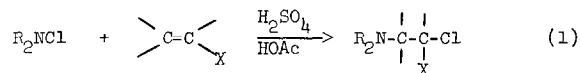THE CHEMISTRY OF NITROGEN RADICALS. III.[a] THE ADDITION
OF DIALKYL-n-CHLORAMINES TO SUBSTITUTED OLEFINS.

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We have recently reported the addition of dialkyl-N-chloramines in

a highly acidic medium to various unsaturated aliphatic hydrocarbons;[1,2]

these free radical processes involve protonated nitrogen radicals $R_2\overset{+}{N}H$ as

the chain carrying intermediate common to all the reactions   However, electro-

philic chlorination can sometimes compete effectively with radical addition

of chloramines to allenes and simple olefins, and we are presently studying

how the latter process can be enhanced and broadened in scope. In this re-

port we describe the remarkable facility with which radical addition occurs

to certain substituted olefins and the resulting syntheses of novel types of

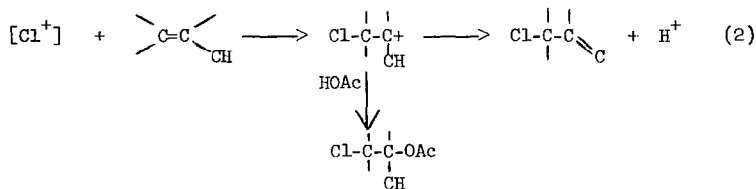chlorinated, tertiary amines according to eq. 1.

$$R_2NCl \quad + \quad \overset{\diagdown}{\diagup}C{=}C\overset{\diagup}{\underset{X}{\diagdown}} \quad \xrightarrow[\text{HOAc}]{H_2SO_4} \quad R_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{\underset{X}{C}}}{-}Cl \qquad (1)$$

In order to achieve more efficient additions of chloramines to

monoolefins it was desirable to identify the side reactions responsible for

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[a] The papers considered to constitute parts I and II of this series are,
respectively: R. S. Neale and M. R. Walsh, J. Am. Chem. Soc. 87, 1255
(1965); R. S. Neale, M. R. Walsh, and N. L. Marcus, J. Org. Chem. 30,
3683 (1965).

the low yields of adducts commonly observed. Thus, the reaction between cis-2-butene and dibutylchloramine under nitrogen (Table 1) afforded 17% of the neutral ionic reaction product 2-acetoxy-3-chlorobutane,[a] 60.5% of di-n-butylamine (DBA) and 1.5% of N-n-butylpyrrolidine (NBP), the Hofmann-Loeffler radical rearrangement product. No radical addition product was detected. Significantly, in the presence of air the reaction still gave only 15% of the chloroacetate and no NBP. 1-Butene behaved similarly as the % yields of [free radical adduct]/DBA/NBP changed from 12/56/12 under nitrogen to < 1/68/5 under air, while the yield of 1-chloro-2-acetoxybutane increased slightly from 18 to 22%.

These results show that the observable radical reactions were inhibited by oxygen, although the yields of one of the ionic chlorination products were hardly affected. We therefore believe that the only radical reactions present were chloramine addition or rearrangement, since the elimination by oxygen of significant hydrogen abstraction due to radical chain reactions would have produced a correspondingly large increase in the competing ionic reaction products, including the isolated chloroacetate. The reacted olefins not recovered as products from these reactions were doubtless converted to chloroolefins[b] by ejection of a proton from an initially formed chlorinated carbonium ion (eq. 2); solvolysis of this carbonium ion gave the observed chloroacetates.

$$[Cl^+] \;+\; \underset{CH}{\overset{}{\diagdown}} C{=}C \diagup \longrightarrow \; Cl{-}\underset{CH}{\overset{|}{\underset{|}{C}}}{-}\overset{|}{C}^+ \longrightarrow \; Cl{-}\overset{|}{\underset{|}{C}}{-}C{\diagdown}_C \;+\; H^+ \quad (2)$$

HOAc ↓

$$Cl{-}\underset{CH}{\overset{|}{\underset{|}{C}}}{-}\overset{|}{\underset{|}{C}}{-}OAc$$

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[a] The yield was similar (21%) from the reaction with N-chlorodiethylamine.[2]

[b] By analogy to 1,1-diphenylethylene, which gave 66% of 1-chloro-2,2-diphenylethylene,[1] and 1,1-dimethylallene, which gave 51% of 2-chloro-3-methyl-1,3-butadiene.[2]
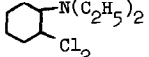
The absence of allylic hydrogen abstraction was further implied by the yields of adducts from diethylchloramine with propylene (42%), 1-butene (33%), and t-butylethylene (16%); the latter olefin with no allylic hydrogens gave the poorest yield of adduct. That this was not an overcompensating steric effect is shown by the successful addition of the chloramine to ethylene substituted with other similarly bulky groups (Table 1, experiments 8 and 10; also compare 4 and 10).

Finally, the reaction of diethylchloramine with allylbenzene demonstrated most directly that allylic hydrogens usually reactive toward radical abstraction are not so activated toward dialkylaminium radicals; thus, experiments 1 and 6 show that more addition of the radical $Et_2\overset{+}{N}H$ occurred to allylbenzene whose allylic hydrogens are also secondary and benzylic, than to propylene, whose allylic hydrogens are simply primary. It is therefore certain that facile intermolecular hydrogen abstraction is not a reaction characteristic of the aminium radical, which prefers instead to add to unsaturated carbon bonds[1,2] in H_2SO_4-HOAc. This behavior of chloramines proves false, at least in our systems, an earlier prediction[3] that hydrogen abstraction reactions of $R_2\overset{+}{N}H$ will generally predominate over addition to olefins.

Thus, electrophilic chlorination and not radical hydrogen abstraction is the process that so effectively competes with radical addition of chloramines to olefins. It therefore appeared that higher yields of free radical adducts might be realized from olefins substituted with groups that destabilize the potential carbonium ions more than the corresponding radicals. The experiments summarized in Table 1[a] illustrate the dramatic success of this approach; those olefins bearing electron withdrawing groups (relative to

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[a] The new structures shown therein were assigned on the basis of elemental analyses (C, H, Cl and N), infrared and, especially, n.m.r. spectra.

TABLE 1

Chloramination of Substituted Olefins in

$4 \underline{M} H_2SO_4$-HOAc at 30° under Nitrogen.

Experiment	Chloramine	Olefin	Adduct	% Yield
1	$(C_2H_5)_2NCl$	$CH_2=CHCH_3$	$(C_2H_5)_2NCH_2CHClCH_3$	42[a]
2	$(C_2H_5)_2NCl$	$CH_2=CHCl$	$(C_2H_5)_2NCH_2CHCl_2$	82[b]
3	$(C_2H_5)_2NCl$	$CH_2=C(CH_3)_2$	--	0
4	$(C_2H_5)_2NCl$	$CH_2=CClCH_3$	$(C_2H_5)_2NCH_2CCl_2CH_3$	84[c]
5	$(\underline{n}-C_5H_{11})_2NCl$	$CH_2=CClCH_3$	$(\underline{n}-C_5H_{11})_2NCH_2CCl_2CH_3$	41[d]
6	$(C_2H_5)_2NCl$	$CH_2=CHCH_2C_6H_5$	$(C_2H_5)_2NCH_2CHClCH_2C_6H_5$	57[e]
7	$(C_2H_5)_2NCl$	$CH_2=CH-\underline{t}-C_4H_9$	$(C_2H_5)_2NCH_2CHCl-\underline{t}-C_4H_9$	16[f]
8	$(C_2H_5)_2NCl$	$CH_2=CHSi(CH_3)_3$	$(C_2H_5)_2NCH_2CHClSi(CH_3)_3$	65[g]
9	$(C_2H_5)_2NCl$	$CH_2=CHCH_2Si(CH_3)_3$	--	0[h]
10	$(C_2H_5)_2NCl$	$CH_2=CCl-\underline{t}-C_4H_9$	$(C_2H_5)_2NCH_2CCl_2-\underline{t}-C_4H_9$	80[i]
11	$(C_2H_5)_2NCl$	$CH_2=CHCH_2CN$	$(C_2H_5)_2NCH_2CH=CHCN$	67[j]
12	$(C_2H_5)_2NCl$			60[k]
13	$(C_2H_5)_2NCl$	$CH_2=CBrCH_3$	$(C_2H_5)_2NCH_2CClBrCH_3$	46[l]

[a] B.p. 72° (38 mm.), $n^{24}D$ 1.4315, picrate m.p. 125-126.5° (lit. b.p. 69° (35 mm.), $n^{20}D$ 1.4332, picrate m.p. 125.5-126°, J. F. Kerwin et al., <u>J. Am. Chem. Soc.</u> <u>69</u>, 2961 (1947)). [b] B.p. 61.8° (10 mm.), $n^{24}D$ 1.4527, hydrochloride m.p. 115.5-117.0°, picrate m.p. 109-110.5°. [c] B.p. 71° (11 mm.), $n^{24}D$ 1.4522, hydrochloride m.p. 144-145°, picrate m.p. 92-95.5°. [d] B.p. 77-81° (0.1 mm.), $n^{25}D$ 1.4577, picrate m.p. 83.0-84.5°; also isolated was 43% of 2-methyl-N-<u>n</u>-pentylpyrrolidine. [e] B.p. 72-74° (0.02 mm.), $n^{25}D$ 1.5090, picrate m.p. 95.5-97°. [f] Picrate m.p. 117-118.5°. [g] B.p. 53° (1.5 mm.), $n^{24}D$ 1.4505, hydrochloride m.p. 92.5-96.0°, picrate m.p. 126.5-127.5°. [h] Main product was 42% of hexamethyldisiloxane. [i] B.p. 48.5° (0.2 mm.), $n^{25}D$ 1.4682, hydrochloride m.p. 190.5-191.0°. [j] B.p. 62-71° (2 mm.), mixture 50% <u>cis</u>-($n^{24}D$ 1.4554) and 50% <u>trans</u>-isomer ($n^{24}D$ 1.4569), picrate (<u>trans</u>-isomer) m.p. 140-141.5°. [k] B.p. 76-79° (0.5 mm.), $n^{24}D$ 1.4894, hydrochloride m.p. 151-154°. [l] B.p. 31-31.5° (0.05 mm.), $n^{24}D$ 1.4770, hydrochloride m.p. 120-123.5°, picrate m.p. 91-93°.

methyl) which do not place a π-electron system in conjugation with the olefinic bond gave adducts in synthetically useful yields. The five substituents[4] illustrated are Cl, Br, $Si(CH_3)_3$, CH_2CN, and $CH_2C_6H_5$. Some other substituted olefins C=C-X were either inert to any reaction (X=CN or $CONH_2$) or reacted very rapidly without affording any insolable adduct (X=OCH_3, $OCOC_2H_5$, or 4-pyridinyl). Minisci[5] has also observed the inertness of acrylic derivatives in certain of his reactions of chloramines with olefins. An obvious exception to our definition of a useful substituent is the vinyl group, since chloramine additions to 1,3-dienes that are not highly alkylated, such as butadiene[1] or 1,3-cyclooctadiene, occur in > 60% yield.

The experiments which utilized chloroolefins are particularly informative. Replacement of methyl by chloro (experiments 1, 2 and 3, 4) led to the preparation of β,β-dichloramines in very good yield; these adducts are the first representatives of this class of compound. In fact, the -Cl group actually may enhance the radical addition as well as discourage the ionic reaction. Thus, dipentylchloramine in the presence of propylene gave 80% of the Hofmann-Loeffler rearrangement product and no addition or ionic reaction products,[2] although addition of this chloramine to 2-chloropropene now competed well with the Hofmann-Loeffler rearrangement (experiment 5). Experiment 10 shows that the radical addition to chloroolefins is facile even with the bulky t-butyl group attached to the chain carrying carbon radical $R_2\overset{+}{N}HCH_2\overset{.}{C}Cl\text{-}t\text{-}$ C_4H_9, and experiment 12 demonstrates the usefulness of 1,2-dialkyl-1-chloroolefins. A β-brom-β-chloramine, another novel composition, was obtained from 2-bromopropene, although with somewhat reduced efficiency (experiment 13). The β,β-dihalamines are easily separated from other basic products by the addition of base to the diluted reaction mixture;[a] the weakly basic dihal-

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[a] The reactions reported in this paper were carried out according to the general method described in ref. 2.

amines are liberated at pH 5-6, leaving amines of ordinary basicity in solution.

The substituent effect was also demonstrated in the reactions of t-butylethylene and trimethylvinylsilane (experiments 7, 8), wherein the bulky but now overall electron-withdrawing group $(CH_3)_3Si$ enhanced the addition of the chloramine to give the β-chloro-β-silylamine, another novel type of compound.

Methyl groups substituted by electronegative substituents also disposed an olefin toward the radical addition; this effect is illustrated by experiment 11, which spotlights the cyanomethyl group, and by experiment 6, already discussed. The initial adduct from 3-butenenitrile dehydrohalogenated on exposure to aqueous acid to give the acrylonitrile derivative shown.

In conclusion, the addition of chloramines to substituted olefins via free radical chain reactions offers an attractively simple and powerful synthetic route to several novel, substituted amines which are difficult to obtain by other methods. Thus, these results further[1,2] illustrate the remarkable versatility of nitrogen radicals as synthetic intermediates.

REFERENCES

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

2. R. S. Neale, ibid. 86, 5340 (1964).

3. F. Minisci and R. Galli, Tetrahedron Letters, 167 (1964).

4. The overall electron withdrawing effect of the first three of these groups relative to methyl is illustrated by their σ-substituent constants   R. W. Taft, Jr. in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, 1956, p. 595.

5. F. Minisci and R. Galli, Chim. Ind. (Milan) 46, 546 (1964).