quantitative sense. The stoichiometry of the reaction leading to aldehyde production is given by eq 7, but benzaldehyde is present in the products in much smaller amount than acetyl bromide because of its further reaction with N-bromosuccinimide. This is not sur-

$$C_{6}H_{5}CH_{2}OCOCH_{3} \xrightarrow{\text{NBS}} CH_{3}COBr + C_{6}H_{5}CHO$$
(7)

prising. Using the relative reactivities of benzaldehyde and ethylbenzene as determined in this investigation and those for ethylbenzene and benzyl acetate which are reported elsewhere,<sup>10</sup> it can be shown that the relative reactivities of benzaldehyde and benzyl acetate with respect to N-bromosuccinimide in carbon tetrachloride (77°) are in the ratio 8:1. The corresponding ratio for benzaldehyde and benzyl methyl ether is 0.07:1. The acetyl bromide in the product mixture is, incidentally, easily identified through its characteristic nmr absorption and through its ready conversion to CH<sub>3</sub>COOD on exposure to D<sub>2</sub>O (see Table IV). The  $\alpha$ -bromobenzyl acetate is also easily recognized through its conversion to benzaldehyde on hydrolysis.

The mixture of products obtained through brief heating at reflux of benzyl acetate and N-bromosuccinimide in carbon tetrachloride contains appreciably more acetyl bromide than  $\alpha$ -bromobenzyl acetate. Prolonged further heating of this mixture results in little change in the quantities of these products. Therefore breakdown of the bromo acetate (eq 1) does not occur readily. It appears that this bromide is significantly more stable thermally than  $\alpha$ -bromobenzyl methyl ether, and this may be a reflection of the relative stabilities of the ion pairs, C6H5C+HOCOCH3 Br- and  $C_{6}H_{5}C^{+}HOCH_{3}$  Br<sup>-</sup> (cf. eq 5). The pathway of eq 2 is important—even dominant—in the reaction of benzyl acetate with N-bromosuccinimide, although this is not the case for the reaction of benzyl methyl ether. A possible explanation for this difference can be made by considering the relative reactivities of the acetate and the ether with N-bromosuccinimide  $(1/116 \text{ at } 77^{\circ} \text{ in carbon})$ tetrachloride<sup>10</sup>). It is reasonable to conclude, on the basis of this large reactivity difference, that of the two radical intermediates, C6H5CHOCOCH3 and C6H5-CHOCH<sub>3</sub>, the former is much less stable and should be more susceptible to direct breakdown to benzaldehyde (eq 2) than the latter.

#### Registry No.—N-Bromosuccinimide, 128-08-5.

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# Chemistry of N-Halamines. XII. Amination of Alkyl Halides with Trichloramine-Aluminum Chloride<sup>1</sup>

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Treatment of alkyl halides with trichloramine-aluminum chloride provided various types of amine products. With t-butyl chloride or bromide, high yields of t-butylamine were obtained. A minor product, 2,2-dimethylaziridine, was also formed. Other t-halides similarly produced the corresponding t-carbinamines. Skeletal rearrangement was noted with isobutyl chloride which afforded t-butylamine, sec-butylamine, and 2,2-dimethylaziridine. Primary and secondary amines, as well as N-alkylaziridines, were generated from sec-halides. meso-2,3-Dibromobutane gave trans-2,3-dimethylaziridine. Rationalizations of the results are provided.

Recent reports from this laboratory have revealed that the direct amination of aromatic compounds with N-halamines under Friedel-Crafts conditions leads to products of unusual orientation. When monoalkylbenzenes were treated with trichloramine and aluminum chloride or aluminum bromide, the corresponding malkylanilines were formed.<sup>5-8</sup> The proposed mech-

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- (5) P. Kovacic, R. M. Lange, J. L. Foote, C. T. Goralski, J. J. Hiller, Jr., and J. A. Levisky, J. Amer. Chem. Soc., 86, 1650 (1964).
- (6) P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *ibid.*, **87**, 1262 (1964).
  - (7) P. Kovacic, J. A. Levisky, and C. T. Goralski, *ibid.*, **88**, 100 (1966).
  - (8) P. Kovacic and J. A. Levisky, ibid., 88, 1000 (1966).

anism,  $\sigma$  substitution, accounts for the selective meta orientation. Further work showed that dialkylbenzenes,<sup>9</sup> biphenyl,<sup>10</sup> and napthalene<sup>10</sup> behaved similarly. With halobenzenes and anisole,<sup>11</sup> o- and p-chloroanilines were detected in addition to the meta-substituted aniline derivatives. The substitution of N-halo- or N,Ndihaloalkylamines for trichloramine in the amination of toluene resulted in the formation of the corresponding N-alkyl- or N,N-dialkylanilines.<sup>12</sup> Although meta orientation generally predominated, the ortho and para isomers were observed in appreciable quantities in certain cases.

<sup>(1)</sup> For a preliminary report see P. Kovacic and M. K. Lowery, *Chem. Commun.*, 651 (1966); presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

<sup>(9)</sup> P. Kovacic, K. W. Field, P. D. Roskos, and F. V. Scalzi, J. Org. Chem., **32**, 585 (1967).

<sup>(10)</sup> P. Kovacic and A. K. Harrison, *ibid.*, **32**, 207 (1967).
(11) P. Kovacic, J. J. Hiller, Jr., J. F. Gormish, and J. A. Levisky, *Chem.*

<sup>Commun., 580 (1965).
(12) V. L. Heasley, P. Kovacic, and R. M. Lange, J. Org. Chem., 31, 3050 (1966).</sup> 

The detection of 8-amino-p-cymene from the reaction of p-cymene with trichloramine-aluminum chloride opened a new field of investigation.<sup>13</sup> Various dialkylbenzenes containing a t-benzylic hydrogen could be successfully aminated at the side chain, thus providing a convenient synthesis for this class of *t*-carbinamines.<sup>14,15</sup> By analogy, hydrocarbons were also found to be suitable substrates.<sup>16</sup> The conversion of 1-methylcyclohexane to 1-amino-1-methylcyclohexane is an example of this novel method of substitution.

The present study deals with the amination of alkyl halides with trichloramine-aluminum chloride. Representative, simple primary, secondary, and tertiary halides were investigated with emphasis on the mechanistic and synthetic aspects.

## **Results and Discussion**

t-Alkyl Halides.—Of the compounds in this category, most attention was focused on t-butyl chloride. Optimum reaction conditions involved addition of the alkyl halide to trichloramine-aluminum chloride (vide infra, t-octyl chloride section) at  $-10^{\circ}$ . From a study entailing variation in the concentration of organic substrate, best results were achieved at a 4/1/2 molar ratio of t-butyl chloride/trichloramine/aluminum chloride (Table I). This procedure, with methylene

#### TABLE I

EFFECT OF VARIATION IN CONCENTRATION OF t-BUTYL CHLORIDE ON YIELD OF t-BUTYLAMINE t-BuCl, Ma t-BuNH2, % 1 39 2 61

	4		ę	90			
<sup>a</sup> With	NCl <sub>3</sub> /AlCl <sub>3</sub> ,	1/2.	<sup>b</sup> Based	on	weight	of	distilled
material.							

75

3

chloride as solvent, was employed as the standard for the other alkyl halides. Work-up included treatment with acid and then with base.

t-Butyl chloride gave a 90% yield (based on trichloramine) of distilled *t*-butylamine which upon glpc analysis was found to be greater than 99% pure. With the alkyl halide as reference, best yields (39%) were realized with 1 mol of the starting material. The crude basic product was also subjected to glpc analysis and found to contain a minor component which was identified as 2,2-dimethylaziridine. The authentic compound was prepared by the method of Campbell and Sommers:<sup>17</sup> concentrated sulfuric acid was added to 2-amino-2-methyl-1-propanoi, and the resulting zwitterion was then treated with strong caustic.

Table II lists the absolute yields (glpc analysis) from amination of t-butyl chloride and t-butyl bromide.

- (14) P. Kovacic and R. J. Hopper, Tetrahedron, 23, 3977 (1967).
- (15) P. Kovacic, J. F. Gormish, R. J. Hopper, and J. W. Knapczyk, J. Org. Chem., 33, 4515 (1968).

TABLE II ANIMATION PRODUCTS FROM & BUTTLE HALTER

CT MILIN.	TION	TU	0000019	FROM	C-D01	ГTГ	TIALIDE
AND	TRICH	ILO	RAMINE	-ALUM	INUM	Сн	LORIDE

	Basic	products, %
		NH
-Butyl Halide	(CH <sub>2</sub> ) <sub>3</sub> CNH <sub>2</sub>	CH2-C(CH3)2
(CH <sub>3</sub> ) <sub>3</sub> CCl	90	8
(CH₃)₃CBr	85	15

The neutral portion from the *t*-butyl chloride reaction was investigated. The indicated major components of the gross mixture were isolated and characterized: 1,2,3-trichloro-2-methylpropane, 1,1,2,3-tetrachloro-2methylpropane, 1,2,3-trichloro-2-chloromethylpropane, and 2,5-dichloro-2,5-dimethylhexane. Identification was accomplished by comparison with physical properties of the authentic substances reported in the literature,<sup>18</sup> elemental analyses (Table III) and nmr spectra (Table IV).

When the concentration of t-butyl chloride was reduced to 1 mol and the reaction mixture was quenched with ice water immediately after addition was complete, distillation of the organic phase provided a 30% yield of N,N-dichloro-t-butylamine. Zimmer and Audrieth<sup>19</sup> have prepared this compound. Isolation of N,Ndichloro-t-butylamine from the reaction of t-butyl chloride with trichloramine-aluminum chloride suggests that the nucleophile is trichloramine, dichloramine, or the dichloramide ion. The decomposition of trichloramine by hydrogen chloride, which in all likelihood occurs via a stepwise process, has been shown to give ammonium chloride and chlorine.<sup>20</sup> Hydrogen chloride is generated by dehydrohalogenation of t-butyl chloride under the catalytic influence of aluminum chloride. However, the presence of N,N-dichloro-t-butylamine cannot be taken as conclusive evidence for participation of a chlorine-containing nucleophile since attack of chlorine or a halamine on t-butylamine would give N.Ndichloro-t-butylamine. Existing data argue against trichloramine as the actual nucleophile.<sup>7</sup>

With this foundation, a plausible mechanism for the formation of t-butylamine and 2,2-dimethylaziridine is presented (eq 1-3). The nitrogenous nucleophile is tentatively designated as  $NCl_2^{\delta-}$ .

$$Cl_{3}N + AlCl_{3} \rightleftharpoons Cl_{3}N \cdots AlCl_{3} \rightleftharpoons Cl^{\delta+}(Cl_{2}NAlCl_{3})^{\delta-}$$
 (1)

$$(CH_3)_3CNCl_2 \xrightarrow{+H^+} (CH_3)_3CNH_2$$

$$(CH_3)_3CCl \xrightarrow{AlCl_4} (CH_3)_3C^+$$

$$(CH_3)_2C = CH_2 \xrightarrow{Cl^+} (CH_3)_2CCH_2Cl$$

 $-Cl^+$ 

(2)

$$(CH_{3})_{2}\overset{\dagger}{C}CH_{2}Cl \xrightarrow{NCl_{2}^{-}} (CH_{3})_{2}CNCl_{2} \xrightarrow{+H^{+}} \\ \downarrow \\ CH_{2}Cl \xrightarrow{-Cl^{+}} \\ (CH_{3})_{2}C \xrightarrow{-NH_{2}} (CH_{3})_{2}C \xrightarrow{N} CH_{2} \quad (3)$$

- (18) A. O. Rogers and R. E. Nelson, J. Amer. Chem. Soc., 58, 1027 (1936).
- (19) H. Zimmer and L. F. Audrieth, ibid., 76, 3856 (1954).

(20) W. A. Noyes, ibid., 42, 2173 (1920).

<sup>(13)</sup> J. A. Levisky, M. S. Thesis, Case Institute of Technology, 1965.

<sup>(16)</sup> P. Kovacic and S. S. Chaudhary, Tetrahedron, 23, 3565 (1967); Org. Syn., 48, 4 (1968).

<sup>(17)</sup> K. N. Campbell, A. H. Sommers, and B. K. Campbell, ibid., 37, 12 (1947).

TABLE III

PROTON MAGNETIC RESONANCE DATA FOR CHLORINATED ALKANES FROM t-BUTYL CHLORIDE-TRICHLORAMINE-ALUMINUM CHLORIDE

		~~ <u>~</u>	Chemical sł	nifts, δ, ppm <sup>a,o</sup>		_
Compound	Registry no.	CH1	CH <sub>2</sub>	CH <sub>2</sub> Cl	CHCl <sub>2</sub>	<b>Relative intensities</b>
(CH <sub>2</sub> Cl) <sub>3</sub> CCl	18963-00-3			4.41		
CH <sub>3</sub> C(CH <sub>2</sub> Cl) <sub>2</sub> Cl	1871-58-5	1.90		3.98		3/4
	18963-01-4	2.15		4.20	6.31	3/2/1
$\mathbf{CH}_{2}\mathbf{Cl}$						
$(CH_3)_2C(CH_2)_2C(CH_3)_2$	6223-78-5	1.50	1.83			3/1
Cl Cl						

<sup>a</sup> Tetramethylsilane was used as an external reference standard. <sup>b</sup> Only singlets observed.

TABLE IV

ELEMENTAL ANALYSES OF	Chlorinated	ALKANES FROM	t-BUTYL	CHLORIDE	-Trichloramine-Aluminum	CHLORIDE
-----------------------	-------------	--------------	---------	----------	-------------------------	----------

		<i></i>				-Found, %	
Compound	Formula	С	н	Cl	С	н	Cl
$CH_{3}C(Cl)(CH_{2}Cl)_{2}$	$C_4H_7Cl_3$	29.7	4.4	65.9	29.61	4.45	66.09
(CH <sub>2</sub> Cl) <sub>3</sub> CCl	C4H6Cl4	24.6	3.0	72.4	24.74	3.20	72.28
$CH_{3}C(CHCl_{2})Cl$	$C_4H_6Cl_4$	24.6	3.0	72.4	24.76	3.07	72.13
1							

CH<sub>2</sub>Cl

We are uncertain as to whether the aziridine is generated in the reaction mixture or during the work-up procedure. Coleman<sup>21</sup> found that trichloramine in the absence of aluminum chloride combined with isobutylene to form 1-chloro-2-amino-2-methylpropane. Stoichiometrically, the product is the result of addition of trichloramine across the double bond, followed by conversion of RNCl<sub>2</sub> to RNH<sub>2</sub>. Further evidence for the pathway leading to 2,2-dimethylaziridine was provided by its synthesis from either isobutylene or 1,2-dichloro-2-methylpropane in the presence of trichloramine-aluminum chloride. The latter reaction can be envisioned as first an ionization to the dimethylchloromethyl carbonium ion, followed by the same pathway as outlined in the t-butyl chloride case. Aziridine formation from N-halamine and olefins  $(\alpha,\beta$ -unsaturated ketones) has been reported previously, along with the theoretical considerations.<sup>22</sup>

The chlorinated hydrocarbons found in the neutral portion of our amination reaction mixture can be accounted for quite simply by well-established ionic processes involving some of the same intermediates as for the amination sequence.

Various other *t*-alkyl chlorides were employed in the reaction with trichloramine-aluminum chloride. The results are listed in Table V.

#### TABLE V

AMINATION PRODUCTS FR	OM <i>t</i> -Alkyl Chlorides
AND TRICHLORAMINE-	ALUMINUM CHLORIDE
R in RCl	RNH2, % <sup>a</sup>
t-Amyl	82
t-Octyl	356

1-Methyl-1-cyclohexyl 33° <sup>a</sup> Based on weight of distilled material. <sup>b</sup>*t*-Butylamine (15%) was also formed. <sup>c</sup>A large amount of residue was present from distillation.

The presence of t-butylamine in the amination of toctyl chloride can be explained by degradation<sup>23</sup> of t-octyl cation to isobutylene and t-butyl cation, followed by attack of the carbonium ion by the nitrogenous nucleophile. In the 1-chloro-1-methylcyclohexane reaction, there was also a large amount of basic distillation residue which contained the hydrochloride of 1-amino-1methylcyclohexane. This salt could only have been formed during distillation, and, therefore, points to the presence of labile chlorine as a constituent of the crude basic product. The chlorine may have resulted from addition of trichloramine to a double bond, perhaps in 1-methylcyclohexene, with subsequent loss of hydrogen chloride during distillation (conceivably accompanied by aziridine formation). A possible explanation of the decreasing yield of *t*-alkylamine with increasing alkyl substitution at the  $\beta$ -carbon atoms may be due to the greater ease of olefin formation. Brown<sup>24</sup> found that the amount of olefin arising from solvolysis of various t-alkyl chlorides increased with increasing alkyl substitution at the  $\beta$  carbon.

In the initial stages of the over-all study, we found that the mode of addition used in earlier work (introduction of trichloramine into a mixture of substrate and aluminum chloride) gave extremely low yields of basic product. Examination of various modes of addition was carried out with *t*-octyl chloride (Table VI).

## TABLE VI

#### EFFECT OF MODE OF ADDITION ON

YIELD	OF <i>t</i> -Octylamine	
Mode of addition <sup>a</sup>	RX/AlCl <sub>3</sub> /NCl <sub>3</sub>	Yield, % <sup>b</sup>
RX to AlCl <sub>3</sub> /NCl <sub>3</sub>	4/2/1	35
RX/NCl <sub>3</sub> to AlCl <sub>3</sub>	5/2/1	25
NCl <sub>3</sub> to RX/AlCl <sub>3</sub>	5/2/1	1
<sup>a</sup> $RX = t$ -octyl chlorid	le. <sup>b</sup> Based on weight	of distille

<sup>a</sup>  $\mathbb{R}X = t$ -octyl chloride. <sup>b</sup> Based on weight of distilled material.

 <sup>(21)</sup> G. H. Coleman, G. M. Mullins, and E. Pickering, *ibid.*, **50**, 2739 (1928).
 (22) N. H. Cromwell, R. P. Cahoy, W. E. Franklin, and G. D. Mercer, *ibid.*, **79**, 922 (1957).

<sup>(23)</sup> P. Kovacic and H. C. Volz, ibid., 81, 3261 (1959).

<sup>(24) (</sup>a) H. C. Brown and R. S. Fletcher, *ibid.*, **72**, 1223 (1950); (b) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

As a consequence of these findings, addition of the alkyl halide to a mixture of trichloramine and aluminum chloride was incorporated into the standard procedure. Preliminary mixing of the alkyl halide and catalyst apparently leads to poor results because of gross conversion to olefin before entry of the nucleophile.

The reaction of trichloramine-aluminum chloride with t-alkyl halides provides a novel method for the synthesis of t-alkyl amines. The interesting specificity of the nucleophile is emphasized by the easy elimination which occurs on treatment of t-alkyl halides with amines.<sup>25</sup> With few exceptions, e.g., the Ritter reaction, the classical routes to t-carbinamines are characterized by a multiplicity of steps.<sup>25</sup> The Ritter technique usually entails use of an olefin or alcohol as the substrate.<sup>26,27</sup>

**Primary Alkyl Halide.**—Since the reaction of *t*-butyl chloride and trichloramine-aluminum chloride proceeded so well, the analogous transformation with isobutyl chloride was attempted. The results in terms of absolute yields are *t*-butylamine (69%), sec-butylamine (11%), and 2,2-dimethylaziridine (eq 4-6). Presumably, the similarity of some aspects of the findings from *t*-butyl chloride reflects the participation of common intermediates.

$$(CH_3)_2CHCH_2CI \xrightarrow{AlCl_3} O (CH_3)_3C^+ \longrightarrow (CH_3)_3CNH_2 \quad (4)$$

$$(CH_3)_2CHCH_2CI \xrightarrow{NCl_3} O (CH_3CH_2CHCH_3 \longrightarrow CH_3CH_2CHCH_3 \quad (5)$$

$$(CH_3)_2C=CH_2 \longrightarrow CH_3)_2C-CH_2 \quad (6)$$

Comparison with related literature investigations proves informative. The results of nitrous acid deamination of isobutylamine in protic and aprotic media<sup>28</sup> are summarized in Table VII.

#### TABLE VII

## CATIONIC PRECURSORS FOR PRODUCTS FROM NITROUS ACID DEAMINATION OF ISOBUTYLAMINE<sup>28</sup> Solvent (CH3)3C CH3CH2CHCH3 (CH3)3CHCH2

CH3COOH	55	37	8
HCCl <sub>3</sub>	19.7	15.9	64.4

Product composition in the aprotic medium is interpreted as resulting from kinetic control of the reaction, whereas in the protic case one is approaching thermodynamic control which, in the extreme situation, would lead to substances from t-butyl precursor. The large amount of isobutyl-containing material from the aprotic environment is attributed to SN2 substitution. Our results indicate the absence of backside displacement since no isobutyl-derived products were found. The large amount of t-butylamine suggests that the reaction is thermodynamically controlled for the most part.

(25) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry,"
John Wiley & Sons, Inc., New York, N. Y., 1953, Chapter 24.
(26) J. J. Ritter and J. Kalish, J. Amer. Chem. Soc., 70, 4048 (1948).

vic-Alkylene Dihalides.—The investigation of aziridine production from reaction of vicinal dihalides with trichloramine-aluminum chloride was pursued. Addition of bromine to cis- and trans-2-butene provided dl-2,3-dibromobutane and meso-2,3-dibromobutane, respectively. Amination of the meso form gave rise to trans-2,3-dimethylaziridine in 40% yield, whereas the racemic disastereomer gave no organic amine product. The indicated mechanism (eq 7) is proposed to rationalize the positive result.



If the same mechanism were operative with dl-2,3dibromobutane, generation of the resonance-stabilized bridged ion from neighboring-group participation would force the methyl groups into a stereochemically unfavorable *cis* relationship. It appears, therefore, that anchimeric assistance by the second bromine is important, since if simple ionization occurred, rotation about the C<sub>2</sub>-C<sub>3</sub> bond would place the methyls *trans* to one another. Hence, it seems plausible that there is an energetically more favorable alternative pathway, perhaps elimination of hydrogen bromide.

sec-Alkyl Halides.—Isopropyl chloride reacted with trichloramine-aluminum chloride to give isopropylamine (18%), diisopropylamine (48%), and N-isopropylpropylenimine (20%). Proposed pathways for the formation of these products are illustrated (eq



8-10). The intermediate N,N-dichloroisopropylamine might conceivably be derived from either the isopropyl cation and  $NCl_2^-$ , or from SN2 attack on the alkyl halide.

An oversimplified stoichiometric relationship for the reaction is illustrated (eq 11). This equation is

$$(CH_2)_2 CHCl + NCl_4 \xrightarrow{AlCl_3} (CH_3)_2 CHNCl_2 + Cl_2 \quad (11)$$

consistent with the fact that iodometric titration of the reaction mixture immediately after addition of isopropyl chloride demonstrated the presence of all of the positive chlorine. Another possible interpretation, namely,

 <sup>(27)</sup> M. Mousseron, R. Jacquier, and H. Christol, Bull. Soc. Chim. Fr., 600 (1957).

<sup>(28)</sup> A. Jurewicz, Ph.D. Thesis, Case Institute of Technology, 1967.

that no reaction had occurred, was discounted by the visible and ultraviolet spectra of the reaction mixture. A maximum was recorded at 320 m $\mu$ , which gradually shifted with time to  $312 \text{ m}\mu$  and decreased in intensity. If the positive chlorine in the initial stages were in the form of trichloramine, the maximum should be at 345 mµ. Chlorine and N,N-dichloroisopropylamine absorb at 335 and 312 m $\mu$ , respectively.<sup>12,29</sup> Therefore, the maximum recorded at 320 m $\mu$  may be ascribed to a mixture of the three components (trichloramine, chlorine, and N,N-dichloroisopropylamine) or a combination of two components, N,N-dichloroisopropylamine and either trichloramine or chlorine. The shift of the maximum to  $312 \text{ m}\mu$  as time elapsed indicated the presence of N,N-dichloroisopropylamine, with the decrease in peak intensity reflecting conversion to amine products.

It was found that, after addition of isopropyl chloride to trichloramine-aluminum chloride, the catalyst dissolved. This observation prompted an investigation of the reaction of N,N-dichloroisopropylamine with aluminum chloride. Treatment of isopropylamine with hypochlorous acid yielded N,N-dichloroisopropylamine which produced a homogeneous mixture on exposure to an equimolar amount of aluminum chloride at  $-30^{\circ}$ . The nmr spectrum of the solution at  $-30^{\circ}$  was identical with that of N,N-dichloroisopropylamine. However, on warming to  $-10^{\circ}$  two new peaks appeared at 2.95 ppm at the expense of the methyl doublet at 1.60 ppm associated with N,N-dichloroisopropylamine. After several hours, the two peaks at 2.95 ppm were the only ones detectable. The nmr spectrum can be interpreted as due to N-chloroisopropylimine (nonequivalent methyl groups). Hydrolysis of the reaction mixture gave a 42% yield of acetone. The illustrated reaction scheme appears appropriate (eq 12). The conversion

$$(CH_3)_2 CHNCl_2 \xrightarrow{AlCl_3} (CH_3)_2 C = N \xrightarrow{Cl} \xrightarrow{H_2O} (CH_3)_2 C = O \xrightarrow{(12)}$$

of primary amines to carbonyl compounds via halamines has been studied previously.<sup>30</sup> The N-chloramine, derived from the amine and t-butyl hypochlorite, was treated with sodium ethoxide, followed by hydrolysis of the resulting imine to the desired ketone. The dehydrohalogenation of N,N-dichloroisopropylamine is apparently set in motion by coordination of the aluminum chloride with a chlorine substitutent. In contrast, with base catalysis hydrogen suffers initial attack by alkoxide ion. The literature records a similar conversion of N-chloroisopropylamine to acetone and ammonia by dehydrohalogenation followed by hydrolysis.<sup>31</sup>

Amination of cyclopentyl bromide with trichloraminealuminum chloride gave cyclopentylamine (20%), dicyclopentylamine (37%), and N-cyclopentyl-6-azabicyclo[3.1.0]hexane (23%). Mechanistic pathways completely analogous to those postulated for amination of isopropyl chloride appear to be applicable. The reaction of sec-butyl chloride with trichloraminealuminum chloride afforded eight products including sec-butylamine, the two diastereomers of di-sec-butylamine, and uncharacterized materials. The unknown bases may be N-alkylaziridines formed from reaction of N,N-dichloro-sec-butylamine with cis- or trans-2-butene, or 1-butene.

In the case of *sec*-alkyl halides, it appears that two nitrogenous nucleophiles are involved. The second species, which was not encountered as a reactant in the *t*-alkyl halide series, would appear to be  $RR'CHNCl_2$ . Steric arguments can be advanced to account for participation of only one nucleophilic entity in the *t*-alkyl halide case. The steric factor pertains to the nucleophile and substrate, both of which contain the bulky *t*-alkyl moiety (the hypothetical end product would be di-*t*-alkylamine, a highly crowded molecule). There is also the reasonable possibility that formation of secondary amines arises from backside attack, a pathway which is not available to the tertiary series.

There are certain similarities and differences in the reactions of alkanes<sup>16</sup> and alkyl halides with trichloramine-aluminum chloride. One of the principal differences involves the mode of generation of the carbonium ion. With the alkyl halides, aluminum chloride catalyzes ionization in a well-established manner. In the amination of alkanes, carbonium ion formation is not so well defined. It is postulated that chloronium ion abstracts hydride.<sup>16</sup> Another important difference is the experimental procedure employed. With alkanes, trichloramine is added to a mixture of the hydrocarbon and aluminum chloride, whereas in amination of alkyl halides, the substrate is introduced into a mixture of trichloramine and aluminum chloride. Thus the concentrations of trichloramine and substrate in the two systems differ prior to the final stages of reaction.

#### **Experimental Section**

Melting points and boiling points are uncorrected.

Materials.—The alkyl halides, which were generally subjected to gas chromatographic examination, were greater than 98% pure. t-Octyl chloride and 1-chloro-1-methylcyclohexane were prepared by bubbling dry hydrogen chloride through diisobutylene<sup>32</sup> and methylcyclohexene,<sup>33</sup> respectively. The preparation of 1,2-dichloro-2-methylpropane was accomplished by refluxing a mixture of concentrated hydrochloric acid and methallyl chloride.<sup>34</sup> Addition of bromine to *cis*- and *trans*-2-butene afforded the respective diastereomeric dibromides, *dl*-2,3-dibromobutane and *meso*-2,3-dibromobutane.

Analytical Procedures.—Infrared spectra were recorded with a Beckman IR-8 spectrophotometer on neat samples. Nmr spectra were obtained on a Varian A-60 or A-60A unit, and ultraviolet and visible spectra with a Beckman DB spectrophotometer. Galbraith Laboratories, Knoxville, Tenn., performed the elemental analyses. Gas chromatography was carried out with an Aerograph A-90-P (columns 1-3) or Aerograph Hy-Fi 1200 (columns 4, 5) gas chromatograph (Table VIII).

Trichloramine Solution.—A published procedure' (method B) was used with methylene chloride as solvent. *Caution:* exercise the necessary precautions when working with N-halamines.

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## TABLE VIII

## GLPC COLUMNS

	Dimensions,	
Column	ft:in.	Packing
1	15:0.25	15% Carbowax 20M on base-coated (5% KOH) Chromosorb P (30/60 mesh)
2	15:0.25	20% Carbowax 1540 on base-coated (5% KOH) Chromosorb P (30/60 mesh)
3	6:0.25	15% Apiezon L on base-coated (5% KOH) Chromosorb P (30/60 mesh)
4	15:0.13	15%Carbowax 1540 on base-coated (5% KOH) Chromosorb P (60/80 mesh)
5	6:0.13	Poropak Q (80/100 mesh)

Amination of Alkyl Halides and Dihalides .--- In reactions involving alkyl bromides, a nitrogen flow was maintained throughout the course of reaction. The purge was not necessary in the case of alkyl chlorides.

A. t-Alkyl Halides.—A slurry of 26.6 g (0.2 mol) of aluminum chloride in 100 ml of methylene chloride was cooled to  $-10^{\circ}$  in a three-necked flask equipped with a stirrer, thermometer, condenser, and dropping funnel. A solution of trichloramine (0.1 mol) in methylene chloride (150 ml) was added quickly. The t-alkyl halide (0.4 mol) in an equal volume of methylene chloride was added dropwise between -5 and  $-10^{\circ}$ . The reaction mixture was stirred for 1 hr after addition was complete, and then poured over hydrochloric acid and ice.

B. sec-Alkyl Halides, Dihalides, and Isobutyl Chloride.—The same general procedure as for the amination of t-alkyl halides was followed except that the temperature was allowed to rise to 15° during the hour of stirring after addition was complete.

C. Isobutylene.-In a 125-ml erlenmeyer flask cooled to  $-30^{\circ}$ , 22.4 g (0.4 mol) of isobutylene was collected. The flask was fitted with a one-hole rubber stopper and tube leading to a three-necked flask equipped with a gas inlet tube, thermometer, stirrer and condenser. A slurry of 26.6 g (0.20 mol) of aluminum chloride in 100 ml of methylene chloride was cooled to  $-10^{\circ}$  in the reaction flask and a solution of trichloramine (0.10 mol) in methylene chloride (150 ml) was added quickly. The isobutylene was then vaporized into the reaction mixture by gentle warming. The temperature was kept at  $-10^{\circ}$  during the addition, and then allowed to rise to  $15^{\circ}$  during the hour of stirring after addition was complete. Following the appropriate work-up procedure, glpc analysis showed one product, 2,2-dimethylaziridine, in 10% yield.

Work-Up Procedures .-- Two work-up procedures were employed in the isolation of amine products. After standing overnight, the two layers were separated, and the organic layer was The aqueous layer washed twice with dilute hydrochloric acid. and washings were extracted twice with ether.

Method A .- In the case of water-insoluble amines, the aqueous layer was made basic with 50% sodium hydroxide. The basic products were extracted with ether and dried over anhydrous sodium sulfate. Following removal of ether by rotary evaporation, distillation of the crude amine product was carried out with a "Minilab" apparatus.

Method B.—For water-soluble amines, the aqueous layer was cooled, made basic with 50% sodium hydroxide, and then steam distilled into a hydrochloric acid solution until the distillate was no longer basic. Water was removed from the amine hydro-chloride solution by rotary evaporation. When distillation was feasible, the amine hydrochloride salt was dissolved in 10 ml of water and made basic with 40 ml of 50% sodium hydroxide. The amine product was distilled from the basic aqueous solution in a "Minilab" apparatus. If distillation was not possible, the amine hydrochloride salt was dissolved in water, made basic, and extracted with ether. Analysis of products was made by gas chromatography.

Product Identification. 1. Amines.-The indicated aliphatic amines were identified by comparison with authentic materials on the basis of glpc retention time, and infrared, and nmr spectra: t-butylamine, t-octylamine, sec-butylamine, isopropylamine, diisopropylamine, t-amylamine, cyclopentylamine, and dicyclopentylamine. The remainder of the amine products were synthesized as described.

A. 1-Amino-1-methylcyclohexane.--We are grateful to Dr. S. S. Chaudhary for an authentic sample which was prepared by the Ritter method from 1-methylcyclohexene and sodium cyanide.16

B. 2,2-Dimethylethylenimine.—The method of Campbell and Sommers<sup>17</sup> gave a 20% yield, bp 70-72° (lit.<sup>17</sup> bp 71-72°). C. trans-2,3-Dimethylaziridine.-The method of Dickey, Fickett and Lucas<sup>35</sup> was followed.

D. N-Isopropylpropylenimine. a. 1-Isopropylamino-2propanol.—A mixture of 118 g (2 mol) of isopropylamine in 65 ml of water was placed in a three-necked flask equipped with stirrer, thermometer, condenser and dropping funnel. Propylene oxide (58 g, 1 mol) was added dropwise over a period of 30 min. After the mixture was heated under reflux for 90 min, the product was distilled: bp 75-76.5° (22 mm) [lit.<sup>36</sup> bp 75.5-76° (22 mm)]; 65% yield.

b. Ring Closure.—The method of Campbell and Sommers<sup>17</sup> was followed. Since solidification of the zwitterion did not occur, the resulting viscous liquid was treated with base. Distillation of the crude product gave 5 g (21% yield) of desired material, bp 80-82°

Anal. Calcd for C<sub>6</sub>H<sub>13</sub>N: C, 72.70; H, 13.15; N, 14.15. bund: C, 72.64; H, 13.23; N, 14.01. Found:

E. N-Cyclopentyl-6-azabicyclo[3.1.0]hexane. a. Cyclopentene Oxide.-The method of Emmons and Pagano<sup>87</sup> was used. The product was formed in 45% yield, bp 97-99° (lit.<sup>37</sup> bp 98-100°)

b. 1-Cyclopentylamino-2-cyclopentanol.-The procedure described for 1-isopropylamino-2-propanol was followed. The

product was isolated by distillation, bp 100-102° (1 mm). Anal. Calcd for  $C_{10}H_{19}NO$ : C, 71.00; H, 11.20; N, 8.30. Found: C, 70.85; H, 11.34; N, 8.15.

c. Ring Closure.—The method of Campbell and Sommers<sup>17</sup> was followed. After the mixture solidified, base was added and the solution was heated at reflux for 5 min. The base was extracted with ether, and distilled, bp 52-53° (2 mm), n<sup>25</sup>D 1.4734. Anal. Calcd for  $C_{10}H_{17}N$ : C, 79.50; H, 11.30; N, 9.20. bund: C, 79.42; H, 11.47; N, 9.41.

Found:

2. Neutral Products from Amination of t-Butyl Chloride.-The amination of t-butyl chloride was carried out according to the procedure for t-alkyl halides. After the neutral organic layer was dried over anhydrous sodium sulfate and the methylene chloride and ether were removed by rotary evaporation, the residue was subjected to vacuum distillation. The individual entities were collected and identified by the infrared spectra, indices of refraction,<sup>18</sup> nmr spectra (Table III) and elemental analyses (Table IV).

Authentic 2,5-dichloro-2,5-dimethylhexane<sup>38</sup> was prepared by the procedure of Johnston and Quayle,39 60% yield, mp 64° (lit.38 mp 64-65°)

Isolation of N,N-Dichloro-t-butylamine.-In a 500-ml, threenecked flask equipped with thermometer, stirrer, condenser and dropping funnel, a mixture of 26.6 g (0.2 mol) of aluminum chloride and 100 ml of methylene chloride was cooled to  $-10^{\circ}$ . Trichloramine (0.1 mol) in methylene chloride (150 ml) was added quickly. With the temperature between -5 and  $-10^{\circ}$ , 9.25 g (0.1 mol) of t-butyl chloride in an equal volume of methylene chloride was added dropwise. After addition, the reaction mixture was quenched with ice water, and the organic layer was separated and dried over anhydrous sodium sulfate. Following separation of the solvent by rotary evaporation, vacuum distillation afforded N,N-dichloro-t-butylamine in 30% yield, bp 37° (16 mm),  $n^{26}$ D 1.4611. The infrared and nmr spectra were identical with those of the authentic material.

Preparation of Authentic N,N-Dichloro-t-butylamine.-In a 1-l., three-necked flask equipped with thermometer, stirrer, condenser and dropping funnel were placed 50 g (0.23 mol) of "HTH" (70% calcium hypochlorite) in 200 ml of methylene chloride and 150 ml of water. A solution of 21.9 g (0.2 mol) of t-butylamine hydrochloride in 20 ml of water and 37.5 ml of concentrated hydrochloric acid was added dropwise below 10°.

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When addition was complete, the mixture was stirred for an additional 15 min, and then the layers were separated. The organic layer was dried over anhydrous sodium sulfate, methylene chloride was removed by rotary evaporation, and vacuum distillation of the residue gave the desired product in 55% yield:

bp 34° (16 mm),  $n^{26}$ D 1.4609 [lit.<sup>19</sup> bp 30° (16 mm),  $n^{19}$ D 1.4639]. Reaction of N,N-Dichloroisopropylamine<sup>40</sup> with Aluminum Chloride.—The preparation of N,N-dichloroisopropylamine was the same as that described for N,N-dichloro-t-butylamine. In a 250-ml, three-necked flask equipped with stirrer, thermometer, dropping funnel, and condenser were placed 6.7 g (0.05 mol) of aluminum chloride and 26 ml of methylene chloride. The mixture was cooled between -25 and  $-30^\circ$ , and 56 ml of a methylene chloride solution of N,N-dichloroisopropylamine (0.05 mol) was added quickly. An aliquot of the reaction mixture (homogeneous) was taken and the nmr spectrum recorded at  $-22^{\circ}$ . The spectrum showed a heptet at 3.95 ppm for the methyl groups, 1/6 ratio for CH/CH<sub>3</sub>, and was the same as that of N, N-dichloroisopropylamine. When the solution in the nmr tube was allowed to warm to  $-10^{\circ}$ , a new doublet appeared at 2.95 ppm which increased with time, whereas the doublet due to the methyl protons of N,N-dichloroisopropylamine decreased and then disappeared. The reaction mixture was subjected to the same conditions as for the sample. Aliquots were taken periodically until the nmr spectrum showed the disappearance of the peaks attributed to N.N-dichloroisopropylamine.

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After addition of water, the layers were separated. Glpc analysis of the organic layer revealed a single product which was collected and identified as acetone from the infrared and nmr spectra. By means of an internal standard, the yield was calculated to be 42%.

Visible and Ultraviolet Spectra of the Reaction Mixture from 2-Chloropropane and Trichloramine-Aluminum Chloride.-The general amination procedure for sec-alkyl halides was followed. After addition was complete, the temperature of the reaction mixture was kept at -5 to  $-10^{\circ}$ . There was no solid remaining in the reaction mixture. A 2-ml aliquot was taken and placed in a separatory funnel containing 10 ml of water and 8 ml of methylene chloride. The spectrum of the organic layer showed a maximum at 320 m $\mu$ . The temperature was allowed to increase to 20°. At 10-min intervals, aliquots were taken, quenched, and the spectrum recorded. The maximum shifted to 312 m $\mu$  with a decrease in intensity until after 230 min there was no discernible maximum.

Registry No.-Trichloramine, 10025-85-1; aluminum chloride, 7446-70-0; t-butyl chloride, 507-20-0; t-butyl bromide, 507-19-7.

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# Reactions of Difluoramine with *a*-Hydroxy Ketones<sup>1</sup> and $\alpha,\beta$ -Diketones in the Presence of Sulfuric Acid

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 $\alpha$ -Hydroxy ketones in fuming sulfuric acid undergo reaction with difluoramine to form substituted 4-difluoramino-1,3-dioxa-2-thiolane 2,2-dioxides. Under similar conditions,  $\alpha,\beta$ -diketones give substituted 4,5-bis(difluoramino)-1,3-dioxa-2-thiolane 2,2-dioxides. Difluoramine was generated in situ by the interaction of N,N-difluorourea with sulfuric acid.

The preparation of a large number of organic compounds containing difluoramino groups has been reported in the past several years. Most of these compounds have been synthesized either by direct fluorination<sup>2-7</sup> or by reactions involving tetrafluorohydrazine.<sup>8-15</sup> The use of difluoramine<sup>16-19</sup> for intro-

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ducing difluoramino groups into organic molecules<sup>20-22</sup> has been reported in the literature in only a few cases. It is believed that the latter reactions involve the formation of an intermediate carbonium ion, which subsequently alkylates the diffuoramine. A new reaction has been found that is in agreement with this theory. This reaction involves the condensation of  $\alpha$ -hydroxy ketones or  $\alpha,\beta$ -diketones with diffuoramine and fuming sulfuric acid. The main products of this reaction are substituted 4-difluoramino-1,3-dioxa-2thiolane 2,2-dioxides (1) and substituted 4,5-bis-(difluoramino)-1,3-dioxa-2-thiolane 2,2-dioxides (2), respectively.

The compounds are prepared in a one-step procedure. A solution of N,N-diffuorourea<sup>2</sup> and the ketone in methylene chloride is treated with concentrated sulfuric

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