1.4316 (lit.[51] bp 51–53° (11 mm)), 2-ethoxyhexaldehyde 2,4-dinitrophenylhydrazone mp 106–107.5°.

Anal. Calcd for $C_{14}H_{20}N_4O_5$: C, 51.84; H, 6.22; N, 17.28. Found: C, 52.09; H, 6.13; N, 17.51.

From diethylchloramine and 3-hexyne was obtained **2-chloro-3-hexanone**, bp 88° (70 mm), $n^{25}D$ 1.4310, 2,4-dinitrophenylosazone mp 288° (lit.[52] bp 49° (15 mm), dinitrophenylosazone mp 259–260°); **2-chloro-3-hexyne**, which was identified solely from its infrared and nmr spectra, had bp ~74° (70 mm), $n^{25}D$ 1.4504.

Anal. Calcd for $C_9H_9N_4O_4$: C, 45.57; H, 3.82; N, 23.63. Found: C, 45.65; H, 4.02; H, 23.61.

Registry No.—**1**, 13422-82-7; **1** picrate, 13422-83-8; **2**, 13422-84-9; **3**, 13422-85-0; **4**, 13440-87-4; **4** picrate, 13422-86-1; **5**, 761-22-8; **5** hydrochloride, 869-26-1; **6**, 761-38-6; **7**, 13422-89-4; **8**, 13444-57-0; **9**, 13422-90-7; **9** picrate, 13422-91-8; **10**, 761-21-7; **11**, 761-36-4; **11** picrate, 1041-72-1; **12**, 5929-85-1; **12** picrate, 5929-91-9; **13**, 13429-70-4; **13** picrate, 13429-71-5; **14**, 13429-72-6; **14** dipicrate, 13639-77-5; **15**, 13429-73-7; **15** dipicrate, 13429-74-8; **15** dihydrochloride, 13429-66-8; **16**, 13429-76-0; **16** dipicrate, 13429-77-1; **17**, 13429-78-2; **18**, 13429-79-3; **19** dipicrate, 13639-78-6; **20**, 13429-75-9; **21**, 13422-66-7; **22**, 760-98-5; **23a**, 13429-85-1; **23b**, 13429-86-2; **24**, 13422-59-8; **25**, 13429-81-7; **26**, 13429-82-8; **27**, 13440-83-0; **28**, 13422-60-1; **30**, 13422-61-2; **31**, 760-86-1; **32**, 13422-63-4; **33**, 13422-67-8; **34**, 13422-65-6; 2-ethoxy-3,3-dimethylbutyraldehyde 2,4-dinitrophenylhydrazone, 13440-84-1; 3-diethylaminocyclooctene, 13422-66-7; 2-ethoxyhexaldehyde 2,4-dinitrophenylhydrazone, 13422-68-9; 2-chloro-3-hexyne, 763-91-7; 1-chloro-2,2-diphenylethylene, 4541-89-3.

Acknowledgment.—The author thanks Dr. R. L. Hinman[1a] for many helpful discussions in the early phases of this study and Miss N. L. Marcus for carrying out the experimental work involving some of the acetylenic hydrocarbons.

(51) L. Herzfeld, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, **36**, 1842 (1953).

(52) S. H. Zaheer, B. Singh, B. Bhushan, I. K. Kacker, K. Ramachandran, and N. S. Rao, *J. Chem. Soc.*, 1706 (1955).

The Chemistry of Nitrogen Radicals. VI. The Free-Radical Addition of Dialkyl-N-chloramines to Substituted Olefins

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Received April 28, 1967

The facile synthesis of a variety of substituted β-chloramines has been accomplished in 46–92% yield by the free-radical addition of N-chlorodialkylamines to vinyl and allyl compounds in sulfuric acid–acetic acid. These one-step reactions are sufficiently general to constitute the method of choice for the preparation of the novel adducts described. The results are also of mechanistic significance, since they demonstrate further[1] that addition to carbon–carbon multiple bonds is a reaction characteristic of aminium radicals generated from chloramines under the present conditions. The results also provide information pertaining to the steric requirements of the addition reaction with vinyl chlorides and to previously recognized[1] competitive processes involving either aminium radical rearrangement or electrophilic chlorination by the protonated chloramine.

In the preceding article[1] we described the addition of dialkyl-N-chloramines across the double and triple bonds of unsaturated, aliphatic hydrocarbons in the solvent 4 *M* sulfuric acid–acetic acid. These additions proceeded *via* free-radical chain reactions that involved protonated amino radicals $R_2\dot{N}H^+$ as the chain-carrying species. For example, simple 1,3-dienes gave the chloramination product I in yields up to 68% (eq 1).

$$R_1R_2NCl + R_3CH{=}CHCH{=}CHR_3 \xrightarrow[HOAc]{H_2SO_4} \underset{I}{R_1R_2NCHCH{=}CHCHCl} \quad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad R_3 \qquad\qquad R_3$$

However, simple olefins gave only 0–42% yields of β-chloramines as the result of a competing ionic reaction,[2] in which electrophilic chlorination of the olefin was effected by the protonated chloramine.

We thought that an olefinic double bond bearing an electronegative group X, such as chloro, might avoid this ionic reaction, since the developing carbonium ion intermediate III (eq 2) would be destabilized[3] by such a

$$[Cl^+] + \underset{II}{CH_2{=}C<^{R}_{X}} \longrightarrow \underset{III}{Cl{-}CH_2{-}\overset{R}{\overset{|}{C}}^+{-}X} \quad (2)$$

group. The stabilization of the free radical IV, which is a necessary intermediate in the desired chloramination reaction (eq 3), however, was not expected to decrease owing to the presence of such a substituent.[4] Furthermore, if substituted olefins II could be utilized generally, a route to many new β-substituted aliphatic β-chloramines would be opened. In the present article we describe[5] the successful generalization of

$$R_2\dot{N}H^+ + CH_2{=}C<^{R}_{X} \longrightarrow \underset{IV}{R_2\overset{+}{N}HCH_2\overset{R}{\overset{|}{C}}\cdot{-}X} \xrightarrow{R_2\overset{+}{N}HCl} \underset{V}{R_2\overset{+}{N}HCH_2\overset{R}{\overset{|}{C}}Cl{-}X} \quad (3)$$

(1) R. S. Neale, *J. Org. Chem.*, **32**, 3263 (1967).

(2) R. S. Neale, *Tetrahedron Letters*, 483 (1966).

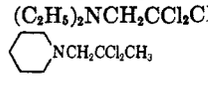
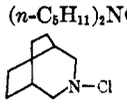
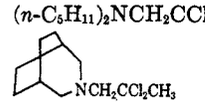
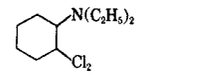
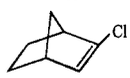
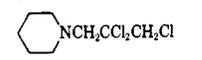
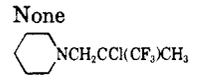
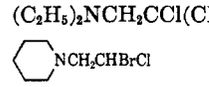
(3) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 50, 120–121.

(5) Preliminary mention of this work was made in paper III of this series.[2]

TABLE I

LIGHT-CATALYZED ADDITION OF CHLORAMINES TO SIMPLE VINYL COMPOUNDS IN 4 *M* SULFURIC ACID–ACETIC ACID AT 30°[a]

Chloramine	Olefin	Time, min	Adduct	No.	% yield
$(C_2H_5)_2NCl$	$CH_2=CHCl$	48	$(C_2H_5)_2NCH_2CHCl_2$	1	82
$(C_2H_5)_2NCl$	$CH_2=C(Cl)CH_3$	<15	$(C_2H_5)_2NCH_2CCl_2CH_3$	2	84
	$CH_2=C(Cl)CH_3$	12		3	92
$(n\text{-}C_5H_{11})_2NCl$	$CH_2=C(Cl)CH_3$	<12	$(n\text{-}C_5H_{11})_2NCH_2CCl_2CH_3$	4	28[b]
	$CH_2=C(Cl)CH_3$	5		5	76
$(C_2H_5)_2NCl$	$CH_2=C(Cl)C(CH_3)_3$	19	$(C_2H_5)_2NCH_2CCl_2C(CH_3)_3$	6	80
$(C_2H_5)_2NCl$		12		7	60
$(C_2H_5)_2NCl$		10	None		
$(C_2H_5)_2NCl$	$CHCl=CHCH_3$	105	$(C_2H_5)_2NCH(CH_3)CHCl_2$	8	54
	$CH_2=CClCH_2Cl$	90		9	85
$(C_2H_5)_2NCl$	$CH_2=CHF$	60	$(C_2H_5)_2NCH_2CHClF$	10	80
$(C_2H_5)_2NCl$	$CH_2=CFCH_3$	5	None		
	$CH_2=C(CF_3)CH_3$	240		11	88
$(C_2H_5)_2NCl$	$CH_2=C(CF_3)CH_3$	120[c]	$(C_2H_5)_2NCH_2CCl(CF)_3CH_3$	12	85[c]
	$CH_2=CHBr$	270		13	77
$(C_2H_5)_2NCl$	$CH_2=CBrCH_3$	20	$(C_2H_5)_2NCH_2CBrClCH_3$	14	46
$(C_2H_5)_2NCl$	$CH_2=CHSi(CH_3)_3$	20	$(C_2H_5)_2NCH_2CHClSi(CH_3)_3$	15	65

[a] All reactions were run with 200 ml of solution 0.5–0.7 *M* in both the chloramine and the total olefin added. [b] Also obtained was 43% of N-pentyl-2-methylpyrrolidine. [c] The reaction was terminated after ~30% decomposition of the chloramine.

the chloramination reaction along these lines, and we also present data dealing with the effect on the process of dialkylchloramine structure and the nature of the acid solvent.

Results

Vinyl Compounds (Table I).—The reactions realized between simple dialkylchloramines and substituted olefins $R^1CH=CXR^2$ can be conveniently grouped into those involving either vinyl or allyl (X = CH_2Y) substrates. Most of the reactions were carried out in 4 *M* sulfuric acid–acetic acid under the conditions employed previously[1] with unsubstituted hydrocarbons, although some reactions in other acidic media are described in a following section. Vinyl chlorides were chosen as substrates in the initial experiments; the results demonstrated convincingly that the use of electronegatively substituted olefins does lead to enhanced efficiencies of free-radical chloramination. For example, in each of three sets of reactions (eq 4), a chloro olefin gave far

$$Et_2NCl + R_1CH=C\begin{matrix}R_2\\X\end{matrix} \xrightarrow[\substack{HOAc,\\ h\nu}]{H_2SO_4} Et_2NCH\overset{R_1}{\underset{X}{C}}\overset{R_2}{Cl} \qquad (4)$$

Olefin	X	R_1	R_2	% yield
Propylene	CH_3	H	H	42
Vinyl chloride	Cl	H	H	82
Isobutylene	CH_3	H	CH_3	0
2-Chloropropene	Cl	H	CH_3	84
cis-2-Butene	CH_3	CH_3	H	0
1-Chloropropene	Cl	CH_3	H	54

more adduct than the corresponding alkyl olefin, *e.g.*, vinyl chloride gave twice as much adduct as propylene, and both 2- and 1-chloropropene gave adducts in contrast to isobutylene and *cis*-2-butene, which gave[1] none. Good to excellent yields of adducts **6**, **7**, and **9** (Table I) were also obtained from 2-chloro-3,3-dimethyl-1-butene, 1-chlorocyclohexene, and 2,3-dichloro-1-propene.

The chloramination of vinyl chlorides and analogous chloraminations of allyl and other vinyl compounds, reported in Tables I–IV, are undoubtedly free-radical chain processes with the propagation steps shown in eq 5 and 6. Such chain reactions are directly related to those[1] involving unsubstituted olefins and acetylenic hydrocarbons, although initiation by ultraviolet light was now required in nearly every example. Furthermore, the reactions were fast, often requiring only 10–20 min for completion at 30°, and they did not occur in the presence of air. The chain-carrying species again[1] must have been the aminium radical, which was always found on the terminal carbon atom of the adducts.

A high yield of adduct **6** was realized from an olefin bearing both the bulky *t*-butyl group and a chlorine atom on the same carbon (X = Cl, R = $t\text{-}C_4H_9$ in eq 5 and 6); this suggests that the second step in the chain

$$>\overset{+}{N}H + CH_2=\overset{R}{\underset{R}{C}}-X \longrightarrow >\overset{+}{N}HCH_2\overset{R}{\underset{X}{C}}\cdot \qquad (5)$$

$$>\overset{+}{N}HCH_2\overset{R}{\underset{X}{C}}\cdot + >\overset{+}{N}HCl \longrightarrow >\overset{+}{N}HCH_2\overset{R}{\underset{X}{C}}Cl + >\overset{+}{N}H \qquad (6)$$

reaction (eq 6) is not unduly affected by steric crowding at the chlorinated carbon radical. Furthermore, it appears that only very severe steric shielding of the

aminium radical (eq 5) or the $>N^+HCl$ center (eq 6) has a detrimental influence on the chloramination process. Thus, 78% of the adduct **28** was obtained from N-chloro-*t*-butylethylamine and 2-chloropropene, although the yield of adduct **29** finally fell off sharply to 35% in the case of N-chloro-2,2,6,6-tetramethylpiperidine, a model for N-chlorodi-*t*-butylamine. It is interesting that the chemical shift of the $>NCH_2CCl_2$ hydrogens in the most sterically crowded adduct (**29**) occurred at unusually low field, τ 6.40, in contrast to the absorption of the nonmethylated piperidine adduct **3** at τ 7.12 and of related adducts at τ 6.8–7.0.

The aliphatic β,β-dichloramines obtained by the chloramination of vinyl chlorides are examples of a new type of substituted, tertiary amine. Their structures were readily apparent from elemental analyses, infrared and nmr spectra, and stability. Thus, the isomeric α,β-dichloramine structures could be ruled out on the basis of their nmr spectra, in which the NCH_2 hydrogen resonances in adducts **1**, **3**, **6**, and **9** occurred at slightly lower field than in the β-monochloramines[1,6,7] (and in the same range as in the 2-butenylamines[1]) but at higher field than that at which the $-CH_2Cl$ hydrogens[1,6,7] of the α,β-dichloro isomers would be expected to absorb. Furthermore, the β,β-dichloramines are characterized by an enhanced thermal stability relative to β-monochloramines, a failure to yield a precipitate with slightly acidified alcoholic silver nitrate solution, and inertness to attack by organic bases; α-chloramines, in contrast, have been shown to react readily with secondary amines[8] and with silver perchlorate in acetonitrile.[9]

Vinyl compounds other than the chlorides that gave adducts are shown in Table I; all the resulting compounds R_2NCH_2CClXR are again the first reported members of their respective classes. Although vinyl fluoride gave 80% of the expected adduct **10**, 2-fluoropropene unexpectedly failed to give any adduct, although it caused the rapid decomposition of diethylchloramine.[10] Both vinyl bromide and 2-trifluoromethylpropene gave good yields of adducts, but these reactions were considerably slower than expected, owing probably to inefficient introduction of the gases into the acid mixtures. The structure of silyl adduct **15** was assigned on the basis of its nmr spectrum, which contained a lowest field peak at τ 6.72 due to a *single* hydrogen. The alternative structure to **15** would have contained the grouping $\equiv SiCH(NR_2)$-CH_2Cl, but the resonance of this tertiary hydrogen should certainly be shifted *up*field by the silyl group from its normal position of τ >7.0.

Of particular interest was the nmr spectrum of N,N-diethyl-2-chloro-2-fluoroethylamine (**10**). The rather complex spectrum of **10** (Figure 1) is best described[11] as that of a four-spin ABMX system plus normal N-

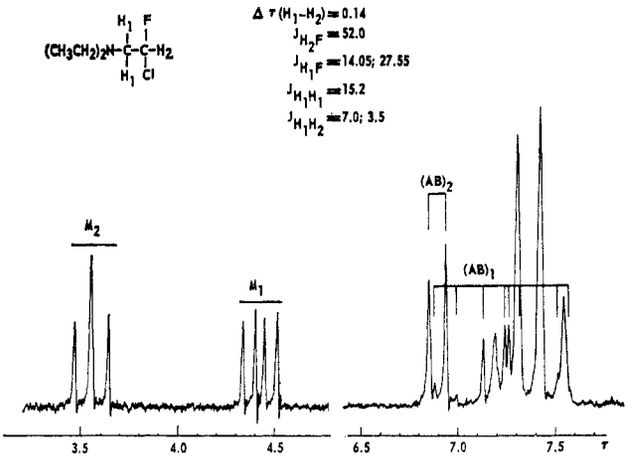


Figure 1.—The nmr spectrum of diethyl-2-chloro-2-fluoroethylamine in CCl_4.

ethyl group absorption in which the ABM part refers to the three hydrogens $>NCH_2CHClF$ and the X part to ^{19}F. There are two different ABM subspectra corresponding to ^{19}F spin states of $+1/2$ and $-1/2$. One of the ABM subspectra [$(ABM)_1$ in Figure 1] is normal in appearance, but the other [$(ABM)_2$] is "deceptively simple,"[12] since it accidentally resembles an A_2M system (triplet and doublet) even though the two AM coupling constants are quite different (3.5 and 7.0 cps). All the lines of the two ABM subspectra were located, using double resonance techniques as necessary, and the coupling constants (see Figure 1) were then derived from the energy level equations in a straightforward manner. The methylene hydrogen (H_1) shifts were found to differ by 8.5 cps, that with the larger H_1H_2 coupling appearing at lower field. The ^{19}F spectrum contained the expected eight lines; the chemical shift was 26.4 ppm downfield from an external perfluorobenzene reference.

Certain vinyl compounds failed to yield adducts, either causing the spontaneous decomposition of the chloramine or remaining inert to any reaction whatsoever at 25–30° despite continued ultraviolet irradiation. The former type of olefin was represented by 1,1-diphenylethylene,[1] methyl vinyl ether, vinyl acetate, 2-chloronorbornene, and α-chlorostyrene; the last named olefin gave 37% of α-chloro- and 25% of α,α-dichloroacetophenone on reaction with diethyl chloramine. Unreactive olefins included acrylonitrile, acrylamide, α-chloroacrylonitrile, α-methacrylonitrile, *cis*- and *trans*-1,2-dichloroethylenes, and perfluoro-2-butene.

One further experiment involving a vinyl compound should be specially noted. Since it had recently been proposed and apparently substantiated from competition reactions that a vinylic chlorine atom deactivates an olefin toward radical addition of a dialkylchloramine in a sulfuric acid–iron(II) salt system,[13] we carried out an analogous competition to test the applicability of this conclusion to our system. When liquid 2-chloropropene was introduced into an irradiated acid solution of diethylchloramine while a fivefold excess of gaseous propylene was simultaneously passed through the mixture, 51% of the chloropropene adduct **2** was obtained (83% based on chloropropene) accom-

(6) P. L. Levins and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **87**, 826 (1965).

(7) N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **30**, 821 (1965).

(8) H. Böhme, *Chem. Ber.*, **92**, 1608 (1959).

(9) H. Böhme, E. Mundlos, and O. Herboth, *ibid.*, **90**, 2003 (1957).

(10) This result could derive from the greatly heightened reactivity of vinyl fluorides *vs.* vinyl chlorides toward formation of a halocarbonium ion on protonation or chlorination of the olefin. The reactivity difference toward addition of trifluoroacetic acid, for example, is about 200-fold (value reported by P. E. Peterson and R. J. Bopp, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S-3).

(11) The authors are indebted to Dr. E. B. Whipple of this laboratory for the analysis of the nmr spectrum of **10**.

(12) R. S. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(13) F. Minisci, R. Galli, and M. Cecere, *Tetrahedron Letters*, 3163 (1966).

TABLE II

LIGHT-CATALYZED ADDITION OF CHLORAMINES TO SIMPLE ALLYL COMPOUNDS IN 4 *M* SULFURIC ACID–ACETIC ACID AT 30°[a]

Chloramine	Olefin	Time, min	Adduct	No.	% yield
$(C_2H_5)_2NCl$	CH_2=$CHCH_2Cl$	35	$(C_2H_5)_2NCH_2CHClCH_2Cl$	16[b]	83
$(C_2H_5)_2NCl$	CH_2=$CHCH_2OH$	17	$(C_2H_5)_2NCH_2CHClCH_2OAc$	17	48
$(C_2H_5)_2NCl$	CH_2=$CHCH_2OAc$	12	$(C_2H_5)_2NCH_2CHClCH_2OAc$	17	60
$(C_2H_5)_2NCl$	CH_2=$CHCH_2O$–C$_6$H$_5$	15	$(C_2H_5)_2NCH_2CHClCH_2O$–C$_6$H$_5$	18	6
			$(C_2H_5)_2NCH_2CHClCH_2O$–C$_6$H$_4$–Cl	19	14
N–Cl	CH_2=$CHCH_2O$–C$_6$H$_3$Cl$_2$	23	N–$CH_2CHClCH_2O$–C$_6$H$_3$Cl$_2$	20	87
N–Cl	CH_2=$CHCH_2OC_2H_5$	12	N–$CH_2CHClCH_2OC_2H_5$	21	88
$(C_2H_5)_2NCl$	CH_2=$CHCH_2C_6H_5$	5	$(C_2H_5)_2NCH_2CHClCH_2C_6H_5$	22	57
$(C_2H_5)_2NCl$	CH_2=$CHCH_2CN$	50	$(C_2H_5)_2NCH_2CH$=$CHCN$	23	84[c]
N–Cl	CH_2ClCH=$CHCH_2Cl$	330	N–CH(Cl)–$CHCH_2Cl$ (CH_2Cl)	24	73
N–Cl	SO_2	310	N(Cl)–SO_2	26	51
N–Cl	O	70	N(Cl)–O	27	6

[a] See footnote *a*, Table I. [b] Bp 78° (6 mm), $n^{25}D$ 1.4595, picrate mp 95–96° (lit.[24] picrate mp 96–97°). [c] Mixture of 50% *cis*–50% *trans*-olefin.

panied by only 8% of the propylene adduct. It is therefore evident that (a) the chloro olefin was now the more reactive toward radical chloramination or (b) propylene was preferentially destroyed without reaction with the chloramine or was insoluble. The second alternative is unlikely in view of the known, rapid reaction[1] of propylene with chloramines and since a large excess of propylene was used. Consistent with the resulting view that chloro olefins may be generally *more* reactive in our system than their alkyl counterparts, for whatever reason, is the fact that 2-chloropropene can partially divert N-chlorodipentylamine from the Hofmann–Loeffler rearrangement by reacting with the intermediate aminium radical to give adduct **4**, although the presence of propylene had no effect[1] on the chloramine rearrangement. We should note that the reactivity of 2-chloropropene with N-chlorodipentylamine is similar to that of allene but intermediate between that of 1,3-dienes, which completely divert the rearrangement, and simple olefins or acetylenes, which cannot divert it at all.[1]

Allyl Compounds (Table II).—Simple allyl compounds were found to afford the same good yields of adducts as did the vinyl monomers; now the electron-withdrawing group was insulated from the double bond in each case by a methylene group, but the over-all electronegative character of such substituted methyl groups relative to a simple alkyl group[14] was obviously adequate to inhibit electrophilic chlorination and thereby promote the radical chloramination. The variety of substituents that proved effective for reaction 7 is illustrated in Table II; all the adducts except that with Y = Cl are the first representatives of their particular types of substituted amine.

$$R_2NCl + R_1CH{=}CR_2CH_2Y \xrightarrow[h\nu]{H_2SO_4\text{–}HOAc} R_2NCH(R_1)CR_2(Cl)CH_2Y \quad (7)$$

Both allyl alcohol and allyl acetate gave the same adduct **17** with diethylchloramine; it is more probable that allyl alcohol was acetylated prior to its chloramination than after, since the acetylation of the adduct should be slower[15] than that of allyl alcohol owing to the presence of the nearby protonated amino group in the adduct. A related problem was encountered when allyl phenyl ether was allowed to react with diethylchloramine; ring chlorination of the starting material or the reaction products occurred to give 30% of allyl *p*-chlorophenyl ether and 14% of its chloramination product **19**. As expected, allyl 2,4-dichlorophenyl ether gave a good yield (87%) of the desired adduct **20** and allyl ethyl ether gave 88% of **21**.

Allyl cyanide gave a crude product which had spontaneously undergone dehydrohalogenation to a marked degree; the elimination of HCl was, therefore, completed to give equal amounts of the *cis*- and *trans*-aminocrotononitriles (**23**).

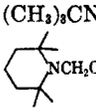
An adduct (**24**) from 1,4-dichloro-2-butene was observed to undergo an interesting cyclization on heating to give a salt whose spectral data best fit the quaternary structure **25**. A reasonable rationalization of the formation of **25** is that an initially formed aziridinium salt was opened as shown in eq 8 on attack by chloride

(14) According to the polar substituent constants σ^*, for example: R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 619.

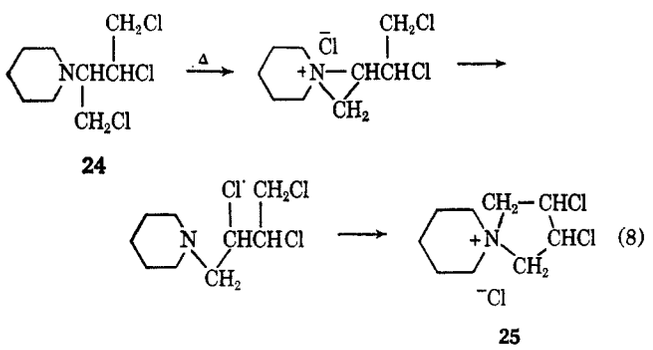
(15) See discussion of β-chloramine reactivities in acidic *vs.* basic media given in paper V.[1]

TABLE III

LIGHT-CATALYZED ADDITION OF SPECIALLY SUBSTITUTED CHLORAMINES TO 2-CHLOROPROPENE IN 4 *M* SULFURIC ACID–ACETIC ACID AT 30°

Chloramine	Adduct	Time, min	Compd	% yield
$(CH_3)_3CN(Cl)CH_2CH_3$	$(CH_3)_3CN(C_2H_5)CH_2CCl_2CH_3$	13	**28**	78
		45	**29**	35
$(CH_3)_3CN(Cl)CH_2C_6H_5$	None[a]	10		
$CH_3N(Cl)CH_2C_6H_5$	$C_6H_5CH_2N(CH_3)CH_2CCl_2CH_3$	~15	**30**	27
$CH_3N(Cl)CH_2$-*p*-Cl-C_6H_4	None	5		
$CH_3N(Cl)CH_2CH_2C_6H_5$	$C_6H_5CH_2CH_2N(CH_3)CH_2CCl_2CH_3$	5	**31**	75
c-$C_6H_{11}N(Cl)CH_2CH{=}CH_2$	None	20		76[b]
$CH_3N(Cl)(CH_2)_{1-2}{-}CN$	None	8–10[c]		
$CH_3N(Cl)CH_2X$ (X: C≡CH, CH_2OH, $CH(OCH_3)_2$)	None	5–10		
	None	15[c]		
$CH_3N(Cl)(CH_2)_{2-3}{-}N(Cl)CH_3$	None[d]	10		
$CH_3N(Cl)(CH_2)_4N(Cl)CH_3$	$(CH_3CCl_2CH_2N(CH_3)CH_2CH_2\rightarrow_2$	10	**32**	49
$CH_3N(Cl)(CH_2)_6N(Cl)CH_3$	$(CH_3CCl_2CH_2N(CH_3)CH_2CH_2CH_2\rightarrow_2$	10	**33**	72

[a] Temperature 18°. [b] Yield of recovered allylcyclohexylamine. [c] Spontaneous reaction. [d] N,N′-Dimethylethylenediamine sulfate precipitated on addition of the bischloramine to the acid medium.



24 **25** (8)

ion at the more substituted carbon,[16] then recyclized to the five-membered ring compound finally isolated.

We had expected the radical chloramination of allyltrimethylsilane to fail, despite the successful use of trimethylvinylsilane (Table I), since an allylic trimethylsilyl group is electron donating, in contrast to its electron-withdrawing effect as a vinyl substituent.[17] However, we did not anticipate the formation of 42% of hexamethyldisiloxane ($(CH_3)_3SiOSi(CH_3)_3$) as the only silicon-containing product of significance. The presumably ionic process that gave the siloxane may have involved the addition of Cl^+ to the allylsilane followed by attack of a base (acetate or bisulfate ion) at silicon[18] to effect cleavage of the chloroalkyl group and give a trimethylsilyl ester. This would have readily hydrolyzed[19] on work-up to trimethylsilanol, which is well known[20] to dehydrate spontaneously to the disiloxane.

(16) Although most nucleophilic opening of azirdinium rings occurs *via* attack at the less substituted carbon, chloride ion constitutes a consistent exception: J. F. Kerwin, G. E. Ullyot, R. C. Fuson, and C. L. Zirkle, *J. Am. Chem. Soc.*, **69**, 2961 (1947); R. C. Fuson and C. L. Zirkle, *ibid.*, **70**, 2760 (1948); E. G. Brain, F. P. Doyle, and M. D. Mehta, *J. Chem. Soc.*, 633 (1961). In the case of ring openings that preferentially give tertiary rather than primary chlorides, the driving force is thought to be the formation of the tertiary carbonium ion, and a displacement reaction is probably not involved.[7]

(17) E. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p 103.

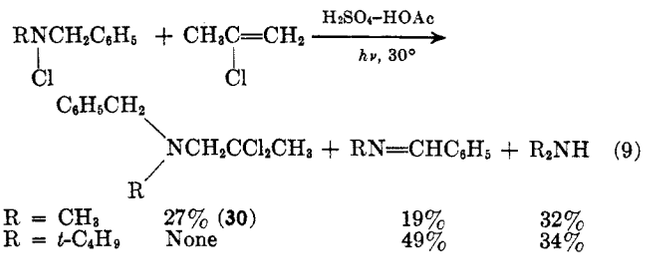
(18) Such a process has been considered often: ref 17, p 141.

(19) Reference 17, p 316.

(20) Reference 17, p 246.

A few other allyl compounds caused the decomposition of N-chloropiperidine, but failed to yield an adduct, *e.g.*, allylurea, allylthiourea, allyl methyl sulfide, and acrolein dimethyl acetal.

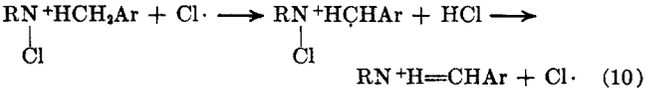
Use of Substituted Chloramines (Table III).—We have noted above the consequences of bulky N-alkyl substituents on the addition of chloramines to 2-chloropropene. The remaining entries in Table III illustrate two further points. When chloramines of the general type $RNClCH_2Z$ were employed, no addition to 2-chloropropene occurred when Z = CH_2OH, $CH(OCH_3)_2$, CN, $CH{=}CH_2$, or C≡CH. The only exception was methylbenzylchloramine (Z = C_6H_5), which struck a balance between addition and dehydrohalogenation to give 27% of the adduct **30** along with 19% (at least) of N-methylbenzaldimine (eq 9); *t*-butylbenzylchloramine, however, gave 49% of the imine and no adduct. Certain homologous chloramines $CH_3NCl(CH_2)_2Z$ were also tried. Whereas methyl-2-phenylethylchloramine gave a good yield of adduct **31**, both of the related compounds methyl-2-cyanoethyl- and -2-hydroxyethylchloramine failed to give any isolable adduct.



(9)

R = CH_3	27% (**30**)	19%	32%
R = *t*-C_4H_9	None	49%	34%

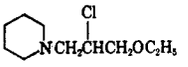
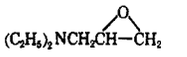
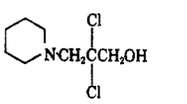
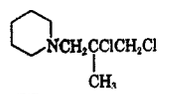
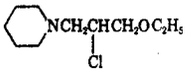
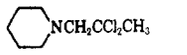
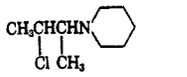
Since all of these reactions were light catalyzed and the chloramines remained stable in strong acid until the olefin was introduced, we believe that the benzaldimines obtained in reaction 9 could have resulted from a radical elimination process (eq 10) and that the parent



(10)

TABLE IV

LIGHT-CATALYZED ADDITIONS OF CHLORAMINES TO OLEFINS IN SOLVENTS OTHER THAN ACETIC ACID[a]

Chloramine	Olefin	Solvent	Temp, °C (time, min)	Adduct	Compd	% yield
	CH_2=$CHCH_2OC_2H_5$	70% (vol) H_2SO_4 in H_2O	27 (30)		21	64
$(C_2H_5)_2NCl$	CH_2=$CHCH_2OH$	70% (vol) H_2SO_4 in H_2O	30 (15)		34	46
	CH_2=CCl-CH_2OH	70% (vol) H_2SO_4 in H_2O	27 (45)		35	72[b]
$(C_2H_5)_2N$—Cl	CH_2=$CHCH_2OC_6H_5$	70% (vol) H_2SO_4 in H_2O	27 (30)	$(C_2H_5)_2NCH_2CH(Cl)CH_2OC_6H_5$	18	7[c]
$CH_3NCH_2CH_2OH$ (Cl)	CH_2=CCl-CH_3	70% (vol) H_2SO_4 in H_2O	27 (45)	None		
	CH_2=CCl-CH_2Cl	70% (vol) H_2SO_4 in H_2O	27 (110)		36	36[d]
	CH_2=$CHCH_2OC_2H_5$	4 *M* H_2SO_4 in CH_3NO_2	30 (30)		21	71
	CH_2=CCl-CH_3	4 *M* H_2SO_4 in CH_3NO_2	27 (10)[e]		3	26
$(n\text{-}C_4H_9)_2N$—Cl	CH_2=CHC_2H_5	CF_3COOH	23 (10)	$(n\text{-}C_4H_9)_2NCH_2CH(Cl)C_2H_5$	37	39[f]
$(n\text{-}C_4H_9)_2N$—Cl	CH_2=$C(CH_3)_2$	CF_3COOH	10 (5)	None		80[g]
	*cis*-CH_3CH=$CHCH_3$	CF_3COOH	15 (15)		38	31[h]
$CH_3NCH_2CH_2C_6H_5$ (Cl)	CH_2=CCl-CH_3	CF_3COOH	20 (30)	None		62[g]
$CH_3NCH_2CH_2C_6H_5$ (Cl)	CH_2=CHC_2H_5	CF_3COOH	30 (10)	None		51[g]

[a] Unless specified, the solutions were 0.6–0.9 *M* in chloramine and in total olefin, which was added slowly to the solution. [b] Yield based on 9 to which 35 was converted with $SOCl_2$. [c] For other products also formed, see Experimental Section. [d] Only 9% yield in H_2SO_4–HOAc. [e] Reaction spontaneous on addition of olefin in the dark. [f] Same yield from reaction at 0°. [g] Yield of recovered dialkylamine. [h] Yield of the derivative 39.

amines were produced in part from the normal reduction[21] of the chloramines by the HCl formed in reaction 10. The addition of methyl-*p*-chlorobenzylchloramine to 2-chloropropene was therefore attempted, since benzylic hydrogen abstraction should now have been less favored than in the case of the unsubstituted benzyl compound on the basis of the usual polar effects.[22] However, no adduct was obtained from this reaction, which gave the expected low yield of imine (7%) but produced the parent amine as the only significant basic product.

A second type of chloramine substitution, in which two chloramino groups were incorporated into the same molecule with intervening methylene groups of 2, 3, 4, and 6 units ($CH_3NCl(CH_2)_nNClCH_3$), was also examined. It is evident from Table III that the ability of both chloramino groups to add to 2-chloropropene is dependent on their separation from one another; a good yield of diadduct (**33**, 72%) was achieved only on use of the hexamethylenediamine derivative. This effect is quite reasonably attributable to the increasing ease of complete diprotonation of the α,ω-bis(chloraminoalkanes) with increasing methylene chain length.

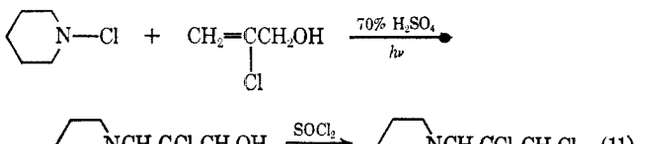
Other Acidic Media.—Some chloramination reactions carried out in acidic media other than the usual 4 *M* H_2SO_4 in acetic acid are grouped in Table IV according to the three different acid systems in which additions occurred. The yields of adducts were generally good but lower by 10–20% relative to those obtained in acetic acid when 70% by volume H_2SO_4 in water (~13 *M*) was used; the usual quantities of chloramines and acid solution were employed, resulting in acid–chloramine molar ratios of over 20:1. Allyl ethyl ether reacted normally, giving 64% of the expected adduct **21**, and allyl phenyl ether gave only 7% of the adduct **18**, which is equivalent to the result in acetic acid. In one example, aqueous sulfuric acid proved to be superior to the acetic acid medium; 36% of the adduct **36** from methallyl chloride was obtained in contrast to only 9% under the usual conditions.

Of most interest were the two experiments with allylic alcohols. From allyl alcohol, which had given 48% of the acetate **17** in acetic acid, was obtained directly the amino epoxide **34** in 46% yield, no doubt as the

(21) R. S. Neale, M. R. Walsh, and N. L. Marcus, *J. Org. Chem.*, **30**, 3683 (1965).

(22) For example, see the data presented by G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

result of ring closure of the initially formed amino-chlorohydrin from the expected chloramination reaction. In contrast, 2-chloro-3-hydroxy-1-propene gave a crude alcoholic product (**35**) which could not be further purified or efficiently acetylated. This adduct was therefore identified by converting it with thionyl chloride to compound **9** (Table I) in an over-all yield of 72% (eq 11). Unfortunately, no adduct was obtained from the secondary allylic alcohol 3-hydroxy-1-butene, so that chloramination fails as a general route to amino epoxides.

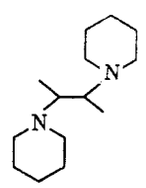


35 **9** (72%) (11)

Two reactions were carried out in 4 *M* H_2SO_4 in nitromethane instead of acetic acid, since this medium had previously been found useful in the Hofmann–Loeffler reaction[21] but not for the chloramination of butadiene.[23] Allyl ethyl ether again gave a good yield of adduct **21** but 2-chloropropene reacted spontaneously and gave only 26% of adduct **3**. Thus, it appears that vinyl halide chloraminations would be generally inefficient in sulfuric acid–nitromethane.

We last investigated neat trifluoroacetic acid (TFA) as a solvent because TFA is useful in Hofmann–Loeffler reactions[24] and promotes a moderately successful chloramination of butadiene.[23] We were particularly interested in whether unsubstituted olefins might be less subject to electrophilic chlorination in TFA than they were[1] in H_2SO_4–HOAc and would consequently give better yields of free-radical chloramination products. It is evident, however, from the last five entries in Table IV that TFA was of only moderate value in this regard since the yield of adduct **37** from 1-butene and dibutylchloramine was raised only twofold relative to the results in acetic acid[1] and isobutylene still gave no adduct. Although *cis*-2-butene now gave 31% of adduct **38**, compared to none in acetic acid,[1] 2-chloropropene failed to yield the expected adduct **31** obtained previously in acetic acid in 75% yield.

The adduct **37** from 1-butene was isolated by stripping the reaction mixture of excess TFA, extracting an ether solution of the residue with bicarbonate solution, and distilling the acid-free product. The adduct **38** could not be so isolated owing to its facile reaction with hydroxide ion or piperidine, which was also a significant reaction product; the product obtained for analysis was therefore **39**, which resulted on treatment of the neutralized ether solution of **38** with excess piperidine.



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(23) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 2666 (1963).

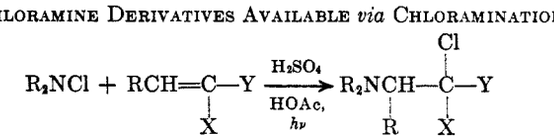
(24) J. F. Kerwin, M. E. Wolff, F. F. Owings, B. B. Lewis, B. Blank, A. Magnani, C. Karash, and V. Georgian, *J. Org. Chem.*, **27**, 3628 (1962).

Discussion Section

The synthetic utility of olefin chloramination for the preparation of various types of β,β- and β,γ-disubstituted alkylamines has been established through the preceding examples. The generality of the method is best brought out by Table V, in which are summarized the 13 new types of substituted amines now readily

TABLE V

β-CHLORAMINE DERIVATIVES AVAILABLE *via* CHLORAMINATION



From vinyl compounds		From allyl compounds
X	Y	Y (X = H)
Cl	H or R	CH_2Cl
Cl	CH_2Cl	CH_2OAc
Cl	CH_2OH[a]	CH_2OR
Br	H or R	CH_2OAr
F	H	CH_2Ar
CF_3	R	CH_2CN
$Si(CH_3)_3$	H	CH_2SO_2R

[a] Best prepared in 70% (by volume) H_2SO_4 in water.

available by the use of this one-step, free-radical process.[25] We have also been able to prepare many, but not all, of the types of compounds listed in Table V in which only one N-alkyl group R is present; examples and details of these reactions, however, will be presented at another time.

The vinyl compounds found useful for chloramination all bore electron-withdrawing substituents (Table I). However, if (a) electron depletion of an olefinic bond became too great, as was probably true[26] of the 1,2-dichloroethylenes or perfluoro-2-butene, or (b) the substituent contained a C–X π-electron system conjugated to the olefin in which X was oxygen or nitrogen, *i.e.*, the acrylates, the olefin was inactive toward any type of attack under the usual reaction conditions. The situation with allyl compounds is even more favorable, since nearly any group $-CH_2Y$ is electron withdrawing relative to a simple alkyl group and conjugated systems are not involved. Thus, carbonium ion stabilizing groups such as alkoxy or aryl, which promoted electrophilic attack on vinyl monomers, and the totally inactivating vinylic cyano group became useful activators of a double bond on relocation in the allylic position (Table II).

Although aminium radical addition to alkyl olefins, styrenes, and vinyloxy compounds cannot compete with ionic chlorination under chloramination conditions, we see no reason why such olefins would not yield adducts in the absence of the ionic reactions, since other hetero radicals readily add to these types of olefins.[27] However, the acrylates and similar derivatives were also reactive toward radical addition in other systems, while

(25) Only the type of adduct derived from allyl chloride was already known (made from 1-bromo-2,3-dichloropropane): M. Ishidate and N. Sakurai, Japanese Patent 3962 (1961); see *Chem. Abstr.*, **58**, 10078 (1963).

(26) The successful chloraminations of 1-chloropropene, 1-chlorocyclohexene, and 1,4-dichloro-2-butene suggest that the present inertness of *cis*- and *trans*-1,2-dichloroethylene is not of steric origin; see ref 4, p 127.

(27) Many examples will be found in the extensive data compiled for HBr, thiol, sulfonyl halide, chlorosilane, phosphine, and other radical additions that yield new carbon–heteroatom bonds: F. W. Stacey and J. F. Harris, Jr., *Org. Reactions*, **13**, 150 (1963).

TABLE VI

PHYSICAL CONSTANTS AND ANALYSES OF NEW COMPOUNDS

Compd and derivative	Empirical formula	Bp (mm) or mp, °C	n_D (temp, °C)	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Halogen, % Calcd	Halogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found
1	$C_6H_{13}Cl_2N$	61.8 (10)	1.4527 (24)	42.37	42.11	7.70	7.68	41.69	42.21	8.24	8.29
1 hydrochloride		115.5–117									
1 picrate	$C_{12}H_{16}Cl_2N_4O_7$	109–110.5		36.10	36.08	4.04	3.99	17.78	17.72	14.04	14.19
2		71.0 (11)	1.4522 (24)								
2 hydrochloride	$C_7H_{16}Cl_2N$	144–145		38.12	37.71	7.31	7.27	48.22	47.95	6.35	6.61
2 picrate	$C_{13}H_{16}Cl_2N_4O_7$	92–95.5		37.78	37.67	4.39	4.33	17.17	17.62	13.56	13.82
3	$C_8H_{15}Cl_2N$	55–56.5 (0.9)	1.4776 (25)	48.99	49.25	7.71	7.77	36.16	35.87	7.14	7.17
3 picrate·$^1/_3C_6H_6$[a]	$C_{16}H_{20}Cl_2N_4O_7$	132.5–134		42.58	42.72	4.47	4.38	15.71	15.67	12.42	12.31
4		77–81 (0.08)	1.4577 (25)								
4 picrate	$C_{19}H_{30}Cl_2N_4O_7$	83–84.5		45.87	45.92	6.08	6.23	14.27	14.10	11.27	11.22
5		39.5–41.5									
5 picrate	$C_{17}H_{22}Cl_2N_4O_7$	142–143.5		43.87	44.08	4.77	4.69	15.25	15.38	12.04	11.95
6		48.5 (0.2)	1.4682 (25)								
6 hydrochloride	$C_{10}H_{22}Cl_3N$	190.5–191		45.71	45.70	8.44	8.37	40.52	40.25	5.33	5.56
7		78.5–80 (0.5)	1.4894 (24)								
7 hydrochloride	$C_{10}H_{20}Cl_3N$	153–154		46.06	46.10	7.73	7.72	40.84	40.54	5.37	5.55
7 picrate	$C_{16}H_{22}Cl_2N_4O_7$	119–120.5		42.39	42.34	4.89	4.91				
8		59–59.2 (6)	1.4586 (23)								
8 picrate	$C_{13}H_{18}Cl_2N_4O_7$	96.5–98.5		37.78	37.91	4.39	4.30	17.17	17.13	13.56	13.49
9	$C_8H_{14}Cl_3N$	63–64 (0.5)	1.4968 (24)	41.67	41.14	6.12	6.12	46.13	45.85	6.08	6.37
9 hydrochloride	$C_8H_{15}Cl_4N$	183 dec		35.98	35.78	5.66	5.77	53.11	52.81	5.25	5.45
10	$C_6H_{13}ClFN$	61–61.5 (40)	1.4160 (25)	46.91	47.02	8.53	8.31			9.12	9.01
10 picrate	$C_{12}H_{16}ClFN_4O_7$	110–111		37.66	37.56	4.21	4.28	14.22	15.06[b]	14.65	14.79
11		84–85 (30)	1.4206 (24)								
11 hydrochloride	$C_9H_{16}Cl_2F_3N$	194–195 dec		40.62	40.54	6.06	6.57	48.06	48.46[b]	5.26	4.87
11 picrate	$C_{15}H_{15}ClF_3N_4O_7$	125–126		39.27	39.46	3.95	4.11			12.21	12.04
12		82–85 (60)	1.3966 (25)								
12 hydrochloride	$C_8H_{16}Cl_2F_3N$	161–162		37.81	37.93	6.35	6.35	50.33	50.59[b]	5.51	5.26
12 picrate	$C_{14}H_{18}ClF_3N_4O_7$	89–90.5		37.64	37.78	4.06	4.07	20.70	21.26[b]	12.54	12.59
13		44 (0.4)	1.4505 (25)								
13 hydrochloride		170–171.5									
13 picrate·$0.5C_6H_6$	$C_{16}H_{19}BrClN_4O_7$	116–117.5		38.84	38.72	3.87	3.99	23.32[c]	23.08	11.33	11.31
14		31–31.5 (0.05)	1.4770 (24)								
14 hydrochloride	$C_7H_{16}BrCl_2N$	121–123.5		31.72	31.66	6.09	6.11	40.13[c]	40.04[d]	5.29	4.83[d]
14 picrate	$C_{13}H_{18}BrClN_4O_7$	84–86		34.11	34.21	3.96	4.17			12.24	12.45
15		53 (1.5)	1.4505 (24)								
15 hydrochloride	$C_9H_{23}Cl_2NSi$	92.5–96		44.24	44.30	9.49	9.55	29.05	29.14	5.73	6.02
15 picrate	$C_{15}H_{25}ClN_4O_7Si$	126.5–127.5		41.25	41.15	5.77	5.50	8.13	8.85	12.83	12.72
17	$C_9H_{18}ClNO_2$	57 (0.1)	1.4445 (25)	52.04	51.64	8.74	8.77	17.07	16.99	6.74	6.55
18		100–104 (0.15)	1.5098 (25)								
18 picrate	$C_{19}H_{23}ClN_4O_8$	76.5–78		48.46	48.49	4.92	4.85	7.53	7.73	11.90	11.59
19		122 (0.15)	1.5219 (25)								
19 picrate	$C_{19}H_{22}Cl_2N_4O_8$	118–119.5		45.16	45.19	4.39	4.44			11.09	11.10
20 hydrochloride	$C_{14}H_{19}Cl_4NO$	125–126.5		46.82	47.12	5.33	5.52	39.49	39.70	3.90	3.75
20 picrate	$C_{20}H_{21}Cl_3N_4O_8$	136–137.5		43.53	43.54	3.84	3.80	19.28	19.10	10.15	10.33
21	$C_{10}H_{20}ClNO$	47–48 (0.05)	1.4637 (25)	58.38	58.14	9.80	10.08	17.23	17.37	6.81	7.08
21 hydrochloride	$C_{10}H_{21}Cl_2NO$	150–151.5		49.59	49.63	8.74	8.82	29.28	29.13	5.78	5.52
21 picrate	$C_{16}H_{23}ClN_4O_8$	93–94.5		44.19	44.17	5.33	5.39	8.15	8.18	12.89	12.63
22	$C_{13}H_{20}ClN$	72–74 (0.02)	1.5090 (25)	69.16	68.80	8.93	8.87	15.71	15.68	6.20	6.45
22 picrate	$C_{19}H_{23}ClN_4O_7$	95.5–97		50.17	50.42	5.10	5.09	7.79	7.68	12.32	11.88
23		62–71 (2)	[e]								
trans-**23** picrate	$C_{14}H_{17}N_5O_7$	141–142		45.77	45.71	4.67	4.60			19.07	19.20
24 hydrochloride	$C_9H_{17}Cl_4N$	149–154		38.46	38.09	6.10	6.08	50.46	50.65	4.90	5.13
25	$C_9H_{16}Cl_3N$	115–116		44.19	44.18	6.59	6.69	43.49	42.26	5.73	5.76
26[f]	$C_9H_{16}ClNO_2S$	97–101		45.47	45.13	6.78	6.81	14.97	14.76	5.89	5.91
26 picrate[g]	$C_{15}H_{19}ClN_4O_9S$	175–176		38.59	38.64	4.10	4.03	7.59	7.63	12.00	11.92
26 hydrochloride		197–198.5									
27		57.5–58 (0.07)	1.4952 (25)								
27 hydrochloride	$C_9H_{17}Cl_2NO$	203–205		47.80	47.38	7.58	7.64	31.36	31.61	6.19	6.18
28	$C_9H_{19}Cl_2N$	33 (0.04)	1.4606 (25)	50.95	50.65	9.03	9.06	33.42	33.47	6.60	6.85
28 hydrochloride	$C_9H_{20}Cl_3N$	146–147		43.48	43.27	8.11	8.09	42.78	42.77	5.63	5.94
29	$C_{12}H_{23}Cl_2N$	86 (0.05)	1.4948 (25)	56.69	56.56	9.91	9.28	27.89	28.28	5.51	5.73
29 hydrochloride	$C_{12}H_{24}Cl_3N$	137–138.5		49.58	50.01	9.01	8.55	36.59	36.92	4.82	4.60
30		76.5–77 (0.09)	1.5222 (24)								
30 hydrochloride	$C_{11}H_{16}Cl_3N$	155–161 dec		49.16	48.75	6.00	6.12	39.62	39.60	5.22	5.80
31		115–120 (0.2)	1.5186 (25)								
31 hydrochloride	$C_{12}H_{15}Cl_3N$	146–147.5		50.99	51.20	6.42	6.48	37.63	37.31	4.96	4.88

TABLE VI (*Continued*)

Compd and derivative	Empirical formula	Bp (mm) or mp, °C	n_D (temp, °C)	—Carbon, %— Calcd	Found	—Hydrogen, %— Calcd	Found	—Halogen, %— Calcd	Found	—Nitrogen, %— Calcd	Found
31 picrate	$C_{13}H_{20}Cl_2N_4O_7$	106–108		45.49	45.42	4.24	4.22	14.92	14.68	11.79	11.78
32 dipicrate	$C_{12}H_{15}Cl_2N_4O_7$	163–165		36.20	36.37	3.80	3.90	17.81	17.48	14.07	13.53
33 dihydrochloride	$C_7H_{15}Cl_3N$	176 dec		38.29	38.63	6.89	6.92	48.44	48.30	6.38	6.03
33 dipicrate	$C_{13}H_{17}Cl_2N_4O_7$	139–140		37.88	37.76	4.16	4.09				
36		65 (1)	1.4834 (24)								
36 picrate	$C_{15}H_{21}Cl_2N_4O_7$	120–121		40.92	41.00	4.81	4.45	16.11	16.06	12.73	12.93
39		126–128 (4)	1.4884 (25)								
39 dipicrate·0.5EtOH	$C_{28}H_{40}N_8O_{15}$	162–163.5		46.15	46.23	5.53	5.43			15.38	15.21

[a] Duplicate analyses performed on repurified picrate, again recrystallized from benzene, gave the same result. [b] Combined Cl and F analyses. [c] Analysis for total halogen (Br + Cl), computed on basis of chlorine alone (*i.e.*, grams of total halogen as chlorine × 100/actual molecular weight). [d] Analysis of second sample. [e] Glpc separated isomers: *cis*, 1.4554 (25); *trans*, 1.4569 (24). [f] *Anal.* Calcd: S, 13.49. Found: S, 13.57. [g] *Anal.* Calcd: S, 6.87. Found: S, 6.92.

in ours they were not. This was quite unexpected in view of the well-known[28] activating effect of C=O or C≡N groups on double bonds toward the addition of carbon radicals; this activation, on the average, is less than that of a vinyl group but more than that of chlorine or $-CH_2Y$ groups. It is unfortunate that more data are not available by which the reactivities of olefins of various types toward addition of other noncarbon radicals could be compared. The present results with aminium radicals suggest that such comparisons might reveal some unanticipated olefin substituent effects of both synthetic and mechanistic interest.

Whether or not an olefin is activated by a vinylic chlorine substituent toward addition of amino radicals is also a point of particular interest in the context of amino radical reactions. Minisci feels from certain of his data[13] that the electrophilic nature of amino radicals requires that the transition state for their addition to olefins be determined more by polar factors than by resonance stabilization of the developing carbon radicals; an electron-rich alkyl olefin was therefore anticipated to react faster than a monochloro analog. This behavior was apparently realized when competitive reactions of cyclohexene and 1-chlorocyclohexene with N-chloropiperidine were carried out with an iron salt in either aqueous sulfuric acid or in methanol, since the adduct derived from cyclohexene was by far the predominant product.[13] These results were taken as confirmation that protonated and unprotonated amino radicals should add better to alkyl than to chloro olefins.

However, this conclusion seems intended to correct our speculation[2] (not "assumption"[13]) that the relative reactivities might be the opposite in our system. Accordingly, we wish to emphasize two of our results that do indeed indicate such an inverse order. First, the 2-chloropropene *vs.* propylene competition described in this paper showed that the chloropropene adduct could be isolated in 83% yield, based on the chloropropene used, even in the apparent presence of a fivefold excess of propylene. The second result was the unexpected finding[2] that the dipentylaminium radical was diverted from the Hofmann–Loeffler rearrangement by reaction with 2-chloropropene, but could not be intercepted by propylene. These experiments show that both free-radical amination of chloropropene and aminium radical rearrangement are processes preferred to either radical or ionic reactions of propylene *under the conditions stated*, and for whatever reason. We do not know whether analogous competitions would yield the same result. Nevertheless, it is obvious without further examples that conclusions derived from one amino radical system cannot be safely extended to others without the support of experimental evidence. The results we have observed are consistent, of course, with copolymerization data[28] involving *carbon* radical additions to substituted olefins, which show a chlorine atom to be a bit better than a methyl group in activating an olefin.

Finally we note that our facile addition of N-chloro(methyl-2-phenylethyl)amine to 2-chloropropene (Table III) contrasts with the reported[29] Fe(II) salt-promoted cyclization in sulfuric acid of the methyl-2-phenylethylaminium radical in the absence of an added substrate to give 27% of N-methyl-2,3-dihydroindole; cleavage of the radical also occurred to produce 44% of benzyl chloride. It would be of interest to determine whether these unimolecular processes are inhibited by added olefins or whether they result from an influence of the metal ion.

Experimental Section

The apparatus and procedures were the same as described in paper V of this series.[1] The physical constants and analytical data of all new compounds and their derivatives have been listed in Table VI according to their reference numbers, which are given in Tables I–IV or in the text. Unless specified otherwise, all the amines and olefins were available from either the Aldrich Chemical Co. or Columbia Organic Chemicals Co., Inc; liquids were redistilled when glpc analysis so dictated. Hydrochlorides of the adducts were prepared from gaseous HCl in ether and were recrystallized from acetone, acetonitrile, or ethanol. Picrates were obtained from ethanolic picric acid solution, usually only after 12–36 hr standing at −30°, and were recrystallized from ethanol, benzene, ethyl acetate, or chloroform. The chloramines were usually prepared from N-chlorosuccinimide in ether, as described in paper V.[1]

Nmr spectra were recorded in carbon tetrachloride, and data representative of the new compounds are summarized in Table VII. No single peak could be identified from the infrared spectra of 30 different β-chloramines or β,β-dichloramines as uniquely characteristic of any one of the several structural types represented (see Tables I and II and adducts previously reported[1]). It was invariably true, however, that either one, two, or three medium to strong bands were present in the region 13.3–15.9 μ in the spectrum (neat liquid) of any given sample and that the strongest band usually occurred at 14.4–14.6 μ. When only a single band was present in the spectrum of a β-monochloramine, it appeared at 14.5–15.0 μ (seven examples).

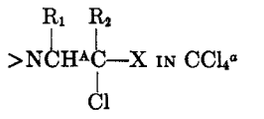
N-2,2-Dichloropropylpiperidine (3).—To 45 ml of sulfuric acid in 144 ml of glacial acetic acid at 15° was added by syringe 0.11 mole of N-chloropiperidine, bp 44° (16 mm), $n^{25}D$ 1.4706, after

(28) Reference 4, pp 118–121.

(29) F. Minisci and F. Galli, *Tetrahedron Letters*, 253 (1966).

TABLE VII

PARTIAL NMR SPECTRA OF SOME SUBSTITUTED β-CHLORAMINES



Compd	R_1	R_2	X	$\tau(H^A)$	$\tau(R_2)$	$\tau(X_{CH_2})$
1	H	H	Cl	7.00 d	4.50 t	
3	H	CH_3	Cl	7.12 s	7.95 s	
6	H	$C(CH_3)_3$	Cl	6.94 s		
28	H	CH_3	Cl	6.85 s	7.90 s	
29[b]	H	CH_3	Cl	6.40 s	7.82 s	
8	CH_3	H	Cl	6.80 (8)	4.36 d	
9	H	CH_2Cl	Cl	6.94 s	5.86 s	
11	H	CH_3	CF_3	7.27 s	8.33 s	
13	H	H	Br	7.03 d	4.41 t	
14	H	CH_3	Br	6.90 s	7.80 s	
15	H	H	$SiC(CH_3)_3$	7.2 to 7.5 m	6.72 (4)	
16	H	H	CH_2Cl	7.15 to 7.35 m	——5.8 to 6.25 m——	
17	H	H	CH_2OAc	7.32 d	——5.5 to 6.2 m——	
19	H	H	CH_2OAr	7.25 m	——5.7 to 6.1 m——	
21	H	H	$CH_2OC_2H_5$	7.1 to 7.7 m	——5.85 to 6.70 m——	
22	H	H	$CH_2C_6H_5$	7.1 to 7.5 m	5.8 to 6.25 m	6.5 to 7.5 m

[a] Line splittings are indicated by s (singlet), d (doublet), t (triplet), or m (multiplet). [b] The α-methyl groups in the piperidine ring produced two equally sized peaks at τ 8.85, 9.00.

the acid mixture had been purged 20 min with nitrogen. The nitrogen flow was reduced after 5 min, and 0.06 mole of 99+% pure 2-chloropropene, bp 23–24°, $n^{25}D$ 1.4044, was added to the vigorously stirred mixture. The Vicor flask was then externally irradiated for 12 min with a 100-w Hanovia ultraviolet lamp as 0.06 mole of remaining olefin was added dropwise to the mixture; the solution temperature was maintained at 30°. The colorless acid solution was then poured into 200 g of ice and 700 ml of water. Extraction of the aqueous solution with pentane yielded no product, but neutralization to pH 6–7 with 230 ml of 12 *N* sodium hydroxide liberated an oil which was extracted into ether. The ether solution was washed with bicarbonate (to remove acetic acid), dried, and evaporated. The 20.3 g of crude **3** thus obtained was distilled without decomposition. No further adduct was obtained on the complete basification of the aqueous solution.

Diethyl-1,1-dichloro-2-propylamine (8).—The above reaction was repeated using an acid solution of diethylchloramine prepared as described in paper V.[1] 1-Chloropropene, bp 32–35°, was obtained in 97% purity (along with 3% of 2-chloropropene) as an approximately 50:50 *cis–trans* mixture by distillation of a mixture containing all the monochloropropenes. The usual work-up as above yielded pure **8** after distillation, which removed a small forerun that spontaneously decomposed to a salt in the receiver while under vacuum. The nmr spectrum of **8** (Table VII) reflected a slight magnetic nonequivalence of the N-methylene hydrogens, whose pattern showed $\Delta\nu$ <4 cps by comparison with spectra[30] of esters with nonequivalent O-methylene groups. The nmr spectrum of **8** hydrochloride showed that no rearrangement occurred on preparation of the salt and its recrystallization from hot acetone.

N-2,2-Dichloropropyl-3-azabicyclo[3.2.2]nonane (5).—3-Azabicyclo[3.2.2]nonane was obtained from Frinton Laboratories and recrystallized from methanol after removal of ether-insoluble material. The sublimation point was 187° in an open capillary.[31] The N-chloro compound, an oil, was somewhat unstable and rapidly formed a precipitate on standing. The reaction of 0.13 mole of the chloramine with 2-chloropropene was carried out in the usual way, although the crude adduct **5** separated completely from the diluted acid reaction mixture after the addition of only 125 ml of 12 *N* sodium hydroxide. The adduct was extracted into pentane and recrystallized from methanol to give 23 g of pure **5**; about 1 g of 3-azabicyclo[3.2.2]nonane hydrochloride was recovered from the methanol on evaporation and crystallized from chloroform, mp 310–312°.

Diethyl-2,2-dichlorocyclohexylamine (7).—A solution of 64 g (0.76 mole) of cyclohexanone in 100 ml of ether was added to 200 g of PCl_5 (0.96 mole) under 500 ml of ether at 0° over 1 hr.[32] The stirred mixture was warmed to 24° over 1 hr and then poured over an excess of ice with rapid stirring. The product (mainly the dichloride) was extracted into ether, washed with 10% NaOH, dried, and dehydrochlorinated by distilling it from quinoline. 1-Chlorocyclohexene, 39 g, was obtained in 99.4% purity, bp 56° (35 mm), $n^{24}D$ 1.4767 (lit.[32] bp 50° (20 mm), $n^{25}D$ 1.4772).

The reaction of 0.12 mole of 1-chlorocyclohexene with diethylchloramine was carried out in the usual way; distillation gave 15 g of the adduct **7**. A 1.1-g forerun decomposed to an insoluble salt in the head of the column.

Preparation of the 2-Chloropropene Adduct 2 in the Presence of Propylene.—To an irradiated standard acid solution containing 0.13 mole of diethylchloramine was added dropwise 0.08 mole of 2-chloropropene while 0.4 mole of propylene was simultaneously passed into the vigorously stirred mixture. No active chlorine remained after 10 min. Work-up in the usual manner gave 15 g of products from the partially neutralized aqueous solution; distillation of 10 g afforded 1.0 g of a forerun, bp 50–62° (11 mm), $n^{24}D$ 1.4404, which was shown to be mainly diethyl-2-chloropropylamine from its infrared spectrum. The yield of the propylene adduct based on the chloramine was therefore only ~7%. The main distillation fraction (8.2 g) was found to be the pure 2-chloropropene adduct **2**, bp 68–69° (11 mm), $n^{24}D$ 1.4520; the yield of **2** based on the chloramine was 51%, or 83% based on 2-chloropropene.

Diethyl-2-chloro-3-acetoxypropylamine (17).—Adduct **17** was obtained in the usual way from allyl acetate; however, it was also the major product when allyl alcohol was the starting olefin. In the latter case, the acetate **17** was obtained from the still slightly acidic aqueous solution on normal work-up, but basification to pH 9–10 liberated an additional basic product which contained both the acetate and an alcohol. Distillation of 6.2 g of the acetate–alcohol mixture gave 2.0 g of a fraction rich in the alcohol, bp 50–57° (0.1 mm), $n^{25}D$ 1.4546, and 3.25 g of **17**. The alcoholic amine was no doubt the desired adduct from allyl alcohol, since it was converted to the acetate **17** on heating under reflux for 2 hr in 15 ml of acetic acid containing 0.5 ml of sulfuric acid. A sample of the purified acetate **17**, in turn, gave an alcohol identical with the one obtained from the chloramination reaction on hydrolysis in 5 *N* H_2SO_4.

Chloramination of Allyl Phenyl Ether.—Addition of 0.13 mole of the olefin to 0.13 mole of diethylchloramine in H_2SO_4–HOAc over 10 min caused a spontaneous reaction; nevertheless, radiation was applied to the solution after 5 min. The light pink reaction

(30) W. L. Meyer, D. L. Davis, L. Foster, A. S. Levinson, V. L. Sawin, D. C. Shew, and R. F. Weddleton, *J. Am. Chem. Soc.*, **87**, 1573 (1965).

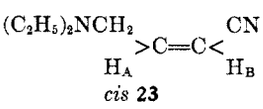
(31) Highly purified material has mp 193.55° under its own vapor: C. A. Wulff and E. F. Westrum, Jr., *J. Phys. Chem.*, **68**, 430 (1964).

(32) M. Mousseron and R. Jacquier, *Bull. Soc. Chim. France*, 648 (1950).

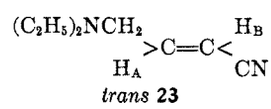
mixture was treated as usual to afford from the pentane extract of the diluted, unneutralized solution 13.6 g of a mixture composed mainly of unreacted allyl phenyl ether (20% recovery) and allyl *p*-chlorophenyl ether (31% yield), bp 70–73° (1.5 mm), $n^{25}D$ 1.5336 (lit.[33] bp 106–107° (12 mm)). Partial neutralization of the aqueous acid solution with 230 ml of 12 *N* NaOH then liberated 8.8 g of another mixture of products, whose distillation afforded two major fractions. The first, 2.1 g (6%) was found from spectral data and elemental analysis of the picrate to be **diethyl-2-chloro-3-phenoxypropylamine** (**18**), whereas the second fraction, 2.25 g (14% based on chloramine), was identified as the *p*-chloro derivative **19**. It was not determined whether **19** was formed by ring chlorination of **18** or by chloramination of allyl *p*-chlorophenyl ether. When the reaction was repeated using a 70:30 mixture by volume of H_2SO_4–H_2O as solvent, very nearly the same yields of all the products were realized.

cis,trans-**Diethylamino-3-cyano-2-propenylamine** (**23**).—The usual procedure was followed for the reaction between 0.13 mole of diethylchloramine and 0.14 mole of 3-cyano-1-propene in H_2SO_4–HOAc, except that the basic products were fully liberated only on complete basification of the diluted reaction mixture. The infrared spectrum of 20 g of crude product contained bands due to both conjugated and nonconjugated cyano groups, and complete dehydrohalogenation was therefore attempted by heating 18 g of the mixture in 40 ml of acetic acid and 100 ml of water at 60°. This gave 16.4 g of product which still contained some nonconjugated cyano compound. After further treatment in aqueous acetic acid for 2.5 days at 23°, the material was distilled to give 11.0 g (74%) of *cis* and *trans* **23** and 2.6 g of residue. The residue was extracted with water, which was filtered and basified to liberate 1.5 g (10%) of a compound whose infrared spectrum was identical with that of *trans*-diethyl-3-cyano-2-propenylamine.

Pure *cis* and *trans* **23** were separated from a mixture by preparative glpc (SF 96 liquid phase, 125°) and differentiated by their nmr spectra, whose differences are summarized below. The compound with the larger $J(H_AH_B)$ was assumed to be *trans*.[34]



cis **23**



trans **23**

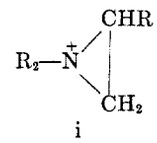
cis **23**	*trans* **23**
$J(H_AH_B)$ = 11.04 cps	$J(H_AH_B)$ = 16.2 cps
$J(H_ACH_2)$ = 6.70	$J(H_ACH_2)$ = 4.98
$J(H_BCH_2)$ = 1.56	$J(H_BCH_2)$ = 1.96
$\tau(H_A)$ = 3.45	$\tau(H_A)$ = 3.30
$\tau(H_B)$ = 4.59	$\tau(H_B)$ = 4.38
$\tau(CH_2)$ = 6.63	$\tau(CH_2)$ = 6.83

The Adduct 24 from 1,4-Dichloro-2-butene.—The olefin was distilled before use, bp 74° (40 mm), and added over 7 min to the standard acid solution containing 0.13 mole of N-chloropiperidine. No reaction ensued until the mixture was irradiated, and the positive chlorine was not completely consumed until 5.5 hr had elapsed. The adduct **24**, which separated from the partially neutralized aqueous solution, decomposed on attempted distillation. The nmr spectrum of **24** was consistent with but not definitive of the structure shown (Table II). The hydrochloride of **24** was prepared for elemental analysis (Table VI) and calculation of the yield of **24** (23 g crude), but the melting point could not be reduced to a range lower than 149–154° even on repeated crystallizations of the salt from acetone. It was therefore entirely possible that the salt, or even the adduct itself, was not homogeneous in one stereochemical isomer. A neat sample of **24** was then heated at steam-bath temperature; a solid which formed was isolated by washing the mixture with ether. The ether solution was evaporated and the residue reheated. Several such cycles converted 85% of **24** to the solid, hygroscopic isomer **25**, which contained ionic chlorine but had no N–H or C=N^+ absorptions in the infrared. The spiro structure **25** was assigned after elimination of the isomeric aziridinium forms on the basis of the nmr spectrum (see below). Although elemental analysis of **25** (Table VI) unexplainedly failed to yield a satisfactory halogen value, the excellent C, H, and N results made any but the empirical formula $C_9H_{16}Cl_3N$ rather unlikely.

(33) Beilstein's "Handbuch der Organischen Chemie," Vol. 61, 4th ed, Julius Springer Publishers, Berlin, 1931, p 101.

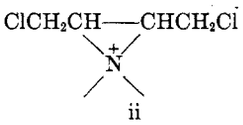
(34) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 193.

The nmr spectrum of **25** was obtained in D_2O with τ values referred to tetramethylsilane: τ 4.95, broad, 2 H, R_2CHCl; τ 5.27–5.88, multiple absorption, 4 H (excluding H_2O peak at τ 5.28), $^+NCH_2R$; τ 6.20, broadened triplet, 4 H, piperidine $^+NCH_2$; τ 7.7–8.5, 6 H. The absence of absorption near τ 7.0 (D_2O) rules out[7] structures containing aziridinium groups of type i



i

and the presence of only two hydrogens at lowest field eliminates structure ii which is isomeric with **25**.



ii

3-Chloro-4-piperidinotetrahydrothiophene 1,1-Dioxide (**26**).—Solid butadiene sulfone was dissolved in 20 ml of acetic acid and added to the standard chloramine–acid mixture. No reaction occurred until irradiation was begun. The work-up liberated 14.5 g of crude **26**, which precipitated on partial neutralization of the diluted reaction mixture, and an additional 2.5 g of adduct on basification to pH 10. The adduct was isolated by extraction into ether and was crystallized from ethanol; it was assigned structure **26** on the basis of consistent spectral data and by analogy to the other adducts. The extent of *cis vs. trans* addition of the chloramine was not determined.

The Reaction of N-Chlorobenzylmethylamine with 2-Chloropropene.—The reaction, carried out as usual, proceeded with the evolution of vapors of HCl, and the work-up afforded no significant product from the diluted reaction mixture prior to neutralization. Partial neutralization liberated a mixture of benzaldehyde and an amine; these were separated by extraction with acid to give 19% of benzaldehyde and the crude adduct **30** (Table III and eq 9), which was distilled. The nmr spectrum of **30** consisted of five singlets in the proper ratios at τ 2.80 (C_6H_5), 6.30 ($NCH_2C_6H_5$), 6.94 (NCH_2CCl_2), 7.67 (NCH_3), and 7.96 (CCl_2CH_3). Benzaldehyde was identified from its infrared spectrum and 2,4-dinitrophenylhydrazone.

N,N′-Dimethyl-N,N′-bis(2,2-dichloropropyl)-1,6-diaminohexane (**33**).—N,N′-Dimethylhexamethylenediamine (Ames Laboratories) was converted to the N,N′-dichloro compound with N-chlorosuccinimide in ether. Addition of 0.13 mole of 2-chloropropene to a mixture of 0.065 mole of the N,N′-dichloramine in 190 ml of 4 *M* H_2SO_4–HOAc followed by irradiation led to complete reaction of the chloramine within 10 min at 30°. The normal work-up gave 19.5 g of crude **33** from the partially neutralized aqueous solution, but the bisadduct decomposed at 180° on attempted distillation at 0.01 mm. The compound was readily identified by comparison of its infrared and nmr spectra with those of the monoadducts of 2-chloropropene; the yield was calculated on the basis of the dihydrochloride.

Diethyl-2,3-epoxypropylamine (**34**).—A solution of 0.14 mole of diethylchloramine in 45 ml of concentrated H_2SO_4 was prepared as described in paper V[1] and added to a solution containing 60 ml of water and 95 ml of concentrated H_2SO_4. No active chlorine was lost on addition of 0.13 mole of allyl alcohol in the dark, but a complete reaction occurred within 15 min after irradiation was begun. The reaction mixture was then poured into 200 g of ice and 700 ml of water. No product was obtained until pH 10 was reached on addition of 270 ml of 12 *N* NaOH. The crude epoxide (8.5 g) was extracted into ether and distilled to give 7.8 g of **34**, bp 54° (20 mm), $n^{25}D$ 1.4303 (lit.[35] bp 42–43° (7 mm), $n^{18}D$ 1.4380). A further 3.9 g of material separated from the basic aqueous solution after 24 hr; this was distilled to give 1.1 g of **34** and 2.0 g of residue. From this residue and that (0.6 g) of the preceding distillation was obtained 2.0 g of another product, bp 90° (1 mm), $n^{25}D$ 1.4475, which was probably a mixture of the diamino alcohols resulting from addition of diethylamine to the epoxide **34**. The nmr spectrum suggested the presence of both the primary and secondary alcohols that could form from **34**, since the low-field OH and H–C–O hydrogen resonances to-

(35) R. Rothstein and K. Binovic, *Compt. Rend.*, **236**, 1050 (1953).

gether reflected 2.5 H instead of the 2 H expected for the 1,3-diamine structure $Et_2NCH_2CH(OH)CH_2NEt_2$, and there were present only 11.5 NCH_2 hydrogens instead of 12.

The epoxide was further identified by conversion to the known diethyl-2-hydroxy-3-cyanopropylamine on treatment of 2.5 g of **34** with 2 g of KCN and 3.7 ml of concentrated HCl in 30 ml of hot ethanol for 6 hr. Distillation afforded 2.2 g of the cyanohydrin, bp 92–93° (2 mm), $n^{25}D$ 1.4528 (lit.[36] bp 108° (2 mm), $n^{32}D$ 1.4473), whose structure was confirmed as the isomer named above by the presence of the expected 2.0 hydrogens at low field in the nmr spectrum: τ 5.75 singlet (1 H), 6.15 multiplet (1 H), 7.2–7.6 (8 H), and 8.97 triplet (6 H).

Reactions of 2-Chloro-3-hydroxy-1-propene.—A good yield of the crude adduct **35** was obtained from a reaction between 0.13 mole each of the olefin and N-chloropiperidine in 70% H_2SO_4. The product, 29.2 g, was extracted into ether from the fully basified aqueous solution but decomposed at 60° on attempted distillaton at 0.05 mm. The alcoholic adduct, which also failed to yield a picrate or hydrochloride, was therefore identified by converting it to **N-(2,2,3-trichloropropyl)piperidine (9)**. From 8 g of crude **35** and 0.02 mole of $SOCl_2$ in 50 ml of chloroform was obtained 9.4 g of crude **9**, whose hydrochloride, picrate, and infrared spectrum were identical with those of the adduct prepared earlier from 2,3-dichloro-1-propene (Table I). The yield of **35**, based on **9** hydrochloride, was 72%.

An adduct similar to **35** was also obtained from diethylchloramine. Several attempts were made to convert 2-g samples of this material to the corresponding acetate, but the following all failed: 20 ml each of HOAc and Ac_2O with 1 ml of H_2SO_4 at 25° for 48 hr or under reflux for 3 hr (no reaction); 5:1 HOAc and H_2SO_4 at 25° for 48 hr (no reaction) or under reflux for 3 hr (very little material recovered).

N-2-Chloro-3-ethoxypropylpiperidine (21) from CH_3NO_2–H_2SO_4.—To the usual reaction flask was charged 145 ml of nitromethane, then 44 ml of concentrated H_2SO_4 with cooling, and finally 0.13 mole of N-chloropiperidine. No change in positive chlorine titer had occurred after 10 min of purging the solution with nitrogen or after the subsequent addition over 10 min of 0.13 mole of allyl ethyl ether. Irradiation initiated the reaction, which was completed in 30 min at 30°; the acid mixture was then poured into 200 g of ice and 500 ml of water. The usual pentane extracts and an emulsified phase were diluted with ether and back-extracted with water to give ultimately only 0.8 g of residual material (immediate precipitation with $AgNO_3$) upon neutralization, drying, and evaporation of the organic solvents. The aqueous phase, which now contained very little nitromethane, was partially neutralized with 100 ml of 12 *N* NaOH to liberate 15.7 g of crude **21**; basification to pH 10 liberated a further 7.0 g of adduct. The product (71%) was purified by distillation and found to be identical with that obtained in H_2SO_4–HOAc (Table II).

2,3-Dipiperidinobutane (39).—To 125 ml of Eastman trifluoroacetic acid (TFA) in the Vicor flask was added 0.11 mole of N-chloropiperidine, and the resulting solution was treated with *cis*-2-butene at 0–10° with rapid stirring under irradiation. When the reaction was complete, excess TFA was removed at 30° (1 mm) and half of the residue was dissolved in 300 ml of ether. The ether solution was extracted with 3 *N* NaOH and dried, whereupon 0.25 mole of piperidine was added, the solution was stripped, and the residue was distilled to give 3.58 g (31%) of the diamine **39**.

The other half of the TFA reaction mixture residue was dissolved in ether, neutralized, and evaporated as above. The residue was heated at 60° for 4 hr with 40 g of KCN in 300 ml of ethanol. The solids were removed by filtration and the liquid residue (3.2 g) was evaporated and distilled, bp 54–55° (0.1 mm), $n^{25}D$ 1.4680. An apparently pure sample of the β-cyanoamine **40**, obtained by preparative glpc (silicone column SF 96), was not analyzed, but its infrared and nmr spectra were straightforward. The yield of **40** was 30% based on the chloramine.

Attempts to secure the initial β-chloramine **38** failed owing to partial hydrolysis on washing ether solutions of **38** and TFA with base; bicarbonate washes failed to remove TFA completely.

Registry No.—**1**, 13426-57-8; **1** hydrochloride, 13426-58-9; **1** picrate, 5992-92-7; **2**, 5929-82-8; **2** hydrochloride, 5929-88-4; **2** picrate, 5921-89-5; **3**, 13426-63-6; **3** picrate, 13444-38-7; **4**, 5929-83-9; **4** picrate, 5929-94-2; **5**, 13444-39-8; **5** picrate, 13426-66-9; **6**, 5929-95-3; **6** hydrochloride, 5929-99-7; **7**, 5929-97-5; **7** hydrochloride, 5930-00-7; **7** picrate, 13426-70-5; **8**, 13426-71-6; **8** picrate, 13426-72-7; **9**, 13444-40-1; **9** hydrochloride, 13426-73-8; **10**, 13426-74-9; **10** picrate, 13426-75-0; **11**, 13426-76-1; **11** hydrochloride, 13426-77-2; **11** picrate, 13426-78-3; **12**, 13426-79-4; **12** hydrochloride, 13426-80-7; **12** picrate, 13437-78-0; **13**, 13426-81-8; **13** hydrochloride, 13426-82-9; **13** picrate, 13444-41-2; **14**, 5929-98-6; **14** hydrochloride, 5930-01-8; **14** picrate, 5930-02-9; **15**, 5929-86-2; **15** hydrochloride, 5929-92-0; **15** picrate, 5929-93-1; **16**, 13426-88-5; **17**, 13444-43-4; **18**, 13426-89-6; **18** picrate, 13426-90-9; **19**, 13444-44-5; **19** picrate, 13444-45-6; **20** hydrochloride, 13444-46-7; **20** picrate, 13444-47-8; **21**, 13444-48-9; **21** hydrochloride, 13444-49-0; **21** picrate, 13449-04-2; **22**, 5929-84-0; **22** picrate, 5929-90-8; *cis* **23**, 5929-96-4; *trans* **23**, 5931-58-8; *trans*-**23** picrate, 13426-30-7; **24**, 13426-31-8; **24** hydrochloride, 13426-32-9; **25**, 13426-33-0; **26**, 13444-51-4; **26** picrate, 13444-52-5; **26** hydrochloride, 13449-05-3; **27**, 13426-34-1; **27** hydrochloride, 13426-35-2; **28**, 13426-36-3; **28** hydrochloride, 13444-53-6; **29**, 13426-37-4; **29** hydrochloride, 13426-38-5; **30**, 13426-39-6; **30** hydrochloride, 13426-40-9; **31**, 13426-41-0; **31** hydrochloride, 13426-42-1; **31** picrate, 13426-43-2; **32** dipicrate, 13463-47-3; **33** dihydrochloride, 13444-54-7; **33** dipicrate, 13444-55-8; **34**, 2917-91-1; **36**, 13426-45-4; **36** picrate, 13426-46-5; **39**, 782-07-0; **39** dipicrate, 13444-56-9.

(36) H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **68**, 1291 (1946).