THE JOURNAL OF Organic Chemistry®

VOLUME 32, NUMBER 11

NOVEMBER 15, 1967

The Chemistry of Nitrogen Radicals. V. The Free-Radical Addition of Dialkyl-N-chloramines to Olefinic and Acetylenic Hydrocarbons

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Received April 28, 1967

The addition of dialkyl-N-chloramines to aliphatic 1,3-dienes, 1,2-dienes, terminal olefins, and acetylenes in sulfuric acid–acetic acid is described. These facile, free-radical chain reactions all involve the addition of an aminium radical $R_2\dot{N}H^+$ to a carbon–carbon multiple bond as the key step in the process, which affords 1:1 adducts in 15–68% yield. Since addition, not hydrogen abstraction, is characteristic of aminium radical reactions with these unsaturated hydrocarbons, chloramination provides a useful, direct route to β-chloroalkyl-, β-chloroalkenyl-, and δ-chloroalkenylamines in those cases in which nonradical reactions or the Hofmann–Loeffler chloramine rearrangement do not compete successfully with the free-radical addition.

During a general study designed to define and utilize the potential of amino radicals as synthesis intermediates, we have explored a remarkable reaction whereby protonated aliphatic N-chlorodialkylamines add to unsaturated hydrocarbons in one step to produce chlorinated tertiary amines.[1] In the present paper we describe the application of this free-radical process to unsubstituted olefins, 1,3-dienes, 1,2-dienes, and acetylenes in the solvent sulfuric acid–acetic acid; in the following paper we present our results using both substituted olefins and other acidic solvents. These papers together define the scope and limitations of the chloramination reaction, which provides ready access to a large number of previously unavailable compounds. As will be shown below, all these chloraminations are the consequence of a free-radical chain sequence of the type shown in eq 1 and 2, in which the key propagation

$$R_2NH^+ + >C{=}C< \longrightarrow R_2NH^+{-}\overset{|}{C}{-}\overset{|}{C}\cdot \qquad (1)$$

$$R_2NH^+{-}\overset{|}{C}{-}\overset{|}{C}\cdot + R_2NH^+{-}Cl \longrightarrow R_2NH^+{-}\overset{|}{C}{-}\overset{|}{C}{-}Cl + R_2NH^+ \qquad (2)$$

step is the addition of a protonated dialkylamino (*i.e.*, dialkylaminium) radical to a carbon–carbon multiple bond, whether or not allylic hydrogens are present. We wish to emphasize immediately that this characteristic preference of aminium radicals for addition does not necessarily, or even probably, reflect the behavior of most other kinds of amino radicals. We anticipate, however, that the results of some studies with which we are presently involved, along with the existing data reviewed below, will increase our understanding of what constitutes the "characteristic behavior" of a given type of nonprotonated amino radical.

Few additions similar to those presently reported of aminium radicals or closely related species to unsaturated hydrocarbons have been described. The major effort apart from ours has been made by Minisci and co-workers,[2] who have been actively studying the chemistry of amino radicals generated from reactions between precursor amine derivatives and transition metal salts, usually in methanolic solution; we shall consider those aspects of the work which deal specifically with chloraminations of unsaturated hydrocarbons in the light of our own results in the Discussion section. Little work with amino radicals has been carried out in acidic media, whether or not with added substrates, with the obvious exception of the Hofmann–Loeffler rearrangement of protonated N-chloramines.[3] Thus, in only a single paper[4] have simple amino radicals been reported to add to olefinic hydrocarbons. Here the radicals generated from hydroxylamines by reduction with titanium or vanadium salts in acidic methanol added to 1,3-dienes or 2-butene to afford aminoallyl or aminoalkyl radicals; these then dimerized, since no chain-carrying step analogous to reaction 2 was possible. An additional example of aminium radical

(1) We have given two preliminary accounts of this work: (a) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 2666 (1963); (b) R. S. Neale, *ibid.*, **86**, 5340 (1964).

(2) The most descriptive, although not the earliest, account of their work is given in F. Minisci, R. Galli, and G. Pollina, *Chim. Ind.* (Milan), **47**, 736 (1965).

(3) (a) The bulk of the work is reviewed by M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963); see also subsequent articles, *e.g.* (b) R. S. Neale and M. R. Walsh, *J. Am. Chem. Soc.*, **87**, 1255 (1965); (c) R. S. Neale, M. R. Walsh, and N. L. Marcus, *J. Org. Chem.*, **30**, 3683 (1965); (d) G. Adam and K. Schreiber, *Chem. Ind.* (London), 989 (1965); (e) E. Schmitz and D. Murawski, *Chem. Ber.*, **99**, 1493 (1966).

(4) C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).

addition to olefins may be Chow's photolysis of nitrosamines in acidic methanol in the presence of olefins to give α-amino oximes.[5] The occasional attempts to effect aromatic aminations *via* amino radicals in acidic media[4,6] are also noteworthy, since in a sense they qualify as examples of double-bond amination.

The chemistry of neutral, unmodified amino radicals, on the other hand, has received somewhat more attention, but in very few cases was addition to carbon–carbon multiple bonds specifically sought. Most pertinent is the liquid phase thermal decomposition of tetramethyltetrazene in the presence of olefins carried out by Cowley and Waters,[7] who failed to observe amination products of 1-octene. Amination products were obtained from α-methylstyrene, however, but these cannot be unequivocally attributed to dimethylamino radical addition to the double bond. Similarly, amino radicals from photolyzed amines failed to add to propylene in the vapor phase.[8]

Most of the work dealing with a third class of amino radicals—those modified by the presence of an electron-withdrawing N substituent other than a proton—is somewhat ambiguous in regard to illustrating characteristic tendencies of these radicals for addition to simple olefins. Bis(trifluoromethyl)amino radicals, $(CF_3)_2N\cdot$, are reported to add to halo olefins, but reactions with alkyl olefins unfortunately were not described.[9] The related difluoramino radicals $\cdot NF_2$ apparently formed from N_2F_4 under two types of conditions and reacted with alkyl olefins in two different ways. In the first, dark reactions under autoclave conditions led to α-N-fluoriminonitriles in the presence of sodium fluoride, no doubt *via* dehydrofluorination of initially formed 1,2-bis-N,N-difluoraminoalkanes.[10a] However, no evidence that these particular reactions involved $\cdot NF_2$ radicals was presented. The second type of $\cdot NF_2$ radical reactions with olefins was observed under photolytic conditions. When irradiated, $\cdot NF_2$ radicals apparently decomposed to fluorine atoms which in turn attacked an olefin, *e.g.*, 2-butene, by either hydrogen abstraction or addition; the resulting radicals then combined with $\cdot NF_2$ radicals to give the observed products $CH_3CH{=}CHCH_2NF_2$ and $CH_3CHFCH(NF_2)CH_3$.[10b]

Anilino radicals $C_6H_5\dot{N}H$ generated from the thermal decomposition of percarbamates were found to efficiently initiate the polymerization of styrene,[11] but that this involved amino radical addition to the double bond can only be assumed.

Finally, although a few reported examples of N-bromosuccinimide to olefins[12] may have involved succinimidyl radicals, simple amide radicals did not add to olefins under the influence of weak ultraviolet radiation.[13a] The only apparent examples of the efficient addition of modified amino radicals to olefins consist of the work of Schrage[13b] and of Swern,[13c] who obtained 1:1 adducts of N-chlorinated urethans in benzene solution.

(5) Y. L. Cho, *J. Am. Chem. Soc.* **87**, 4642 (1965).
(6) F. Minisci, R. Galli, and M. Cecere, *Tetrahedron Letters*, 4663 (1965); H. Bock and K. Kompa, *Chem. Ber.*, **99**, 1361 (1966).
(7) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).
(8) C. H. Bamford, *ibid.*, 17 (1939).
(9) R. N. Hazeldine and A. E. Tipping, *ibid.*, 6141 (1965).
(10) (a) A. L. Logothetis and G. N. Sausen, *J. Org. Chem.*, **31**, 3689 (1966); (b) C. L. Bumgardner, *Tetrahedron Letters*, 3683 (1964).
(11) E. L. O'Brien, F. M. Veringer, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **79**, 6238 (1957).
(12) L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **29**, 1290 (1964); W. J. Bailey and J. Bellow, *ibid.*, **20**, 525 (1955).
(13) (a) R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Am. Chem. Soc.*, **88**, 3051 (1966); (b) K. Schrage, *Tetrahedron*, **23**, 3033 (1967); (c) T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966).

Results

Olefinic Hydrocarbons (Table I). 1,3-Dienes.—The first unsaturated substrate selected for reaction with N-chlorodialkylamines was butadiene, because it is susceptible to the facile addition of free radicals of many types[14] including the *t*-butoxy radical,[15] which ordinarily prefers[16] to abstract allylic hydrogen atoms from simple olefins. In the first experiment, N-chloro-di-*n*-butylamine gave 60% of the adduct **1** when butadiene was bubbled into 200 ml of a stirred solution of the chloramine (0.1 mole) in sulfuric acid–acetic acid in the dark (eq 3). As was also true of the other reactions in Table I, the homogeneous mixture was worked up by pouring it into a mixture of ice and water and removing small amounts of neutral products by extraction with pentane. The major of these products obtained from the butadiene reactions was 3-acetoxy-4-chloro-1-butene (**32**). Sodium hydroxide solution (12 *N*) was then added until the product separated; this often began at pH <7 because of the decreased basicity[17] of the β-halamines, where more strongly basic products separated only on basification to pH 10. The 1,3-diene adducts **1**–**4** were readily identified by spectroscopic methods and by derivatization as noted below and described in the Experimental Section.

$$\underset{0.5\ M}{Bu_2NCl} + CH_2{=}CHCH{=}CH_2 \xrightarrow[\text{HOAc, } N_2,\ 10^\circ,\ 36\text{ min}]{4\ M\ H_2SO_4\text{ in}} \underset{\mathbf{1},\ 60\%}{Bu_2NCH_2CH{=}CHCH_2Cl} + \underset{\mathbf{32},\ \sim 7\%}{CH_2{=}CHCHCH_2Cl\ (OAc)} \quad (3)$$

When reaction 3 was repeated in the presence of a stream of air, instead of nitrogen, the chloramine was consumed twice as fast but no adduct was produced; instead, 72% of dibutylamine was isolated along with three times the usual amount (~1 g) of the chloroacetate **32**.

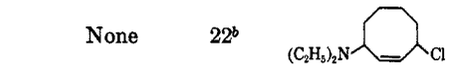
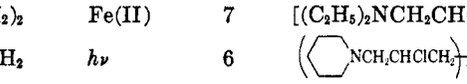
Of the other reactions analogous to eq 3, most significant was the efficient addition of N-chloro-(methyl-4-phenylbutyl)amine to butadiene, since the benzylic hydrogen atoms present in the C-4 position favored in the Hofmann–Loeffler reaction might have caused that process to preempt the desired addition. However, only 2% of the rearrangement products[3c] was obtained along with at least 53% of the addition product, which was unstable and was reduced to **3** with $LiAlH_4$ (eq 4). The addition of chloramines to buta-

$$\underset{\text{Cl}}{C_6H_5(CH_2)_4NCH_3} + CH_2{=}CHCH{=}CH_2 \xrightarrow[2.\ LiAlH_4]{1.\ \text{acid}} \underset{\mathbf{3},\ 53\%}{C_6H_5(CH_2)_4N(CH_3)CH_2CH{=}CHCH_3} \quad (4)$$

(14) M. L. Poutsma, *ibid.*, **31**, 4167 (1966), and references cited therein; J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **84**, 3946 (1962).
(15) (a) J. K. Kochi, *ibid.*, **84**, 2785 (1962); (b) F. Minisci and R. Galli, *Tetrahedron Letters*, 533 (1962).
(16) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).
(17) A. Roedig, K. Grohe, and G. Märkl, *Chem. Ber.*, **99**, 121 (1966); W. E. Hanby, G. S. Hartley, E. O. Powell, and H. N. Rydon, *J. Chem. Soc.*, 519 (1947); B. Cohen, E. R. van Artsdalen, and J. Harris, *J. Am. Chem. Soc.*, **70**, 281 (1948).

TABLE I

FREE-RADICAL ADDITION OF N-CHLORODIALKYLAMINES TO OLEFINIC HYDROCARBONS IN 4 *M* SULFURIC ACID–ACETIC ACID AT 30° UNDER NITROGEN

Chloramine	Olefinic hydrocarbon	Catalyst	Time, min	Adduct	% yield	Compd[a]
$(n\text{-}C_4H_9)_2NCl$	$CH_2{=}CHCH{=}CH_2$	None	42[b]	$(n\text{-}C_4H_9)_2NCH_2CH{=}CHCH_2Cl$	60	1
$(n\text{-}C_5H_{11})_2NCl$	$CH_2{=}CHCH{=}CH_2$	None	10[b,c]	$(n\text{-}C_5H_{11})_2NCH_2CH{=}CHCH_2Cl$	42	2
$C_6H_5(CH_2)_4N(Cl)CH_3$	$CH_2{=}CHCH{=}CH_2$	None	15[b]	$C_6H_5(CH_2)_4N(CH_3)CH_2CH{=}CHCH_3$	53[d]	3
$(C_2H_5)_2NCl$		None	22[b]		68[e]	4
$(C_2H_5)_2NCl$	$CH_2{=}C{=}CH_2$	Fe(II)	55[f]	$(C_2H_5)_2NCH_2C(Cl){=}CH_2$	35	5
$(C_2H_5)_2NCl$	$CH_2{=}C{=}C(CH_3)_2$	None	10	$(C_2H_5)_2NCH_2C(Cl){=}C(CH_3)_2$	11[g]	6
$(n\text{-}C_4H_9)_2NCl$	$CH_2{=}C{=}CH_2$	$h\nu$	15	$(n\text{-}C_4H_9)_2NCH_2C(Cl){=}CH_2$	44	7
$(n\text{-}C_5H_{11})_2NCl$	$CH_2{=}C{=}CH_2$	$h\nu$	26	$(n\text{-}C_5H_{11})_2NCH_2C(Cl){=}CH_2$	8[h]	8
$(n\text{-}C_4H_9)_2NCl$	$CH_2{=}CH_2$	$h\nu$	40	$(n\text{-}C_4H_9)_2NCH_2CH_2Cl$	15[i]	(9)
$(C_2H_5)_2NCl$	$CH_2{=}CHCH_3$	Fe(II)	11	$(C_2H_5)_2NCH_2CHClCH_3$	42	(10)
$(C_2H_5)_2NCl$	$CH_2{=}CHCH_2CH_3$	Fe(II)	14	$(C_2H_5)_2NCH_2CHClCH_2CH_3$	33	11
$(C_2H_5)_2NCl$	$CH_2{=}CHC(CH_3)_3$	$h\nu$	10	$(C_2H_5)_2NCH_2CHClC(CH_3)_3$	16[j]	12
$(n\text{-}C_4H_9)_2NCl$	$CH_2{=}CHCH_2CH_3$	Fe(II)	13	$(n\text{-}C_4H_9)_2NCH_2CHClCH_2CH_3$	16[k]	13
$(C_2H_5)_2NCl$	$(CH_2{=}CHCH_2CH_2)_2$	Fe(II)	7	$[(C_2H_5)_2NCH_2CHClCH_2CH_2]_2$	49[e]	14
	$(CH_2{=}CHCH_2)_2CH_2$	$h\nu$	6		27[e]	15
$(C_2H_5)_2NCl$	$(CH_2{=}CHCH_2)_2O$	$h\nu$	10	$[(C_2H_5)_2NCH_2CHClCH_2]_2O$	40	16

[a] The numbers of previously known compounds are enclosed by parentheses. [b] Reaction spontaneous on addition of diene; temperature 5–15°. [c] Chloramine added to acid over 6 min concurrently with stream of butadiene. [d] Product obtained on reduction of the chloramination product with $LiAlH_4$. [e] Yield of picrate derivative. [f] Temperature 40°. [g] For other products, see text; only 0.6 equiv of the allene gave complete reaction of the chloramine. [h] Not analyzed; major product was 63% of N-pentyl-2-methylpyrrolidine. [i] Also isolated was 53% of N-butylpyrrolidine. [j] Purified as the hydrochloride. [k] Also isolated were 10% of N-butylpyrrolidine and 46% of dibutylamine; a light-catalyzed reaction gave a similar product distribution.

diene, therefore, must be preferred to chloramine rearrangement. Dienes of the type RCH=CHCH=CHR would probably behave similarly, since 1,3-cyclooctadiene gave a good yield of the diethylchloramine adduct **4** (Table I). Adduct **4** was also reduced with $LiAlH_4$; the product, 3-diethylaminocyclooctene (**21**), had been described previously.

Although the structure of adduct **1** was evident from its spectral properties, the compound was unambiguously identified by converting it to the known diamine **18** with dibutylamine in benzene (eq 5). An

$$\mathbf{1} + 2Bu_2NH \xrightarrow[\Delta,\ 27\ hr]{benzene} Bu_2NCH_2CH{=}CHCH_2NBu_2 \quad (5)$$

18, 85%

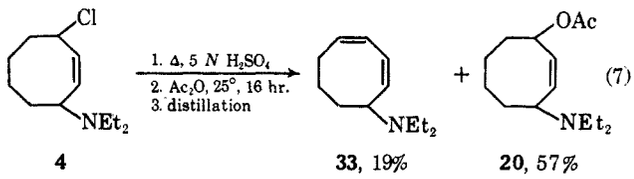
analogous diamine **19** was obtained as a distillation residue when purification of the adduct from N-chloro-di-*n*-pentylamine and butadiene was attempted. The 42% yield of adduct **2** shown in Table I was assigned on the basis of the dipicrate of the diamine **19**, the compound actually isolated. The solvolysis of **1** to the acetate **17** was also carried out (eq 6), but the reaction

$$\mathbf{1} + NaOAc \xrightarrow[85°,\ 26\ hr]{HOAc} Bu_2NCH_2CH{=}CHCH_2OAc \quad (6)$$

17, 83%

was quite slow as the result of the anticipated depression of the solvolysis rate of allylic chlorides that contain a proximate protonated amino nitrogen atom.[18]

The conversion of the 1,3-cyclooctadiene adduct **4** to the acetate **20** (eq 7) was also carried out, but instead of direct acetolysis of the adduct similar to reaction 6, the crude alcohol was first obtained by heating **4** under reflux for 30 min in 5 *N* sulfuric acid. However, acetylation with acetic anhydride at room temperature gave a product whose distillation produced not only the desired acetate but an aminodiene **33** as well (eq 7). The structure of **33** followed from its nmr spectrum, which contained peaks due to four vinyl hydrogens and to the hydrogen —CH(NEt_2)C=C at τ 6.6 also observed in the spectra of **4** and **20**. Compound **33** rearranged quantitatively on attempted glpc purification (Carbowax column, 175°) to a mixture of two isomers in which the amino group was not presumably attached to C-1 and C-2 of the conjugated diene system. The isomeric mixture contained three vinyl hydrogens, and its ultraviolet spectrum ($\lambda_{max}^{isooctane}$ 279 mμ (ϵ_{max} 8550)) was similar to that of a known 1-dialkylamino-1,3-cyclohexadiene.[19]



(7)

4 **33**, 19% **20**, 57%

Although the adducts **1–4** were produced from reactions that required no obvious initiation, the nature of the products and the severe inhibitory effect of air toward the generation of adduct **1** make any except a free-radical chain process analogous to eq 1 and 2 an unlikely mechanism for the reactions. From the well-defined course of the Hofmann–Loeffler rearrangement,[20] we know that the R_2NH^+ radical, not a chlorine atom, must be the chain-carrying species. Furthermore, in the case of the other types of unsaturated substrates described below, the adducts were always of the terminal amino type, as expected for the initial addition of R_2NH^+ to an olefinic or acetylenic bond, and many

(18) C. A. Grob, F. Ostermayer, and W. Raudenbusch, *Helv. Chim. Acta*, **45**, 1672 (1962).

(19) G. Opitz and W. Merz (*Ann.*, **652**, 139 (1962)) gave λ_{max}^{hexane} 281 mμ (ϵ_{max} 13,000) for 1-piperidino-3,5,5-trimethyl-1,3-cyclohexadiene.

(20) S. Wawzonek and P. J. Thelen, *J. Am. Chem. Soc.*, **72**, 2118 (1950); S. Wawzonek and T. P. Culbertson, *ibid.*, **81**, 3367 (1959); E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

of these reactions required initiation by light or an iron(II) salt. Finally, the failure of other basic adducts in this and the accompanying paper to form under radical-inhibiting conditions, with one very interesting exception,[21] confirms the improbability of an ionic route to the chloramine–olefin adducts. Furthermore, when we attempted by various means to add dialkylchloramines to olefins or dienes in an inert medium in the absence of acid (or metal ions[2]), we were unable to detect any addition products. It is pertinent to note that the addition of nitrogen trichloride to olefins[22] in an inert medium occurs *via* an ionic route and is, therefore, apparently a reaction unrelated to those we describe here.

The chloroacetates such as 3-acetoxy-4-chloro-1-butene and the corresponding products from the monoolefins mentioned below no doubt did result from ionic processes owing to the action of protonated chloramines as electrophilic chlorinating agents (eq 8). It was ap-

$$R_2NH^+Cl \longrightarrow [R_2NH + Cl^+] \xrightarrow{>C=C<} Cl-\overset{|}{C}-\overset{|}{C}^+ \quad (8)$$

parently because of the predominance of such chlorination reactions that cyclopentadiene and 2,5-dimethyl-2,4-hexadiene failed to yield adducts, although both dienes caused the spontaneous and rapid decomposition of diethylchloramine.

1,2-Dienes.—Three allenic hydrocarbons were subjected to the chloramination reaction. In contrast to butadiene, allene gave chloramine adducts (**5, 7,** and **8**) only on irradiation with ultraviolet light or on addition of traces of ferrous ammonium sulfate; no reaction occurred between allene and dibutylchloramine on irradiation in the presence of a stream of air. Although it added to butadiene, di-*n*-pentylchloramine rearranged in the presence of allene and gave only 8% of the adduct **8**. Proof that the purified adduct **7** contained a terminal dialkylamino group was afforded on reduction to the known di-*n*-butyl-*n*-propylamine (eq 9). However, the considerable discrepancy be-

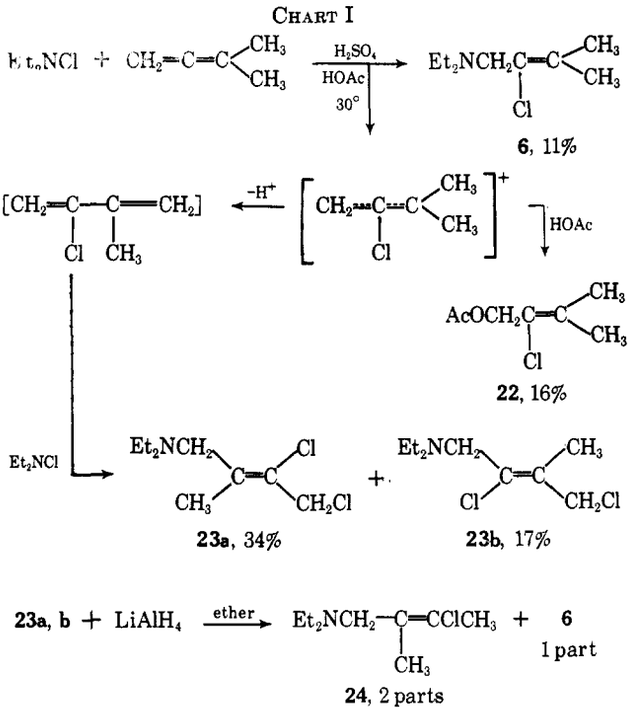
$$Bu_2NCH_2C(Cl)=CH_2 \xrightarrow[40\ psi\ H_2]{Pt\text{-}HOAc,\ 23^\circ} Bu_2NCH_2CH_2CH_3 \quad 64\% \quad (9)$$

7

tween the crude yields (~60%) and the yields following distillation of adducts **5** and **7** (Table I) suggests the presence of some less stable products, most reasonably isomeric adducts resulting from addition of R_2NH^+ to the central carbon of allene. Furthermore, the crude yield of the N,N-diethyl adduct **5** was 63% and that based on the crude hydrochloride of this product was 58%; however, recrystallization to remove low melting material left only 35% of **5** hydrochloride. There are several examples[23,24] of attack on allene by a given radical at both the terminal and internal positions; however, as was true of the present aminium radical reactions, the preferred site of attack was always at the terminal carbon, although the reversibility of terminal attack[23b] sometimes led to the ultimate formation[23c] of major amounts of the product resulting from an irreversible[23b] internal attack.

The reaction between diethylchloramine and 3-methyl-1,2-butadiene was particularly interesting since there was effected, as anticipated, a pronounced decrease in the extent of free-radical addition by the potentially *tertiary* allylic center present in the diene. The course of this reaction is probably that depicted in Chart I. Now the majority of products (**22** and **23a,b**)

CHART I

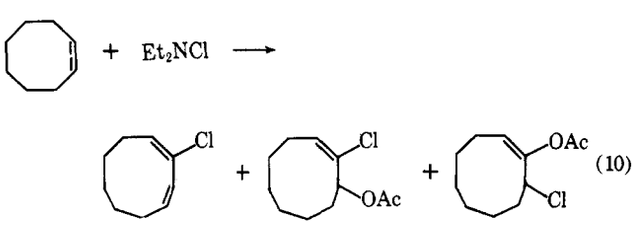


$$\mathbf{23a,b} + LiAlH_4 \xrightarrow{ether} Et_2NCH_2-\overset{CH_3}{\overset{|}{C}}=CClCH_3 \quad (1\ part) + \mathbf{6}$$

24, 2 parts

resulted from ionic chlorination of the allene, and the desired free-radical adduct **6** was formed in only low yield. That **6** was still of the terminal amino type contrasts to prior radical additions to dimethylallene,[24] in which attack at the central carbon was predominant if not exclusive. The isomers **23a,b** were not separated but were identified by reduction with $LiAlH_4$ to a mixture of the original adduct from dimethylallene (**6**) and its isomer **24**, which were separated by preparative glpc. The *cis–trans* isomerism of **23a,b** as shown was assumed.

1,2-Cyclononadiene, a special example of a 1,3-disubstituted allene, failed to yield an isolable adduct with diethylchloramine as it reacted quickly (20 min) and spontaneously to give only ionic chlorination products (eq 10). Although proton elimination might have



given the cyclic diene **25**, the fact that no basic adduct of **25** with the chloramine was observed, analogous to

(21) R. S. Neale and E. B. Whipple, *J. Am. Chem. Soc.*, **86**, 3130 (1964).
(22) G. H. Coleman and H. P. Howells, *ibid.*, **45**, 3084 (1923).
(23) (a) K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele, *J. Org. Chem.*, **28**, 1952 (1963); K. Griesbaum, A. A. Oswald, E. R. Quiram, and P. E. Butler, *ibid.*, **30**, 261 (1965); (b) E. I. Heiba, *ibid.*, **31**, 776 (1966); (c) K. Griesbaum, A. A. Oswald, and D. N. Hall, *ibid.*, **29**, 2404 (1964); P. I. Abell and R. S. Anderson, *Tetrahedron Letters*, 3727 (1964).
(24) H. G. Kuivila, W. Rahman, and R. M. Fish, *J. Am. Chem. Soc.*, **87**, 2835 (1965); T. L. Jacobs and G. E. Illingworth, Jr., *J. Org. Chem.*, **28**, 2692 (1963).

the results with dimethylallene, suggests that **25** may have formed instead on work-up of the reaction, perhaps by elimination of amine from the desired adduct.

Simple Olefins.—Terminal olefins afforded adducts (**9–16**, Table I) in moderate to poor yields which varied with both olefin and chloramine structure. Although spontaneous reactions occurred on addition of the olefins to the acid solutions of the chloramines, initiation by ultraviolet light or an iron(II) salt was required to secure any of the desired free-radical adducts. The chloramination of simple olefins was shown previously[25] to suffer not from abstraction of allylic hydrogen atoms by $R_2\dot{N}H^+$, but from a strongly competitive electrophilic chlorination of the olefins. Thus, dialkyl olefins (*cis*-2-butene or isobutylene, eq 11) and diphenylethylene (eq 12) reacted exclusively *via* the ionic pathway, whereas terminal olefins gave both radical and ionic products, *e.g.*, the chloroacetate **30** and the adduct **13** from 1-butene (eq 13). When the latter reaction was allowed to occur spontaneously in a stream of air at 20°, none of the adduct **13** was obtained.

$$Bu_2NCl + cis\text{-}CH_3CH{=}CHCH_3 \xrightarrow{20^\circ} CH_3\underset{Cl}{C}H\underset{OAc}{C}HCH_3 + Bu_2NH + \text{N-Bu} \quad (11)$$

		(DBA)	(NBP)
$h\nu$, N_2:	**31**, 17%	61%	2%
air:	15%	66%	0%

$$Bu_2NCl + (C_6H_5)_2C{=}CH_2 \xrightarrow[19\ min]{6^\circ,\ N_2} (C_6H_5)_2C{=}CHCl + DBA \quad (12)$$

66% 84%

$$Bu_2NCl + CH_2{=}CHCH_2CH_3 \xrightarrow{20^\circ} ClCH_2\underset{OAc}{C}HCH_2CH_3 + Bu_2NCH_2\underset{Cl}{C}HCH_2CH_3 + DBA + NBP \quad (13)$$

$h\nu$, N_2:	**30**, 18%	**13**, 12%	56%	12%
air:	24%	none	70%	<5%

However, dialkylchloramines which could undergo facile Hofmann–Loeffler rearrangement will probably do so, at the expense of both free-radical addition to and electrophilic chlorination of terminal olefins. Thus, N-chloro-di-*n*-pentylamine in the presence of propylene (which gave 42% of adduct **10** with diethylchloramine) rearranged under the influence of a catalytic amount of an iron(II) salt to yield 80% of N-pentyl-2-methylpyrrolidine and 15% of di-*n*-pentylamine as the only significant products. In the case of nonterminal olefins, however, electrophilic chlorination is the major reaction regardless of chloramine structure, since *cis*-2-butene gave only ionically derived products from dipentylchloramine as well as from the diethyl and dibutyl homologs.

The variation in yield of adduct with olefin structure probably is a consequence of steric factors. Thus, there was a downward progression of adduct yields in reactions of diethylchloramine with methyl-, ethyl-, and *t*-butylethylene (42, 33, and 16%). However, the yield of adduct from 1-butene and dibutylchloramine was also low, being only half that from the same olefin and diethylchloramine; the alkyl groups in the chloramine must therefore exert their own steric influence. A similar effect was also apparent in Minisci's chloraminations of 1-hexene.[2]

The structures of the β-chloramines **9–13** were readily established by comparison of the spectral properties of the new compounds **11–13** with those of the known amines **9** and **10**. Since the yields of purified adducts were similar to those of the crude products, adducts with nitrogen attached to C-2 of the olefins were either not formed or were not isolable. One adduct, **12**, was reduced with lithium aluminum hydride (eq 14). The

$$Et_2NCH_2\underset{Cl}{C}HCH_2CH_3 \xrightarrow[\text{THF, } \Delta,\ 15\ hr]{LiAlH_4} Et_2N\underset{CH_3}{C}HCH_2CH_3 + Et_2NCH_2CH_2CH_2CH_3 \quad (14)$$

12 **28**, 66% **29**, 4%

product was mainly diethyl-*sec*-butylamine (**28**); this would be expected from the nucleophilic opening by hydride ion of the presumed intermediate aziridinium ring at the less-substituted carbon.[26] The homologous adduct **13** was unaffected by Pt–40 psi of hydrogen in acetic acid at 52° for 6 hr.

Once the extent of radical reactions of chloramines with the simple alkyl olefins had been found[25] to consist mainly of addition and not of hydrogen abstraction, our interest turned to further studies designed to probe the properties of the $R_2\dot{N}H^+$ radical and the susceptibility of other types of olefins to the addition process under our standard conditions of reaction. We did not attempt, therefore, to enhance the addition process in the case of simple olefins, and there are now procedures whereby this may be accomplished in both strongly[27] and weakly[2] acidic media.

The principal studies carried out in regard to further defining the characteristic behavior of aminium radicals are described in the accompanying paper. A question pertinent to the present results arose, however, when diethylchloramine was found to form a bisadduct (**14**) with 1,7-octadiene just as efficiently as it added to propylene; thus, might addition occur with ring closure on reaction of the chloramine with diolefins $(CH_2{=}CHCH_2)_2X$, as has been documented[28] for other radicals? Unfortunately, reactions between 1,6-heptadiene or diallyl ether and a simple chloramine gave no isolable ring-closed products; instead, lowered yields of the normal diadducts were obtained (eq 15). An-

$$R_2NCl + (CH_2{=}CHCH_2{-}_2X \xrightarrow{h\nu} (R_2N\underset{Cl}{C}HCH_2)_2X \quad (15)$$

15 (X = CH_2), 27%
16 (X = O), 40%

other related reaction has been previously reported in detail.[21] When norbornadiene, which might have given a ring-closed, free-radical adduct (a nortricyclene derivative), was allowed to react with diethylchlora-

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

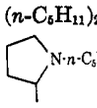
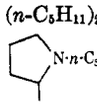
(26) S. D. Ross, *J. Am. Chem. Soc.*, **69**, 2982 (1947); P. Charpentier, *Compt. Rend.*, **225**, 306 (1947); R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. France*, 736 (1958); J. H. Biel, W. K. Hoya, and H. A. Leiser, *J. Am. Chem. Soc.*, **81**, 2527 (1959); E. G. Brain, F. P. Doyle, and M. D. Mehta, *J. Chem. Soc.*, 633 (1961).

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

(28) N. O. Brace, *J. Am. Chem. Soc.*, **86**, 523 (1964); D. H. Hey and A. O. S. Hock, *Chem. Ind.* (London), 753 (1964).

TABLE II

REACTIONS BETWEEN CHLORAMINES AND ACETYLENES IN SULFURIC ACID–ACIDIC ACID AT 30° UNDER NITROGEN

Chloramine	Acetylene	Catalyst	Time, min	Products	% yield
$(C_2H_5)_2NCl$	n-$C_4H_9C{\equiv}CH$	None	90	n-$C_4H_9CHClCHO$	45
$(n$-$C_4H_9)_2NCl$	n-$C_4H_9C{\equiv}CH$	None	60	n-$C_4H_9CHClCHO$	37[a]
				$(n$-$C_4H_9)_2NH$	89
					4
$(n$-$C_5H_{11})_2NCl$	n-$C_4H_9C{\equiv}CH$	None	75	$(n$-$C_5H_{11})_2NH$	25
					52
$(C_2H_5)_2NCl$	n-$C_3H_7C{\equiv}CCH_3$	None	75	n-$C_3H_7CHClCOCH_3$	33
				n-$C_3H_7COCHClCH_3$	29
$(C_2H_5)_2NCl$	$C_2H_5C{\equiv}CC_2H_5$	None	35	$C_2H_5CHClCOC_2H_5$	59
				$C_2H_5CH_2COC_2H_5$	3
				$C_2H_5C{\equiv}CCHClCH_3$	4
$(n$-$C_5H_{11})_2NCl$	$C_2H_5C{\equiv}CC_2H_5$	None	18	$(n$-$C_5H_{11})_2NH$	18
					63
$(n$-$C_4H_9)_2NCl$	$C_6H_5C{\equiv}CH$[b]	None	8	$C_6H_5COCH_3$	59
				$C_6H_5COCH_2Cl$	23
$(C_2H_5)_2NCl$	$(CH_3)_3CC{\equiv}CH$	$h\nu$	22	$(CH_3)_3CCHClCHO$ (**34**)	60
$(n$-$C_4H_9)_2NCl$	$(CH_3)_3CC{\equiv}CH$	$h\nu$	30	$(CH_3)_3CCOCH_3$	8
				$(CH_3)_3CCH_2CHO$	7
				$(CH_3)_3CCHClCHO$	16
				$(CH_3)_3CCOCH_2Cl$	5
				$(n$-$C_4H_9)_2NH$	40
					17
$(C_2H_5)_2NCl$	$ClCH_2C{\equiv}CH$	$h\nu$	90	No reaction	

[a] The yield was 16% when trifluoroacetic acid was used as solvent. [b] Freshly distilled, bp 35° (20 mm), $n^{22}D$ 1.5484.

mine, only products derived from an ionic reaction pathway were produced, although some of these products were chloramine adducts.

Acetylenic Hydrocarbons (Table II).—The reactions summarized in Table II show that dialkylchloramines add to simple acetylenes as well as they do to 1,3-dienes. The addition[29] gives β-chloro enamines, but these hydrolyze to α-chloro aldehydes or ketones on work-up of the reaction mixtures (*e.g.*, eq 16). Trifluoroacetic

$$Et_2NCl + CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[2.\ \text{water}]{1.\ \text{acid}} CH_3CH_2\underset{\underset{Cl}{|}}{\overset{\overset{O}{\|}}{C}}CHCH_2CH_3 + CH_3CH_2C{\equiv}\underset{\underset{Cl}{|}}{C}CHCH_3 \quad (16)$$

59% 4%

acid proved to be an unsatisfactory substitute for sulfuric acid–acetic acid, the usual solvent, and the β-chloro enamines were never isolated. The acetylene reactions, like those of the 1,3-dienes, occurred spontaneously with the exception of those involving *t*-butylacetylene, and these were unusual in another way. Whereas 1-hexyne gave similar product mixtures with either diethyl- or dibutylchloramine, *t*-butylacetylene did not; thus, 2-chloro-3,3-dimethylbutyraldehyde (**34**) was obtained in good yield only from diethylchloramine (eq 17), and the loss in product **34** from

$$R_2NCl + (CH_3)_3CC{\equiv}CH \xrightarrow[2.\ \text{water}]{1.\ \text{acid}} (CH_3)_3\underset{\underset{Cl}{|}}{C}CHCHO \quad (17)$$

34, 60% (R = Et)
16% (R = Bu)

dibutylchloramine was only partly balanced by the competing Hofmann–Loeffler rearrangement (see Table II).

When the chloramine rearrangement can involve a *secondary* side chain methylene group, the chloramination of a triple bond does not occur; thus, the only products from 1-hexyne and N-chlorodi-*n*-pentylamine were 52% of the Hofmann–Loeffler product N-pentyl-2-methylpyrrolidine and 25% of dipentylamine.

The small amount of propargylic substitution product obtained from reaction 16 could have arisen from a hydrogen-abstraction process involving the dialkylaminium radical or from free chlorine formed during the reaction. It is not surprising to have found this substitution product, whose analogs were not sought in other work-ups, since propargylic hydrogens are known to be as reactive toward the *t*-butoxy radical[30] as and probably more reactive toward the bromine atom[31] than allylic hydrogens. We should note that, while it is not an important reaction of olefinic substrates, allylic hydrogen abstraction during chloramine additions could have occurred to a minor extent similar to that in the 3-hexyne reaction.

Finally, we were surprised to find that acetylenes of the type $HC{\equiv}CCH_2X$ gave no addition products and,

(29) First illustrated in our communication on the subject[1b] and also found to occur with phenylacetylene in slightly acidic methanol under the influence of metal ions by F. Minisci and R. Galli, *Tetrahedron Letters*, 1679 (1965).

(30) C. Walling, L. Heaton, and D. D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965).

(31) G. Peiffer, *Bull. Soc. Chim. France*, 537 (1963).

in fact, were completely inert (X = Cl or $SO_2C_6H_5$); this contrasts markedly with the behavior of the favorably reactive allyl compounds described in the next paper.

Discussion

The experiments described above show that three kinds of reactions can occur, depending on the structures of the reactants, when protonated dialkylchloramines are treated with unsaturated aliphatic hydrocarbons in the solvent 4 *M* sulfuric acid–acetic acid. Least desirable of these reactions is electrophilic chlorination, which affords products by a nonradical route in competition with the other two reactions, which are the desired free-radical addition of the chloramine to the carbon–carbon multiple bond and the free-radical rearrangement of the chloramine (the Hofmann–Loeffler reaction). The ionic process predominates to the exclusion of both radical processes in the case of 1,2-dialkylated olefins but competes to varying degrees with chloramine addition in reactions with terminal olefins. The chloramine rearrangement, at least when it involves a secondary side-chain methylene group, is more favorable than either radical addition to or ionic chlorination of terminal olefins. Acetylenes significantly favor radical addition over ionic reactions but, like terminal olefins, cannot divert the progress of the Hofmann–Loeffler rearrangement of a long-chain chloramine. 1,3-Dienes that are not highly alkylated, however, appear to be more susceptible to the free-radical addition than to either of the other two types of reaction. The results obtained with the allenic hydrocarbons suggest that all three types of reaction might be expected to varying extents with other allenes.

It is highly significant that *inter*molecular free-radical hydrogen abstraction is not an important reaction in our systems. Thus, the only type of reaction observed to occur between an aminium radical $R_2\dot{N}H^+$ and a carbon–carbon multiple bond was addition, and we conclude from this result and the prior literature discussed above that *addition is a reaction characteristic of protonated amino radicals* along with *intra*molecular hydrogen abstraction, regardless of the manner in which the radicals are generated. This is not to say that intermolecular hydrogen abstraction will not occur at all, but that the addition or rearrangement reaction is preferred and will take place if the substrates permit. However, we expect, from the admittedly scanty literature on the subject, that neutral, free amino radicals will display a pronounced tendency toward *inter*molecular hydrogen abstraction and disproportionation at the expense of addition to multiple bonds.

There are several ways by which a neutral amino radical can be modified so that its addition to an olefin might become more favorable. One such procedure is to generate N-substituted amino radicals in which the substituents are various electron-withdrawing groups; the study of such a series of radicals might lead to a spectrum of reactivities ranging from that of dialkylamino ($R_2\dot{N}$) through various substituted amino ($R\dot{N}X$) to protonated amino radicals ($R_2\dot{N}H^+$). For example, we have recently completed one aspect of such a study, finding[13a] that neutral, acylamino radicals rearrange efficiently *via* the Hofmann–Loeffler-type process that is characteristic of protonated amino radicals but, unlike aminium radicals, fail to add to unsaturated hydrocarbons. We presently have several other types of substituted amino radicals under active study, and a few other examples have already been mentioned in the introduction.

Another way to modify the reactivity of a given radical is to change the properties of the medium in which it is generated. For example, the judicious use of a solvent[32] or metal ions[33] with which the radical can form a complex may impart to it new types of reactivity. We believe that the reports of Minisci and co-workers on the addition of dialkylchloramines to unsaturated hydrocarbons in methanol should be viewed with this in mind. Among the reactions described by Minisci are the nonchain radical additions[2] of chloramines to simple olefins or butadiene under the influence of molar quantities of copper(I, II) or iron(II, III) redox couples, which gave β-chloramines or the vinylogs just as we have reported above in a strongly acidic medium. The yields of β-chloramines, however, were considerably higher than we observed, since ionic chlorination of the olefins was an unimportant process under the reaction conditions. If an acidic solvent was employed in the redox system, the formation of adducts from simple olefins was now precluded by electrophilic chlorination[34] unless inverse addition of the chloramine to olefin–iron salt mixtures (in 65% aqueous sulfuric acid) was employed.[27] The chloramination of olefins could also be somewhat less efficiently accomplished with hydroxylamine-O-sulfonic acid or hydroxylamine hydrochloride,[35] both in the presence of ferric chloride. In the case of chloramines, the following sequence of reactions is thought[36] to obtain.

$$R_2NCl + Fe^{2+} \longrightarrow R_2\dot{N} + FeCl^{2+}$$

$$R_2\dot{N} + >C{=}C< \longrightarrow R_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot$$

$$R_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot + FeCl^{2+} \longrightarrow R_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Cl + Fe^{2+}$$

Although the reactions with hydroxylamine-O-sulfonic acid have been interpreted in terms of protonated amino radicals,[35] the addition of chloramines to olefins in methanol have consistently been written[36] as involving free, neutral amino radicals as shown, except when a stereochemical preference for *cis* addition to cyclohexene[37] was observed. An amino radical–ferric chloride complex was now considered possible to explain the latter result.[37] However, we feel that *free*, neutral amino radicals cannot be the reactive species in any of the redox systems because of (1) the olefin addition reaction shown in common by the amino radicals produced from a variety of sources, (2) the coincidence of this characteristic addition with the one that we have described above in our system, and (3) the implications of the literature that free, neutral amino radicals possess a strong tendency to abstract hydrogen from

(32) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).
(33) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 606 (1959); ref 15a.
(34) F. Minisci and R. Galli, *Tetrahedron Letters*, 167 (1964).
(35) F. Minisci, R. Galli, and M. Cecere, *Chim. Ind.* (Milan), **48**, 132 (1966).
(36) F. Minisci and R. Galli, *ibid.*, **46**, 546 (1964); F. Minisci and R. Galli, *Tetrahedron Letters*, 167, 3197 (1964); ref 2.
(37) F. Minisci, R. Galli, and M. Cecere, *Chim. Ind.* (Milan), **48**, 347 (1966).

TABLE III

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	Chlorine, % Calcd	Chlorine, % Found	Nitrogen, % Calcd	Nitrogen, % Found
1		99 (1.5)	1.4600 (25)								
1 picrate	$C_{18}H_{27}ClN_4O_7$	87.5–89.5		48.37	48.27	6.07	6.05			12.54	12.77
3	$C_{15}H_{23}N$	62 (0.02)	1.5008 (23.5)	82.89	82.68	10.67	10.60			6.45	6.41
4		63–65 (0.06)	1.4968 (23.5)								
4 picrate	$C_{18}H_{25}ClN_4O_7$	151–154[a]		48.59	48.83	5.66	5.63	7.98	8.30	12.60	12.85
5	$C_7H_{14}ClN$	58–62 (24)	1.4424[b] (24)	56.94	56.98	9.56	9.38	24.02	24.12	9.49	9.65
5 hydrochloride	$C_7H_{15}Cl_2N$	122–126		45.65	45.65	8.21	8.20	38.54	38.50	7.61	7.55
6	$C_9H_{18}ClN$	43 (3)	1.4620[b] (23)	61.51	61.75	10.32	10.29	20.20	19.95	7.97	8.30
7	$C_{11}H_{22}ClN$	53–54 (0.3)	1.4497 (24)	64.88	65.22	10.86	11.04	17.39	17.58	6.86	7.01
9 picrate	$C_{16}H_{25}ClN_4O_7$	101–103		45.66	45.55	5.99	5.89	8.43	8.63	13.32	13.51
11		79 (20)	1.4375 (24)								
11 picrate	$C_{14}H_{21}ClN_4O_7$	76–78		42.80	42.74	5.39	5.40	9.03	9.00	14.27	14.41
12 picrate	$C_{16}H_{25}ClN_4O_7$	117–118.5		45.66	45.71	5.99	5.99	8.43	8.01	13.32	13.22
13		57–59 (0.1)	1.4450 (23)								
13 picrate	$C_{15}H_{29}ClN_4O_7$	76.8–77.6		48.15	48.42	6.51	6.77	7.91	7.95	12.48	12.51
14 dipicrate	$C_{14}H_{20}ClN_4O_7$	151–154.5		42.92	43.19	5.15	5.13	9.05	10.11	14.30	14.17
15 dipicrate	$C_{29}H_{38}Cl_2N_8O_{14}$	194–195		43.89	43.83	4.83	4.88	8.94	8.62	14.12	14.10
15 dihydrochloride	$C_{17}H_{34}Cl_4N_2$	221–222		50.01	50.03	8.39	8.64	34.73	34.41	6.86	6.40
16	$C_{14}H_{30}Cl_2N_2O$	100–101 (0.05)	1.4650 (25)	53.67	53.89	9.65	9.64	22.63	22.41	8.94	8.83
16 dipicrate	$C_{26}H_{36}Cl_2N_8O_{15}$	125.5–127		40.48	40.67	4.70	4.71	9.19	9.26	14.52	14.41
17	$C_{14}H_{27}NO_2$	73 (0.075)	1.4479 (23.5)	69.66	69.88	11.28	11.15			5.80	5.78
19 dipicrate	$C_{18}H_{28}N_4O_7$	144–145		52.41	52.25	6.84	7.00			13.59	13.30
20	$C_{14}H_{24}NO_2$	79 (0.08)	1.4774 (23.5)	70.25	70.56	10.53	10.86			5.85	5.95
22	$C_7H_{11}ClO_2$		1.4585[b] (23)	51.69	52.58	6.81	6.86	21.82	21.86		
23a,b	$C_9H_{17}Cl_2N$	75–77.5 (2.5)	1.4832[c] (23)	51.42	51.59	8.15	8.31	33.77	33.67	6.67	6.43
24	$C_9H_{18}ClN$		1.4585[b] (24)	61.51	61.79	10.32	10.39	20.20	19.84	7.97	8.33
25	$C_9H_{13}Cl$	27–34 (0.1)[c]	1.5123[b] (23)	68.99	68.61	8.36	8.31	22.65	22.87		
26	$C_{11}H_{17}ClO_2$	79–83.5 (0.1)[d]	1.4960[b] (23.5)	60.95	61.28	7.91	8.08	16.38	16.77		
27	$C_{11}H_{17}ClO_2$	79–83.5 (0.1)[d]	1.4910[b] (23.5)	60.95	61.16	7.91	7.93	16.38	16.64		
30	$C_6H_{11}ClO_2$	72–73 (25)	1.4253[b] (23)	47.84	47.68	7.36	7.35	23.56	23.44		
34		80–90 (8.5)	Semisolid								
34 2,4-DNP[e]	$C_{14}H_{20}N_4O_5$	155–157		51.84	51.69	6.22	6.19			17.28	17.31

[a] Variable melting point within the range 151–162°, probably as a result of *cis–trans* isomerism. [b] Glpc purified sample. [c] Mixture with second, unidentified compound. [d] Mixture of two positional isomers. [e] 2-Ethoxy-3,3-dimethylbutyraldehyde 2,4-dinitrophenylhydrazone.

olefins. Thus, we feel that metal ion–amino radical complexes, or even radicals possibly protonated by the weakly acidic[38] medium, must be involved in all the metal salt catalyzed reactions in methanol. One could then rationalize the similar natures of protonated and iron-complexed amino radicals by viewing them both as radicals with the free-electron pair similarly coordinated. This could bestow similar reactivity patterns upon both radicals while allowing for secondary differences between the systems, such as in the product yields or stereochemistry.

We believe that a recognition of the *similarities* between the results obtained from the redox systems and from our experiments in strong acid will be important to the ultimate definition of the characteristic behavior of various types of amino radicals, and we have accordingly emphasized these similarities above. The differences, on the other hand, have already been pointed out by Minisci on several occasions[2,27,34,38] and are the result of the active participation of the metal salts in nonchain redox processes. Some of the products thereby produced compliment those obtained by our procedure.

Once we had established the principle of aminium radical addition to multiple bonds, it seemed worthwhile to define the synthetic applications of this general reaction which had already provided ready access to 4-chloro-2-butenylamines, β-chloramines, and α-chloro aldehydes and ketones in one step from unsaturated hydrocarbons. In the accompanying paper we describe a study based on the premise that the use of properly substituted olefins might avoid the problem of electrophilic chlorination and at the same time lead to the preparation of a large group of novel, substituted amines that could be of interest in their own right.

Experimental Section

Representative procedures for the chloramination reactions are given below. The physical constants and elemental analyses of the new compounds are listed in Table III according to the compound numbers given in Tables I or II or the text, and illustrative A-60 nmr data are recorded in Tables IV and V. Peak area ratios are given in the text in order of increasing chemical shift. Commercial compounds used were obtained from the following sources: gaseous hydrocarbons from the Matheson Co.; the linear actylenes from Farchan Research Laboratories; *t*-butylacetylene from Frinton Laboratories; phenylacetylene from Matheson Coleman and Bell; 3-methyl-1,2-butadiene from Dr. L. Skattebøl,[39] bp 40°, $n^{23}D$ 1.4150; 1,3-cyclooctadiene and 1,7-octadiene from Columbia Carbon Co.; 1,6-heptadiene from Columbia Organic Chemicals Co.; diallyl ether from Aldrich Chemical Co.; and 1,1-diphenylethylene from Distillation Products Industries. All these compounds were used as received. 1,2-Cyclononadiene was prepared according to the published method.[39] Initiation of the reactions was provided by either a

(38) F. Minisci and R. Galli, *Chem. Ind.* (Milan), **45**, 1400 (1963).

(39) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

TABLE IV

NMR DATA FOR AMINES OF TYPE $(RCH^A_2)_2NCH^B(C{=}C)_nCH^C{-}X$ IN CCl_4[a]

Compd	R_1	R_2	R_3	R_4	n	X	τ_A	τ_B	τ_C
1	H	H	H	H	1	Cl	7.80 t	7.08 d	6.08 d
4	$-(CH_2)_4-$		H	H	1	Cl	7.45 q	6.45 m	4.2–4.9[b]
5	H		Cl	H	1		7.45 q	6.88 t	
6	H	H	Cl	CH_3	1	H	7.50 q	6.76 s	8.14 d
17	H	H	H	H	1	OAc	7.68 t	6.97 d	5.55 d
20	$-(CH_2)_4-$		H	H	1	OAc	7.48 q[c]	6.60 m	4.4–4.6[b]
21	$-(CH_2)_4-$		H	H	1	H	7.48 q[c]	6.45 m	7.88 m
24	H	H	CH_3	Cl	1	H	7.58 q	6.90 d	7.92 q
33	$-(CH_2)_2-$		H	H	2	H	7.53 q[c]	6.60 m	7.92 m

[a] Only the principal splitting pattern is given; d = doublet, q = quartet, etc. [b] Coincident with olefinic hydrogen absorption. [c] ~ double pattern, due to magnetic asymmetry.

the two bands at 990, 935 cm^{-1} that are comparable to the unique 985-, 932-cm^{-1} frequencies found[40] in structures $CH_2{=}CHCH_2OCOR$. Glpc analysis on a polypropylene glycol column at 149° suggested the presence of the 1,4 isomer in a later distillation fraction. The chloro acetate **32** has been reported,[41] bp 54–56° (8 mm), $n^{20}D$ 1.4550, but this refractive index appears to be inaccurate.

Anal. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.10; Cl, 23.86. Found: C, 48.23; H, 6.05; Cl, 23.75.

The conversion of **1** to the corresponding acetate **17** in 80–90% yield could be accomplished by heating a mixture of **1**, sodium acetate, and acetic acid in the proportions 1:5:50 at 85° for 26 hr or at 123° for 7 hr. A routine work-up of dilution with water (200 parts), basification with 12 *N* NaOH, and extraction with pentane gave **di-*n*-butyl-4-acetoxy-2-butenylamine**.

When **1** was heated under reflux for 27 hr with 2 moles of dibutylamine in benzene, **1,4-bis(di-*n*-butylamino-2-butene)** (**18**), bp 130° (0.3 mm), $n^{23}D$ 1.4548, was produced in 85% yield and

TABLE V

NMR DATA FOR COMPOUNDS OF TYPE $X{-}CH^ACH^B{-}Y$ IN CCl_4[a]

Compd	R_1	R_2	X	Y	τ_A	τ_B
9	H	H	$(n\text{-}C_4H_9)_2N$	Cl	7.30 t	6.60 t
10	H	CH_3	$(CH_3CH_2)_2N$	Cl	8.54 d	6.15 m
11	H	CH_2CH_3[b]	$(CH_3CH_2)_2N$	Cl	7.42 d	6.25 m (12)
16	H	CH_2OR	$(CH_3CH_2)_2N$	Cl	7.22 d	5.9–6.5 m
22	H	$=C(CH_3)_2$	AcO	Cl	5.30 s	
26	$-CH_2(CH_2)_4CH_2CH=$		AcO	Cl	4.07 t	
27	$-CH_2(CH_2)_4CH_2CH=$		Cl	OAc	4.28 t	
28	CH_3	H	$(CH_3CH_2)_2N$[b]	CH_3	7.2–8.0 m	~8.7 m
30	CH_2CH_3	H	AcO	Cl	5.10 m (5)	6.44 d
31	CH_3	CH_3	AcO	Cl	5.04 m (8)	5.96 m (8)

[a] Only the principal splitting pattern is given; secondary splitting due to coupling or magnetic nonequivalence was usually present. [b] Strong nonequivalence in CH_2 hydrogens.

Vicor-filtered, 100-w Hanovia ultraviolet lamp or by a ferrous ammonium sulfate suspension in acetic acid.

The chloramines were also generally used without purification. All but diethylchloramine were obtained as yellow oils from the parent amine and N-chlorosuccinimide (NCS) in ether[3b] and then added to the acid mixture as described below. Diethylchloramine was prepared as described below in the preparation of **4** from cyclooctene.

Di-*n*-butyl-4-chloro-2-butenylamine (**1**).—A mixture of 44 ml of 96% sulfuric acid and 150 ml of glacial acetic acid was cooled to 10° in a 300-ml Pyrex flask; this was equipped with a strong, paddle-type stirrer, a thermometer, a "coarse" gas dispersion tube as the nitrogen or gaseous reactants inlet, a condenser with gas outlet, and a serum-capped sampling tube. Fifteen grams (0.09 mole) of dibutylchloramine was then added *via* syringe in the dark to the acid mixture, which had been rapidly stirred under a rapid stream of nitrogen for 10 min. The resulting mixture was 4 *M* in sulfuric acid and 0.45 *M* in chloramine. After 5 min of further stirring, the nitrogen flow was terminated and butadiene was introduced directly into the reaction mixture at a rate sufficient to maintain a zero pressure differential at the gas outlet. The ensuing spontaneous and exothermic reaction was maintained at 5–15° with an ice bath and was followed by iodometric titration;[3b] when the chloramine titer had nearly reached zero, butadiene began exiting from the reaction flask. The reaction mixture, which had not darkened during the addition of the diene (0.13 mole total), was swept with nitrogen briefly and then poured over 200 g of ice in 500 ml of water. A small amount of an oil that separated (~2 g) was extracted into pentane. It was from similar pentane extracts, washed with bicarbonate, that the chloro acetates from other reactions were obtained. The aqueous solution was maintained at <25° and basified to pH 9–10 by the addition of ~265 ml of 12 *N* sodium hydroxide. The oil which separated was extracted into ether and distilled to give **1**, identified by spectral data and conversion to **17** and **18** as noted below.

Distillation of the neutral products afforded as the major product **3-acetoxy-4-chloro-1-butene** (**32**), bp 89.5° (50 mm), $n^{22}D$ 1.4410, which was identified from spectral data, in particular was identical with the product obtained from dibutylamine and 1,4-dibromo-2-butene in hot benzene. Both products gave a dipicrate, mp 183–184°, which was identical with that of the known[42] compound.

3-Diethylamino-8-chlorocyclooctene (**4**).—A mixture of 20 g of diethylamine and 20 g of NCS in 200 ml of pentane (permanganate washed) was stirred rapidly for 6 hr. The solids were removed by filtration and the pentane solution was washed free of diethylamine with 2.5 *N* H_2SO_4 and was then chilled over anhydrous sodium sulfate. The cold chloramine solution was extracted with 30 ml and then 14 ml of cold, concentrated sulfuric acid, and the combined, deeply colored acid extracts were filtered under aspirator vacuum through a "medium" fritted-glass funnel to remove pentane. The chloramine–sulfuric acid solution was then added to 150 ml of acetic acid to give a solution 4 *M* in sulfuric acid and 0.68 *M* in the chloramine. After the vigorously stirred solution was swept for 10 min with nitrogen, the gas was slowed and 0.12 mole of 1,3-cyclooctadiene was added to the mixture from a dropping funnel over 21 min at 9°. Work-up as above gave 22 g of the crude adduct **4** which distillation caused to decompose significantly. The yield of **4** was determined *via* the picrate (Table III) and the structure was affirmed *via* spectral data (Table IV) and as follows.

A mixture of **4** (8.5 g, 0.034 mole) and 1.9 g (0.05 mole) of $LiAlH_4$ in 250 ml of ether was heated under reflux for 6.5 hr. After work-up there was still much unreacted **4** remaining. The crude product, an additional 1.8 g of **4**, and 2.9 g of $LiAlH_4$ were then heated under reflux in 100 ml of tetrahydrofuran for 7 hr. The excess hydride was decomposed by the slow addition with violent stirring of 3 ml of water, 6 ml of 10% NaOH, and finally 6 ml of water. The ether solution was filtered from the salts and evaporated to 7.3 g of residue. This was distilled to give 40%

(40) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 49.

(41) B. A. Arbuzov and V. M. Zorastrove, *Compt. Rend. Acad. Sci. URSS*, **53**, 41 (1946); *Chem. Abstr.*, **41**, 3751 (1947).

(42) L. H. Amundsen, R. H. Mayer, L. S. Pitts, and L. A. Malentacchi, *J. Am. Chem. Soc.*, **73**, 2118 (1951).

of **3-diethylaminocyclooctene**, bp 47–48.5° (0.25 mm), $n^{23}D$ 1.4792, picrate mp 123–125.5° (lit.[43] picrate mp 125°).

Anal. Calcd for $C_{18}H_{26}N_4O_7$: C, 52.67; H, 6.39; N, 13.65. Found: C, 52.33; H, 6.35; N, 13.55.

3-Diethylamino-8-acetoxycyclooctene (20).—Ten grams of crude **4** in 250 ml of 5 *N* H_2SO_4 was heated under reflux for 30 min and then allowed to stand at room temperature overnight. The solution was partially neutralized with 12 *N* NaOH, filtered with charcoal, and then basified to liberate 8.55 g (93%) of crude alcohol. To this was added 75 ml of acetic anhydride. After 2 days at room temperature, the solution was poured into 300 ml of water; basification liberated 9.5 g of a red oil which was distilled to give 1.45 g (19%) of a compound believed to be **5-diethylamino-1,3-cyclooctadiene (33)** (see text), bp 39–43° (0.05 mm), $n^{23}D$ 1.4924, and 6.6 g (57%) of the acetate **20**.

Chloramination of 3-Methyl-1,2-butadiene (Chart I).—To an acid solution of diethylchloramine (0.13 mole), prepared according to the preceding example, was added in 10 min 0.1 mole of the allene diluted 1:1 with acetic acid, whereupon no chloramine remained. The usual work-up gave 3.5 g of a neutral product mixture, whose major component was purified by glpc on Carbowax and identified as **1-acetoxy-2-chloro-3-methyl-2-butene (22)** from its nmr spectrum (Table V) and analysis. The major product fraction (12 g) was obtained from the basified aqueous solution and distilled to give two different product mixtures. The first, bp 43° (3 mm), $n^{23}D$ 1.4629, was separated by glpc into the desired adduct **1-diethylamino-2-chloro-3-methyl-2-butene (6)** and a minor component (<10%), which was identified from its nmr spectrum as 2-chloro-3-diethylamino-3-methyl-1-butene.

The second basic product fraction was identified from spectral and elemental analyses as the mixture **23a,b**. The components were not separable by glpc and were reduced to the simpler structures obtained by converting the chloromethyl into methyl groups on heating the mixture with excess $LiAlH_4$ in ether for 4 hr. Work-up afforded 90% of a mixture of the original adduct **6** and an isomer, **1-diethylamino-2-methyl-3-chloro-2-butene (24)**, which were separated by preparative glpc; their relative abundances (1:2) were employed to estimate the yields of **23a** and **23b**.

The Reaction of 1,2-Cyclononadiene with Diethylchloramine.—The allene (0.08 mole) was added neat over 6 min to the usual acid–diethylchloramine mixture; work-up gave no discrete basic product (total 3.3 g of crude mixture) but afforded 9.8 g of neutral products. Distillation then gave fractions from which pure compounds were isolated by glpc (Carbowax on Fluoropak) as follows. From material with bp 27–34°, $n^{23}D$ 1.5109, was obtained **2-chloro-1,3-cyclononadiene (25)**, whose structure was established by elemental analysis, analogy to the dimethylallene reaction above, and the nmr spectrum (hydrogen count calcd 3:4:6, found 3.04:3.19:6.08); the compound had $\lambda_{max}^{isooctane}$ 222 mμ (ϵ_{max} 4920).[44] From the same distillation fraction was also isolated a second compound in too small an amount for elemental analysis; the material had $n^{23}D$ 1.5120, λ_{max} 232 mμ (ϵ_{max} 1000–1400), and an nmr hydrogen count that best fit vinyl H:remainder = 1.96:10.05.

Another distillation fraction, bp 73–79° (0.1 mm), was used for the glpc collection of **2-chloro-3-acetoxycyclononene (26)**, and the next cut, bp 79–83.5° (0.1 mm), for the collection of the isomer **2-acetoxy-3-chlorocyclononene (27)**. These structures were assigned on the basis of elemental analyses (Table III) and the nmr spectra (Table V). Thus, compounds **26** and **27** both had low-field:high-field hydrogen counts of nearly 2:15, but the >CHX hydrogen appeared at lower field in **26** (coinciding with the vinyl hydrogen peaks) and was accordingly attributed[21] to the structure in which X = OAc.

Di-*n*-butyl-2-chloroethylamine (9).—A reaction was carried out as described in the first example, except that ethylene was passed into the irradiated reaction mixture contained in a Vicor flask. Work-up afforded no neutral products but gave a mixture of bases, which was distilled. There was obtained 53% of N-*n*-butylpyrrolidine and 15% of **9**, bp 51° (0.6 mm), $n^{24}D$ 1.4428 (lit.[45] bp 119–120° (30 mm)), whose picrate was analyzed (Table III).

Diethyl-2-chloro-1-propylamine (10).—A reaction with propene was carried out as usual except that 0.2 ml of the iron(II) salt suspension was added as initiator. Distillation of the crude bases gave **10**, bp 72° (38 mm), $n^{24}D$ 1.4315, picrate mp 125–126.5° (lit.[46] bp 69° (35 mm), $n^{20}D$ 1.4332, picrate mp 125.5–126°).

Diethyl-2-chloro-1-butylamine (11).—A reaction of 1-butene with diethylchloramine in the presence of iron(II) proceeded as usual. From the neutal products was obtained 11% of **1-chloro-2-acetoxybutane (30)**, whose structure was evident from the nmr spectrum (Table V) and elemental analysis. Distillation of the basic product gave the adduct **11** whose structure was obvious from the nmr chemical shifts (Table V) and hydrogen count (found 1.15:6.06:2.01:8.88). The splitting patterns in the spectrum of **11** showed the N–CH_2CH_3 hydrogens to be magnetically nonequivalent.

As further proof of structure, however, the β-chloramine **11** (6.8 g, 0.042 mole) was reduced by heating it under reflux in 250 ml of THF with 2.15 g (0.057 mole) of $LiAlH_4$. Normal work-up and distillation afforded 7.2 g of a product, bp 68–71° (110 mm), $n^{23}D$ 1.4111, which was shown by glpc to be a 1:1 mixture of the amines described below with 1-butanol. The alcohol was removed by extraction of the amines into acid, and the crude amines were separated by glpc on a SF 96 column at 92°. The major product (66% yield) was **diethyl-*sec*-butylamine (28)**, $n^{23}D$ 1.4116, picrate mp 113.5–115° (lit.[47] $n^{20}D$ 1.4165, picrate mp 116–117°), whose nmr spectrum contained peaks in the expected ratio 5:14 and disclosed the NCH_2 hydrogens to be magnetically nonequivalent (16 N–C–H lines). The minor product was diethyl-*n*-butylamine (4% yield), nmr area ratio 5.86:13.1.

2-Acetoxy-3-chlorobutane (31).—When either diethyl- or dibutylchloramine was allowed to react with *cis*-2-butene, no adduct was formed. The iron(II)-catalyzed reaction of 0.14 mole of diethylchloramine at 35°, for example, gave 7.3 g of a neutral product, which on distillation afforded 4.6 g (21%) of the chloro acetate **31**, bp 78° (25 mm), $n^{23}D$ 1.4240 (lit.[48] bp 101–102° (100 mm), $n^{20}D$ 1.4270). The structure was defined by its nmr spectrum, from which the following coupling constants were obtained: for $CH_3^C CH^B(OAc)CH^A(Cl)CH_3^D$, J_{AB} = 4.5, J_{BC} = 6.4, J_{AD} = 6.8 cps.

1-Chloro-2,2-diphenylethylene.—To 0.05 mole of dibutylchloramine in 100 ml of the standard acid solution was added 0.05 mole of 1,1-diphenylethylene over 19 min at 5–8° in the usual apparatus. Work-up yielded the results summarized in eq 12. Compound **33** was obtained from the crude neutral products by cooling the liquid directly and by chilling ethanolic solutions of subsequent filtrates. The recrystallized product had mp 38.5–40.5° (lit. mp 38.5–40° [49] and 42–43° [50]); the vinyl hydrogen appeared at τ 3.48 in the nmr spectrum. The basic product was shown to be free of the pyrrolidine by glpc analysis.

2-Chloro-3,3-dimethylbutyraldehyde (34).—To an irradiated solution of 0.11 mole of diethylchloramine in the usual acid mixture was added 0.11 mole of *t*-butylacetylene over 10 min; when the reaction was complete, the acid was diluted with water as usual, but then 100 ml of 12 *N* NaOH was added all at once to the ice-cold solution. The resulting, slightly warm (~30°) mixture was extracted with 200 ml of ether and then with three 100-ml portions over 25 min. The combined ether solutions were neutralized by washing them with saturated $NaHCO_3$ solution and were then dried and distilled with the aid of an antifoaming agent to give 60% of the α-chloro aldehyde **34**. The preparation of the 2,4-dinitrophenylhydrazone derivative resulted in alcoholysis of the chlorine atom (Table III). The other neutral products listed in Table II from the reaction of the acetylene with dibutylchloramine were identified from the nmr spectra of glpc purified samples, and the yields were also determined by glpc analysis.

Other Acetylene Reactions.—Most of the products from reactions between chloramines and other acetylenes had been reported previously. From diethylchloramine and 1-hexyne was obtained 45% of **2-chlorohexaldehyde**, bp 72.5° (45 mm), $n^{23}D$

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(49) M. A. Khaimova, *Compt. Rend. Acad. Bulgare Sci.*, **10**, 371 (1957); *Chem. Abstr.*, **52**, 13689 (1958).

(50) D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.*, **81**, 4714 (1959).

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.

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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

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

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