interfered with the desired reaction. The sigmoid titration curves peculiar only to those reactions involving the observable production of side products support this view.

Although the actual chain terminators are not identified by our results, the implied cause and effect relationship of decreasing NBP with increasing dichloramine formation suggests the involvement of the dichloramine and related materials in chain termination of the desired rearrangement. It therefore appears that excess sulfuric acid is beneficial to the Hofmann–Loeffler reaction because the acid inhibits the too rapid formation of the dichloramine and its possible precursors, which probably act as chain terminators but nevertheless are desirable in low concentration as chain initiators.

(10) S. Wawzonek and J. D. Nordstrom, *J. Org. Chem.*, **27**, 3726 (1962).

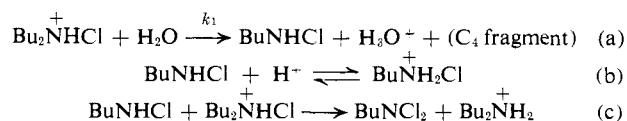
(11) F. Minisci and R. Galli, *Tetrahedron Letters*, 167 (1964); the presence of protonated radicals R_2NH^+ cannot be ruled out however.

An alternative effect of acid in chain termination has been suggested.³ This is the possibility of reduced nitrogen radical coupling due to protonation and electrostatic repulsion, which requires that the basicity of the radical $\text{Bu}_2\text{N}\cdot$ be less than that of the chloramine Bu_2NCl (since the latter is protonated even in the most weakly acidic solutions studied), and that coupling of two charged radicals be disfavored relative to that of the neutral species. However, recent work has shown¹² that the ease of recombination of certain nitrogenous radicals may not greatly depend on the presence or absence of a positive charge situated at or near the radical site. Furthermore, the basicity of $\text{Bu}_2\text{N}\cdot$ may well be greater than that of the parent amine Bu_2NH , and hence considerably greater than that of the chloramine, since Porter¹³ has found the basicity of the anilino radical $\text{C}_6\text{H}_5\text{NH}\cdot$ to exceed that of aniline by greater than 100-fold in aqueous solution. Williams' conclusion¹⁴ that protonation of the neutral hydroxyl, amino, and halogen radicals in aqueous solution is thermodynamically less favorable than protonation of the parent molecules HX was apparently extended from a calculation relating only to the behavior of $\cdot\text{OH}$ vs. $\cdot\text{OH}_2^+$ and hence of $\cdot\text{OH}$ vs. H_2O ; any consideration of the Hofmann–Loeffler reaction in similar terms¹⁴ does not now seem justified in view of both the different solvent involved and Porter's experiment.

A quantitative relationship between the yield of NBP and the extent of dichloramine formation is lacking, despite the qualitative dependence of the two already demonstrated. Since the dichloramine was formed and destroyed more or less continuously, the cumulative yield of this compound cannot be determined for comparison with the yield of undetected products (moles of $\text{I} - (\text{DBA} + \text{NBP})$). Since the maximum amount of the dichloramine present at any time in the 1.5 *M* acid solutions never exceeded 2% of the original monochloramine, although the yield of NBP in 1.5 *M* acid was only 55% that in 4 *M* acid, it appears possible that all the side reactions which detract from the yield of NBP may not be attributable to the dichloramine. An accommodation of this possibility is suggested by a probable mode of dichloramine formation which we now consider.

Dichloramine Formation. The concentration of the dichloramine in the dark at time *t* was determined from $\epsilon^{307} = 320$, and the absorbance of solutions was observed periodically at two acid concentrations at 23°. The rate of consumption of the monochloramine was then computed at each acidity based on the observed production of the dichloramine. The values thus determined obeyed first-order kinetics precisely. The mechanism shown below requires first-order disappearance of dibutylchloramine according to the rate law $-d[\text{Bu}_2\text{N}^+\text{HCl}]/dt = k'[\text{Bu}_2\text{N}^+\text{HCl}][\text{H}_2\text{O}]$, if $d[\text{BuNHCl}]/dt = 0$; the rate constant *k'* equals 1 to $2k_1$, depending on the extent of protonation in step b. However, the apparent rate constants in 0.5 and 1.0 *M* acid (50 and 5% conversion of Bu_2NCl to BuNCl_2)

differed by nearly 100-fold ($4.25 \times 10^{-3} \text{ min.}^{-1}$ vs. $7.8 \times 10^{-5} \text{ min.}^{-1}$). But only a fraction of reaction a was detected kinetically by following reaction c, due to protonation of the intermediate BuNHCl ; thus, the large differences observed in the apparent first-order rate constants as the acidity was varied is reasonable.



The indicated steps for the formation of the dichloramine are therefore consistent with the data; the first may be a Hofmann elimination with loss of a butyl group between the protonated chloramine and water, whose estimated pK_a in these systems is about 10^3 less than that of the chloramine.¹⁵ The monobutylmonochloramine thus formed, being less basic than its dialkyl precursor, would remain somewhat less protonated than dibutylchloramine except at high acidities; the extent of its further reaction c would depend on the equilibrium b. Thus, dichloramine formation may well be inhibited by excess strong acid in two stages: at low acidities by protonation of intermediates and at high acidities by protonation of the Hofmann base which participates in step a of the process. The loss of $\text{Bu}_2\text{N}^+\text{HCl}$ by any but the desired free-radical process may therefore be completely repressed only at very high acidities.

Such a scheme as presented above could account for the very large drop in yield of NBP at acid/chloramine ratios of 3 or less (Table I). At these acidities an intermediate such as BuNHCl may, through deprotonation and increased rate of formation, become available in quantity for participation in radical reactions, although the dichloramine is still not formed in stoichiometric amounts.

Experimental

A typical procedure is outlined below. The NCS received from Matheson Coleman and Bell was colored cream-white; recrystallized material was pure white, m.p. 144–147°. Di-*n*-butylamine was used as received (Eastman White Label), as was glacial acetic acid and reagent grade sulfuric acid. Ultraviolet spectra were obtained on a Beckmann Model DK2 recording spectrophotometer; the quartz cells were either standard 1 cm. or demountable types (0.1 and 0.03 cm.), and reference solutions of sulfuric acid–acetic acid–water were employed. The reactions were carried out in a 300-ml. flask fitted with a mechanical stirrer, thermometer, gas inlet tube (coarse fritted filter stick), a rubber septum for withdrawing samples for iodometric analysis, and a gas outlet tube attached to the top of a Graham reflux condenser.

Rearrangement of *N*-Chlorodi-*n*-butylamine (Table I, Entry 6). The chloramine was prepared³ at room

(15) Our determination as well as the earlier one¹⁶ shows the pK_a of dialkylchloramines referred to water to be 0.5–1.0; the pK_a of urea (+0.5) is similar and exceeds that of water by 2.8 units: H. Lemaire and H. J. Lucas, *ibid.*, 73, 5198 (1951). Since the pK_a of urea also exceeds that of water in sulfuric acid–anhydrous acetic acid by about the same amount (3.1 units) (B. Trémillon, *Bull. soc. chim. France*, 1940 (1960)) the difference $pK_a(\text{R}_2\text{NCl}) - pK_a(\text{H}_2\text{O})$ surely lies in or near the range 2.8–3.1 units in the medium 1.5 *M* water–acetic acid.

(16) I. Weil and J. C. Morris, *J. Am. Chem. Soc.*, 70, 3123 (1949).

(12) G. S. Hammond and R. C. Neuman, *J. Am. Chem. Soc.*, 85, 1501 (1963).

(13) E. J. Land and G. Porter, *J. Chem. Soc.*, 3540 (1961). The effect on the basicity of $-\text{NH}$ of *N*-aryl vs. *N*-alkyl groups, of course, need not be necessarily the same or even in the same direction, but data to probe this point are not available.

(14) T. F. Williams, *J. Am. Chem. Soc.*, 84, 2895 (1962).

temperature from a mixture of 14.2 g. (0.107 mole) of NCS and 150 ml. of ether by the addition of a solution of 12.9 g. (0.10 mole) of di-*n*-butylamine in 50 ml. of ether. The mixture was stirred magnetically for 1 hr. and was then extracted with three 30-ml. portions of water and two 30-ml. portions of 2.5 *N* sulfuric acid (to remove unreacted amine but not the weakly basic chloramine). After brief drying over sodium sulfate, the solution was evaporated to a residual yellow oil (15 g., 0.092 mole). When the residue was distilled, b.p. 59–60° (5 mm.), n_D^{23} 1.5357,¹⁰ no decomposition occurred at pot temperatures below 100°.

The acid solution (16.7 ml. of 96% sulfuric acid, 4.3 ml. of water, acetic acid to total 192 ml. of acid solution) was mixed below 25° and was swept with nitrogen at room temperature for 20 min. to remove oxygen from the system. The chloramine was then added through the septum to the cooled acid mixture (16°) and the resulting solution (20°) was further swept with nitrogen for 10 min. The rate of stirring and nitrogen sweep were then reduced, irradiation was begun (preheated lamp; see Table I, footnote b), and the course of the reaction was followed by titrating 0.5-ml. aliquots added to 20% potassium iodide–40% acetic acid solution with 0.05 *N* sodium thiosulfate solution (ml. $\times 10^{-2}$ = total equivalents of positive chlorine in the reaction mixture). Ultraviolet spectra of samples of the reaction mixture were recorded at 6, 30, 50, 70, and 82% loss of positive chlorine; the broad build-up of absorption near 315 $m\mu$ became noticeable at 30% reaction and was most intense at 70% reaction ($A = 0.19, 0.105$ -cm. cell).

At the end of the reaction, the mixture was poured into 200 g. of ice and 500 ml. of water was then added. Extraction with pentane or pentane–ether yielded solutions which contained the carbonyl components detected by ultraviolet and 2,4-DNP reagent as already described. Basification was accomplished with 245 ml. of 12 *N* sodium hydroxide solution; the addition produced a temperature rise to 51° which was maintained for 1 hr. with stirring to ensure complete cyclization of the δ -chloramine. The cooled mixture was then extracted with pentane and the bases thus isolated were analyzed for the relative amounts of NBP and di-*n*-butylamine.

Analyses were performed in several instances both by g.l.c. and by picrate³ formation; the results agreed each time within 2%. G.l.c. analyses were performed using a 15 ft. \times 1/4 in. column containing Carbowax 6000 on Fluoropak operated at 96° and 28 ml. of helium/min. Under these conditions (retention times NBP 34 min. and DBA 43 min.) the separation of the two bases was nearly but not completely effected; however, good estimates of the individual peaks were possible using calibration curves. The per cent composition was then computed directly from relative peak areas.

Basicity of N-Chlorodi-n-butylamine. Although the pK_a of *N*-chlorodimethylamine (0.47) and of *N*-chlorodiethylamine (1.02) was known,¹⁶ it seemed desirable to determine the pK_a of the dibutyl homolog used here in order to be certain it did not possess an unusual basicity. An approximate value $pK_a = 0.42$ was determined from a plot $-\log [BH^+]/[B]$ vs. H_0' , in agreement with the previous chloramine data; the intercept when $[BH^+]/[B] = 1$ is pK_a referred to water.¹⁷ Values for H_0 in 1.5 *M* water–acetic acid are labeled here H_0' and were estimated as follows. The effect of 0–5.6 *M* water on H_0 values for 1 *m* sulfuric acid in anhydrous acetic acid was reported by Noyce and Castelfranco¹⁸; the dependence was approximately linear for the first 10% by volume of water added. We have therefore assumed that the data of Gold and Hawes⁵ for the effect of 0.055–0.55 *M* water on H_0 in a 0.325 *M* solution of sulfuric acid–acetic acid may be linearly extrapolated to 1.5 *M* water to afford the approximation $H_0' = H_0 + 0.67$. We have used this relationship throughout the acidity range required to determine pK_a (0.0025–0.25 *M*) (Table III). Values of H_0 for sulfuric acid–acetic acid containing 0.05–0.1 *M* water were readily available.¹⁹

Table III. Determination of pK_a of *N*-Chlorodi-*n*-butylamine

| H_2SO_4 , <i>M</i> | H_0' ^a | $[B]/$ $[BH^+]$ ^b | $\log[B]/$ $[BH^+]$ | $10^3 \times$ R_2NCl , <i>M</i> |
|-------------------------|---------------------|---------------------------------|------------------------|---|
| 0.0025 | | 3.36 | | 5.65 |
| 0.005 | 0.55 | 1.43 | 0.156 | 5.65 |
| 0.01 | 0.20 | 0.553 | −0.257 | 5.65 |
| 0.015 | 0.00 | 0.374 | −0.427 | 6.78 |
| 0.02 | −0.10 | 0.253 | −0.597 | 7.91 |
| 0.025 | −0.18 | 0.168 | −0.775 | 13.2 |
| 0.05 | −0.60 | 0.0618 | −1.209 | 13.2 |
| 0.10 | −1.00 | 0.0246 | −1.609 | 13.2 |
| 0.25 | −1.47 | 0.0069 | −2.163 | 13.2 |
| 0.50 | −2.22 | 0 | | 13.2 |

^a Defined $H_0' = H_0 + 0.67$ (see text); H_0 values from ref. 18.

^b Calculated from $\epsilon - \epsilon_{BH^+}/\epsilon_B - \epsilon$ (ref. 16).

The error possible in the present determination due to our estimate of H_0' could be significant, perhaps up to 0.5 pK_a unit. On the basis that the pK_a is 0.4, an indicator quantity of the chloramine in 0.5 *M* sulfuric acid–1.5 *M* water in acetic acid would be 99.7% protonated. It is evident, therefore, that protonation was very extensive in the more acidic solutions (containing larger amounts of the chloramine) actually used for reaction, and that use of anhydrous reaction media raised the effective pK_a of the chloramine by roughly 0.7 unit.

(17) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(18) D. S. Noyce and P. Castelfranco, *J. Am. Chem. Soc.*, **73**, 4482 (1951).

(19) N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940).