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Reactions of 1-Trichloromethyl-substituted Amines with Potassium *tert*-Butoxide

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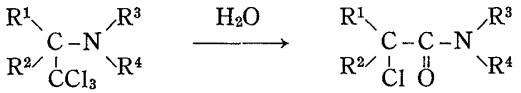
The reaction of 1-trichloromethyl-substituted amines with *tert*-butoxide has been shown to provide important entries into a number of groups of functionalized amines, *i.e.*, 2,2-dichlorovinylamines (which are also convertible into chloroynamines with a large excess of *tert*-butoxide), 2,2-dichloroenamines, N-(α-dichloromethylbenzylidene)-amines and 2,2-dichloroaziridines. The formation of the products in individual cases depends upon the structure of the amine substrate.

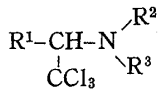
Keywords——1-trichloromethyl-substituted amines; potassium *tert*-butoxide; 2-chloroynamines; 2,2-dichloroenamines; N-(α-dichloromethylbenzylidene)amines; 2,2-dichloroaziridines; elimination of hydrogen chloride

As reported previously, the decarboxylation reactions of trichloroacetic acid with Schiff bases,[2] N,N′-alkylidenebisamines[3,4] and enamines[5] provide ready access to 1-trichloromethyl-substituted amines. However, previous studies on the chemical features of these functionalized amines have been limited to their hydrolysis[4,6,7] to provide 1-chloroacylamines with rearrangement. This hydrolysis has been reported[4,7] to be induced readily on heating in a solvat-



(A)

ing medium, but seems to depend upon the structure of the amine substrate. The reactive amines previously reported are represented by the structure A, where R^1, R^2 and R^3 are alkyl groups and R^4 is an alkyl group or hydrogen, but no report has appeared on the hydrolysis of amines possessing hydrogen at the C^1 carbon, except for some more-reactive 1-tribromomethyl-substituted analogs.[4,8]



(B)

R^1, R^2, R^3:	H	phenyl or alkyl	phenyl or alkyl
	alkyl	alkyl	alkyl or aryl
	alkyl	alkyl	H

We therefore began an investigation on the reactions of a variety of 1-trichloromethyl-substituted amines of type B, which can be obtained synthetically, to determine how these amines behave in a strongly basic medium such as potassium *tert*-butoxide. It was found

1) Location: *2-2-1 Oshika, Shizuoka 422, Japan.*
2) A. Lukasiewicz, *Tetrahedron*, **20**, 1 (1964).
3) M. Sekiya, O. Matsuda, and K. Ito, *Chem. Pharm. Bull.*, **23**, 1579 (1975).
4) A. Lukasiewicz, *Tetrahedron*, **20**, 1113 (1964).
5) A. Lukasiewicz and J. Lesinka, *Tetrahedron*, **24**, 7 (1968).
6) G.H. Alt and A.J. Speziale, *J. Org. Chem.* **31**, 1340 (1966).
7) A. Lukasiewicz and J. Lesinska, *Tetrahedron*, **21**, 3247 (1965).
8) A. Lukasiewicz, *Tetrahedron*, **21**, 193 (1965).

that the reaction with *tert*-butoxide provides novel entries into a number of groups of functionalized amines, *i.e.*, 2,2-dichlorovinylamines, 2,2-dichloroenamines, N-(α-dichloromethylbenzylidene)amines and 2,2-dichloroaziridines; the former three types of compounds have not previously appeared in the literature.

Tertiary 2,2,2-trichloroethylamines (**1**), where R^2R^3N: O N (**1a**) and N (**1b**) in B, gave the corresponding 2,2-dichlorovinylamines (**2a** and **2b**) upon reaction with 1.5 molar equivalents of potassium *tert*-butoxide in tetrahydrofuran (THF) at 10—15°. On comparing

$$\underset{\mathbf{1}}{Cl_3CCH_2\text{-}N(R^2)(R^3)} \xrightarrow{\textit{tert}\text{-BuOK}} \underset{\mathbf{2}}{CCl_2{=}CH\text{-}N(R^2)(R^3)} \xrightarrow{\textit{tert}\text{-BuOK}} \underset{\mathbf{3}}{ClC{\equiv}C\text{-}N(R^2)(R^3)}$$

the reaction times (given in parentheses)**1a** (1 hr) was more reactive than **1b** (20 hr), giving **2a** and **2b** in 45% and 30% yields, respectively. The products, **2a** and **2b**, gave infrared (IR) and nuclear magnetic resonance (NMR) spectra consistent with the proposed structures (see Table IV).

In the reaction of **1a** with two molar equivalents of *tert*-butoxide under similar conditions, the formation of N-(2-chloroethynyl)morpholine (**3a**) is suggested by the intense peak at 2200 cm^{-1} characteristic of a carbon-carbon triple bond in the IR spectrum of the residue of the concentrated reaction solution freed of potassium chloride. However, our attempts to isolate **3a** in a sufficiently pure state encountered difficulties. Among compounds of this chloroynamine type, only N,N-diphenyl-N-(2-chloroethynyl)amine is known.[9] Presumably resonance of its N-phenyl substituents contributes to its thermal stability, but an N-alkyl substituent such as that of **3a** may lower its stability. The reactions of **1a**, **1b** and **1c** (R^2R^3N: $(CH_3)_2N$) with greatly increased amounts of *tert*-butoxide resulted in the production of 1-*tert*-butoxy-2-chlorovinylamines (**4a—c**) and, when *tert*-butanol was used as a solvent in place of THF, in the production of 2-*tert*-butoxyacetamides (**5a—c**) (see Table I). The productions of **4a—c** and **5a—c** may be interpreted in terms of chloroynamine intermediates, **3a—c**. Structures of the products, **4a—c** and **5a—c**, were assigned on the basis of the IR and NMR spectral data shown in Table IV.

Table I.

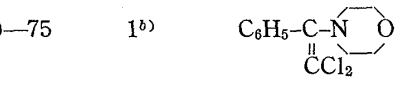
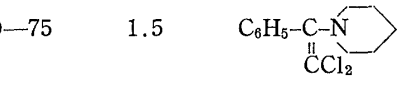
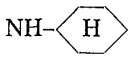
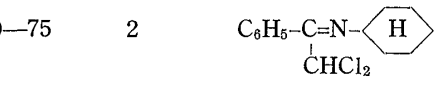
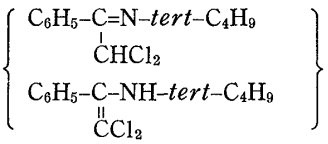
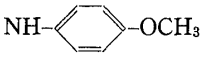
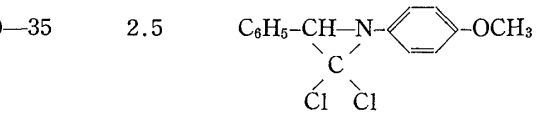
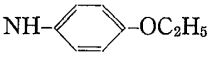
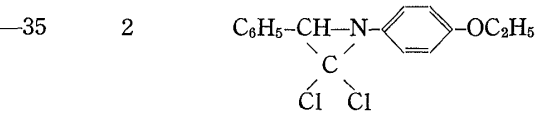
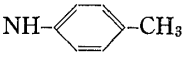
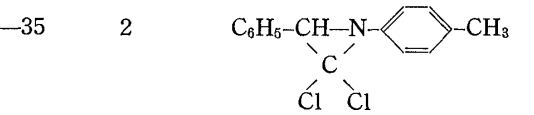
$$\underset{\mathbf{1a—c}}{CCl_3CH_2N(R^2)(R^3)} \xrightarrow[\text{B. } \textit{tert}\text{-BuOK}^{b)} \text{ in } \textit{tert}\text{-BuOH, 75—78°}]{\text{A. } \textit{tert}\text{-BuOK}^{a)} \text{ in THF, 30—40°}} \underset{\mathbf{3a—c}}{[ClC{\equiv}C\text{-}N(R^2)(R^3)]} \rightarrow \begin{cases} \underset{\mathbf{4a—c}}{ClCH{=}C(\textit{tert}\text{-BuO})\text{-}N(R^2)(R^3)} \\ \underset{\mathbf{5a—c}}{\textit{tert}\text{-}BuOCH_2CON(R^2)(R^3)} \end{cases}$$

Substrate	Method A Yield (%)[c] of **4a—c**	Method B Yield (%)[c] of **5a—c**
1a	44 (1)	45 (2)
1b	57 (6)	47 (7)
1c	58 (3)	35 (2)

a) 5 molar equivalents.
b) 4 molar equivalents.
c) Values in parentheses indicate reaction times in hr.

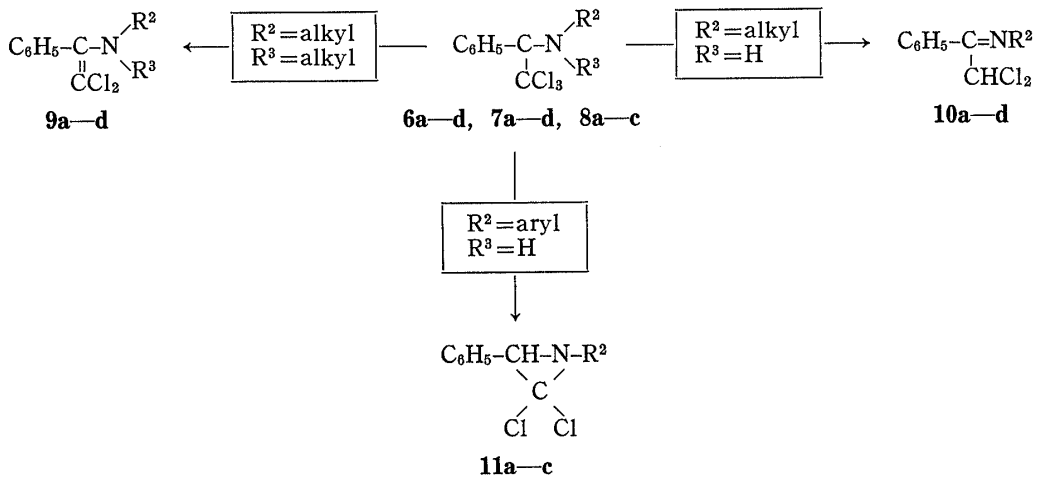
9) J. Ficini, C. Barbara, S. Colodny, and A. Dureault, *Tetrahedron Lett.*, **1968**, 943.

Table II. The *tert*-Butoxide Reaction[a] of $C_6H_5CH(CCl_3)N\langle^{R^2}_{R^3}$

Substrate No.	NR^2R^3	Reaction temp. (°C)	Reaction time (hr)	Product Structure	No.	Yield (%)
6a		70—75	1[b]		**9a**	89
6b		70—75	1.5		**9b**	77
6c	$N(CH_3)_2$	70—75	1	$C_6H_5-C(=CCl_2)-N(CH_3)_2$	**9c**	70
6d	$N(CH_3)CH_2C_6H_5$	70—75	1	$C_6H_5-C(=CCl_2)-N(CH_3)CH_2C_6H_5$	**9d**	82
7a	NH-iso-C_3H_7	70—75	1.5	$C_6H_5-C(CHCl_2)=N$-iso-C_3H_7	**10a**	62
7b		70—75	2		**10b**	64
7c	NH-*sec*-C_4H_9	70—75	4	$C_6H_5-C(CHCl_2)=N$-*sec*-C_4H_9	**10c**	63
7d	NH-*tert*-C_4H_9	70—75	8		**10d** **9e**	72[c]
8a		30—35	2.5		**11a**	37
8b		30—35	2		**11b**	35
8c		30—35	2		**11c**	42

a) The reaction was carried out with 3 molar equivalents of *tert*-butoxide in *tert*-butanol.
b) With 2 molar equivalents of *tert*-butoxide, 5 hours was necessary to complete the reaction, and the yield was 83%.
c) Yield of a mixture of **10d** and **9e**.

A variety of tertiary and secondary 1-phenyl-2,2,2-trichloroethylamines, **6a**—**d**, **7a**—**d** and **8a**—**c**, where R^1 is phenyl in B, were then subjected to the *tert*-butoxide reaction in *tert*-butanol. The results of these experiments are summarized in Table II. Even with a large excess of *tert*-butoxide, the reaction stopped after elimination of one molar equivalent of hydrogen chloride (in practice, 3 molar equivalents of *tert*-butoxide was used in order to speed up the reaction) and the products were of particular interest in that 2,2-dichloroenamine, **9a**—**d**, N-(α-dichloromethylbenzylidene)amine, **10a**—**d**, or 2,2-dichloroaziridine, **11a**—**c**, was produced as the major product, depending on the substrate structure. From the data shown in Table II, it can be generally said that, among the various amine moieties $N\langle^{R^2}_{R^3}$ of the substrates, the cases of R^2,R^3=alkyl give 2,2-dichloroenamines, R^2=alkyl and R^3=hydrogen give N-(α-dichloromethylbenzylidene)amines, and R^2=aryl and R^3=hydrogen give 2,2-dichloroaziridines. In the case of secondary 1-phenyl-2,2,2-trichloroethylamines, it is probable

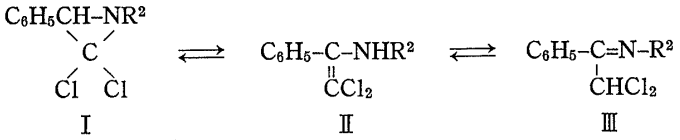


9a—d **6a—d, 7a—d, 8a—c** **10a—d**

11a—c

Chart 1

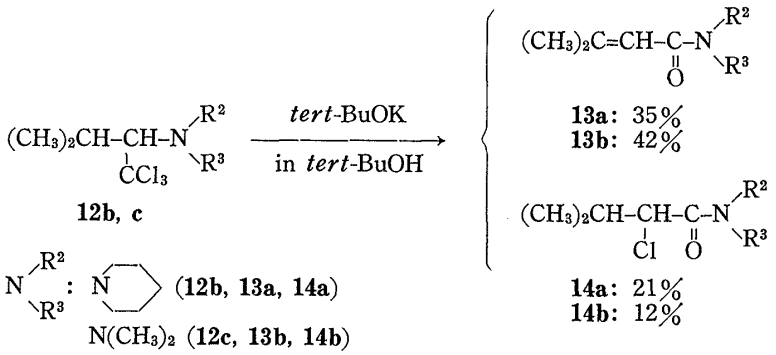
that the three isomers bear the following prototropic relationship to each other, and that the formation of the product in individual cases is governed by thermodynamic control.



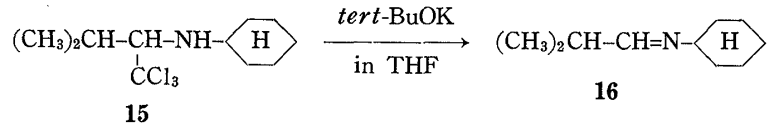
I II III

The satisfactory microanalyses for **9a—d** are sufficient to justify assignment of the 2,2-dichloroenamine structure. Among the three possible structures, the N-(α-dichloromethylbenzylidene)amine structure, III, was assigned to a **10a—c** on the basis of spectral data; in the NMR spectra the methine proton appeared at δ 6.35—6.40 ppm as a singlet, and the IR spectra showed the carbon-nitrogen double bond absorption at 1640—1643 cm^{-1}. Assignment of the 2,2-dichloroaziridine structure, I, to **11a—c** was made on the basis of the appearance of the methine proton at δ 3.60—3.65 ppm as a singlet in the NMR spectra. Further evidence for the aziridine structure was obtained by hydrolysis of a representative compound, **11a**, in aqueous alcohol to yield 2-chloro-2-phenyl-*p*-acetanisidide. Physical, spectral and analytical data for all the products obtained in the reactions in Table II are shown in Table IV. The reaction of 1-phenyl-2,2,2-trichloroethylamine (**7d**) gave a mixture of the prototropic isomers, **9e** and **10d**. Although separation of the mixture was difficult, the proposed composition is supported by the spectral data; in the NMR spectrum the signals of the –NH– proton and the methine proton appear at δ 3.82 ppm as a broad singlet and at 6.27 ppm as a singlet, respectively, and the *tert*-butyl signal appears at δ 1.16 and 1.07 ppm as two signals, while in the IR spectrum the –NH– stretching vibration and the >C=N– stretching vibration appear at 3360 cm^{-1} and 1660 cm^{-1}, respectively.

Next, aliphatic tertiary 2,2,2-trichloroethylamines, where R^1 is isopropyl and the amine moiety, NR^2R^3 is morpholino, **12a**, piperidino, **12b**, or dimethylamino, **12c**, were subjected to reaction with *tert*-butoxide under the conditions used for the reaction of **6a—d**. Among these three substrates, only **12a** gave the corresponding 2,2-dichloroenamine, **9f**, in 81% yield, reacting in the same way as **6a—d**, whereas **12b** and **12c** behaved in a different fashion to give the corresponding α,β-unsaturated, **13a**, **b**, and α-chlorinated amides, **14a**, **b**, as major products. These products, which gave appropriate spectral data (see Table IV), are considered to be formed by the rearrangement and hydrolysis of **12b**, **c** through 2,2-dichloroaziridinium intermediates, as reported previously.[4,6,7] This conversion of **12b**, **c**, different from that of **12a**, may be in the main due to the increasing basicity of the amine moieties, which makes 2,2-dichloroaziridinium formation easier.



The reaction of *tert*-butoxide was further examined with a substrate of aliphatic secondary amine type, **15**, where R^1=isopropyl and NR^2R^3=NH-⟨H⟩. In this case the reaction resulted in the formation of a Schiff base, **16**, with elimination of chloroform.



In view of the above experimental results, the reaction of various 1-trichloromethyl-substituted amines with *tert*-butoxide appears to be capable of producing a number of functionalized amines such as 2,2-dichlorovinylamines, 2,2-dichloroenamines, N-(α-dichloromethylbenzylidene)amines and 2,2-dichloroaziridine, some of which are rarely encountered in the literature. As precursors leading to these functionalized amines, 1-trichloromethyl-substituted amines represent compounds of potential synthetic usefulness.

Experimental

The reaction temperature, period and yield for the *tert*-butoxide reactions described below are recorded in Tables I and II. Physical, spectral and analytical data for the reaction products are recorded in Table IV.

1-Trichloromethyl Substituted Amines——These materials used for the *tert*-butoxide reaction were prepared by the reactions of Schiff bases, N,N′-alkylidenebisamines and enamines with trichloroacetic acid according to the previously reported procedures.[2-5] Among these compounds, amines which have not been described previously are listed in Table III.

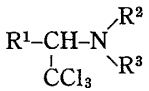
2,2-Dichlorovinylamines (2a, b)——Amine Moiety: morpholine (**2a**), piperidine (**2b**). Procedure: A solution of 0.05 mol of tertiary 2,2,2-trichloroethylamine (**1a, b**)[3] in 50 ml of dry THF was treated dropwise with a solution of 8.4 g (0.075 mol) of *tert*-BuOK in 50 ml of dry THF with stirring at 10—15°. After the addition, the temperature was raised to 20—25° with stirring for 1 hr in the run with **1a** and for 20 hr in the run with **1b**. After filtration, the solvent was removed by evaporation under reduced pressure and the resulting residue was extracted with petr. ether. The solution was dried over $MgSO_4$ and removal of the petr. ether gave an oily residue which was distilled under reduced pressure to give the product (**2a, b**).

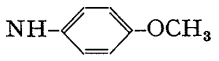
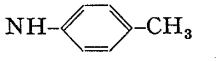
1-*tert*-Butoxy-2-chlorovinylamines (4a—c)——Amine Moiety: morpholine (**4a**), piperidine (**4b**), dimethylamine (**4c**). Procedure: A mixture of 0.05 mol of tertiary 2,2,2-trichloroethylamine (**1a—c**)[3] in 150 ml of dry THF and 28.1 g (0.25 mol) of *tert*-BuOK was heated with stirring. After filtration, the solvent was removed by evaporation under reduced pressure and the resulting residue was extracted with petr. ether. The solution was dried over $MgSO_4$, and removal of the petr. ether gave an oily residue which was distilled under reduced pressure to give the product (**4a—c**).

2-*tert*-Butoxyacetamides (5a—c)——Amine Moiety: morpholine (**5a**), piperidine (**5b**), dimethylamine (**5c**). Procedure: A mixture of 0.05 mol of tertiary 2,2,2-trichloroethylamine (**1a—c**) in 150 ml of *tert*-BuOH and 22.4 g (0.20 mol) of *tert*-BuOK was heated with stirring. After filtration, the filtrate was saturated with CO_2 and the precipitated materials were removed by filtration. Purification of the residual material obtained by removal of the solvent gave the products. The main product (**5a—c**) was obtained by distillation under reduced pressure.

2,2-Dichloro-1-phenylvinylamine (9a—e) and 1-Dichloromethylene-2-methylpropylamine (9f)——Amine Moiety: morpholine (**9a, f**), piperidine (**9b**), dimethylamine (**9c**), methylbenzylamine (**9d**), *tert*-butylamine (**9e**). Procedure: A mixture of 0.05 mol of tertiary or secondary 2,2,2-trichloroethylamine (**6a**,[4] **b**,[4] **c—d,**

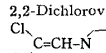
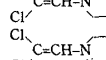
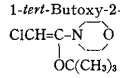
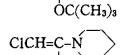
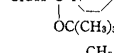
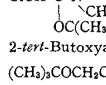
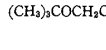
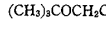
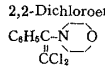
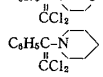
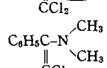
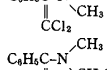
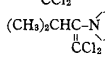
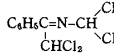
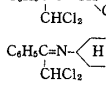
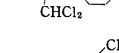
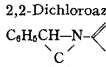
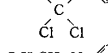
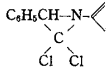
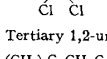
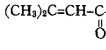
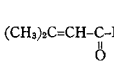
TABLE III. 1-Trichloromethyl-substituted Amines



Compd. No.	R^1	NR^2R^3	Material[a] for preparation	Appearance	bp (°C) (mmHg)	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N
6c	C_6H_5	$N(CH_3)_2$	$R^1CH(NR^2R^3)_2$[b]	Prisms (Hydrochloride)		164—165	$C_{10}H_{13}Cl_4N$	41.56 (41.81	4.52 4.53	4.85 4.85)
6d	C_6H_5	$N(CH_3)(CH_2C_6H_5)$	$R^1CH(NR^2R^3)_2$[b]	Prisms		66	$C_{16}H_{16}Cl_3N$	58.47 (58.38	4.91 4.91	4.26 4.27)
12a	$(CH_3)_2CH$		$(CH_3)_2C{=}CHNR^2R^3$ [c]	Liquid	109—111 (0.15)		$C_9H_{16}Cl_3NO$	41.48 (41.19	6.19 6.08	5.38 5.29)
12b	$(CH_3)_2CH$		$(CH_3)_2C{=}CHNR^2R^3$ [c]	Liquid	99—101 (0.2)		$C_{10}H_{18}Cl_3N$	46.44 (46.21	7.02 6.96	5.42 5.32)
12c	$(CH_3)_2CH$	$N(CH_3)_2$	$(CH_3)_2C{=}CHNR^2R^3$ [d]	Prisms (Hydrochloride)		131—133	$C_7H_{15}Cl_4N$	32.97 (32.89	5.93 5.86	5.49 5.37)
7a	C_6H_5	$NHCH(CH_3)_2$	$R^1CH{=}NR^3$ [e]	Prisms (Hydrochloride)		165	$C_{11}H_{15}Cl_4N$	43.60 (43.43	4.99 4.96	4.62 4.53)
7c	C_6H_5	$NHCH(CH_3)(C_2H_5)$	$R^1CH{=}NR^3$ [e]	Prisms (Hydrochloride)		176	$C_{12}H_{17}Cl_4N$	45.46 (45.62	5.42 5.42	4.42 4.36)
7d	C_6H_5	$NHC(CH_3)_3$	$R^1CH{=}NR^3$ [f]	Prisms (Hydrochloride)		204	$C_{12}H_{17}Cl_4N$	45.46 (45.35	5.42 5.25	4.42 4.40)
8a	C_6H_5		$R^1CH{=}NR^3$ [g]	Prisms		77—78	$C_{15}H_{14}Cl_3NO$	54.49 (54.51	4.27 4.30	4.24 4.23)
8c	C_6H_5		$R^1CH{=}NR^3$ [g]	Prisms		63—64	$C_{15}H_{14}Cl_3N$	57.26 (57.37	4.49 4.45	4.45 4.41)

a) The 1-trichloromethyl-substituted amine was prepared from this material by decarboxylation with trichloroacetic acid.
b) M. Sekiya and H. Sakai, *Chem. Pharm. Bull.*, **17**, 32 (1969).
c) G. Optiz, A. Griesinger, and H.W. Schubert, *Ann.*, **665**, 91 (1963).
d) K.L. Brannock and R.D. Burpitt, *J. Org. Chem.*, **26**, 3576 (1961).
e) R.E. Lutz, P.S. Bailey, R.J. Rowlett, J.W. Wilson, R.K. Allison, M.T. Clark, N.H. Leake, R.H. Jordan, R.J. Keller, and K.C. Nicodemus, *J. Org. Chem.*, **12**, 760 (1947).
f) M. Freifelder, M.B. Moore, M.R. Vernsten, and G.R. Stone, *J. Am. Chem. Soc.*, **80**, 4320 (1958).
g) H.H. Keasling and F.W. Schueler, *J. Am. Pharm. Assoc.*, **39**, 87 (1950).

TABLE IV. Physical, Spectral and Analytical Data for the Products

Product	bp (°C) (mmHg)	mp (°C)[a]	Appearance (recryst. solvt.)	IR $\nu_{max}^{KBr, Liq.}$[b] cm^{-1}	NMR ($CDCl_3$) δ (ppm)[c]	Formula	Analysis (%) Calcd (Found) C	H	N
2,2-Dichlorovinylamines									
 (**2a**)	78—80 (0.7)		Liquid	1630(C=C)	6.11 (1H, s, C=CH) 3.82—3.60 (4H, m, $O(CH_2)_2$) 3.22—3.01 (4H, m, $N(CH_2)_2$)	$C_6H_9Cl_2NO$	39.59 (39.20	4.98 4.94	7.69 7.37)
 (**2b**)	76—78 (4)		Liquid	1632(C=C)	6.13 (1H, s, C=CH) 3.24—2.98 (4H, m, $N(CH_2)_2$) 1.75—1.42 (6H, m, $CH_2(CH_2)_2$)	$C_7H_{11}Cl_2N$	46.69 (46.27	6.16 6.21	7.78 7.72)
1-*tert*-Butoxy-2-chlorovinylamines									
 (**4a**)	92—94 (0.15)	29	Prisms (petr. ether)	3100(H-C=) 1618(C=C)	4.81 (1H, s, CH=) 3.80—3.58 (4H, m, $O(CH_2)_2$) 3.02—2.74 (4H, m, $N(CH_2)_2$) 1.42 (9H, s, $C(CH_3)_3$	$C_{10}H_{18}ClNO_2$	54.67 (54.57	8.26 8.11	6.38 6.59)
 (**4b**)	103—104 (5)		Liquid	3100(H-C=) 1620(C=C)	4.76 (1H, s, CH=) 3.00—2.65 (4H, m, $N(CH_2)_2$) 1.75—1.30 (6H, m, $CH_2(CH_2)_2$) 1.37 (9H, s, $C(CH_3)_3$)	$C_{11}H_{20}ClNO$	60.68 (61.17	9.26 9.27	6.43 6.52)
 (**4c**)	86 (30)		Liquid	3100(H-C=) 1620(C=C)	4.71 (1H, s, CH=) 2.54 (6H, s, $N(CH_3)_2$) 1.40 (9H, s, $C(CH_3)_3$)	$C_8H_{16}ClNO$	54.08 (53.99	9.08 9.04	7.88 7.82)
2-*tert*-Butoxyacetamides									
 (**5a**)	77 (0.04)		Liquid	1650(C=O)	4.01 (2H, s, OCH_2CO) 3.64 (8H, s, $N(CH_2CH_2)_2O$) 1.22 (9H, s, $C(CH_3)_3$)	$C_{10}H_{19}NO_3$	59.68 (59.87	9.52 9.59	6.96 7.06)
 (**5b**)	84 (0.3)		Liquid	1648(C=O)	4.06 (2H, s, OCH_2CO) 3.70—3.30 (4H, m, $N(CH_2)_2$) 1.80—1.30 (6H, m, $CH_2(CH_2)_2$) 1.12 (9H, s, $C(CH_3)_3$)	$C_{11}H_{21}NO_2$	66.29 (66.42	10.62 10.77	7.03 7.17)
 (**5c**)	107 (30)		Liquid	1650(C=O)	4.13 (2H, s, OCH_2CO) 3.05 (3H, s, NCH_3) 2.93 (3H, s, NCH_3) 1.23 (9H, s, $C(CH_3)_3$)	$C_8H_{17}NO_2$	60.35 (59.87	10.76 10.72	8.80 8.79)
2,2-Dichloroenamines									
 (**9a**)		70—71	Prisms (MeOH)		7.31 (5H, s, arom. H) 3.76—3.55 (4H, m, $O(CH_2)_2$) 3.04—2.78 (4H, m, $N(CH_2)_2$)	$C_{12}H_{13}Cl_2NO$	55.83 (56.16	5.08 5.22	5.43 5.49)
 (**9b**)	118—120 (0.07)	24	Prisms (MeOH)		7.35 (5H, s, arom. H) 3.12—2.68 (4H, m, $N(CH_2)_2$) 1.75—1.30 (6H, m, $CH_2(CH_2)_2$)	$C_{13}H_{15}Cl_2N$	60.95 (61.10	5.90 5.96	5.47 5.41)
 (**9c**)	86—88 (0.06)		Liquid		7.25 (5H, s, arom. H) 2.63 (6H, s, $N(CH_3)_2$)	$C_{10}H_{11}Cl_2N$	55.58 (55.55	5.13 5.05	6.48 6.45)
 (**9d**)	148—150 (0.06)	29	Prisms (MeOH)		7.41—7.21 (10H, m, arom. H) 3.96 (2H, s, NCH_2) 2.72 (3H, s, NCH_3)	$C_{16}H_{15}Cl_2N$	65.77 (65.79	5.17 5.24	4.79 4.82)
 (**9f**)	88—90 (0.1)	26	Prisms (petr. ether)		3.75—3.54 (4H, m, $O(CH_2)_2$) 3.10—2.93 (4H, m, $N(CH_2)_2$) 2.05—1.75 (1H, m, >CH) 1.05 (6H, d, J=7.0 Hz, $C(CH_3)_2$)	$C_9H_{15}Cl_2NO$	48.23 (47.91	6.75 6.67	6.25 6.32)
N-(α-Dichloromethylbenzylidene)amines									
 (**10a**)	79—81 (0.8)	61—62	Prisms (*n*-hexane)	1640(C=N)	7.60—7.15 (5H, m, arom. H) 6.40 (1H, s, $CHCl_2$) 3.35 (1H, septet, J=7.0 Hz, NCH) 1.05 (6H, d, J=7.0 Hz, $C(CH_3)_2$)	$C_{11}H_{13}Cl_2N$	57.41 (57.11	5.69 5.60	6.09 6.00)
 (**10b**)		101	Prisms (petr. ether)	1641(C=N)	7.55—7.00 (5H, m, arom. H) 6.35 (1H, s, $CHCl_2$) 3.20—2.80 (1H, m, NCH) 1.90—0.75 (10H, m, $(CH_2)_5$)	$C_{14}H_{17}Cl_2N$	62.23 (62.35	6.34 6.27	5.18 5.22)
 (**10c**)		57—58	Prisms (*n*-hexane)	1643(C=N)	7.51—7.04 (5H, m, arom. H) 6.35 (1H, s, $CHCl_2$) 3.80 (1H, sextet, J=6.0 Hz, NCH) 1.25 (2H, quintet, J=6.0 Hz, CH_2) 1.03 (3H, d, J=6.0 Hz, $>CHCH_3$) 0.74 (3H, t, J=6.0 Hz, CH_2CH_3)	$C_{12}H_{15}Cl_2N$	59.03 (59.04	6.19 6.15	5.74 5.69)
2,2-Dichloroaziridines									
 (**11a**)		90	Prisms (*n*-hexane)		7.45 (5H, s, arom. H) 6.93 (4H, s, arom. H) 3.79 (3H, s, OCH_3) 3.65 (1H, s, CHN)	$C_{15}H_{13}Cl_2NO$	61.24 (61.20	4.45 4.46	4.76 4.88)
 (**11b**)		79—80	Prisms (*n*-hexane)		7.46 (5H, s, arom. H) 6.96 (4H, s, arom. H) 4.01 (2H, q, J=7.0 Hz, OCH_2) 3.63 (1H, s, CHN) 1.37 (3H, t, J=7.0 Hz, CH_3)	$C_{16}H_{15}Cl_2NO$	62.35 (62.47	4.91 4.91	4.54 4.55)
 (**11c**)		61	Prisms (petr. ether)		7.35 (5H, s, arom. H) 7.07 (2H, d, J=8.0 Hz, arom. H) 6.90 (2H, d, J=8.0 Hz, arom. H) 3.60 (1H, s, CHN) 2.31 (3H, s, CH_3)	$C_{15}H_{13}Cl_2N$	64.77 (65.12	4.71 4.77	5.04 5.06)
Tertiary 1,2-unsaturated and 1-chloro-substituted amines									
 (**13a**)	118—120 (4)		Liquid	1630(C=O)	5.76 (1H, s, C=CH) 3.76—3.21 (4H, m, $N(CH_2)_2$) 1.85 (6H, s, $(CH_3)_2C$) 1.70—1.30 (6H, m, $CH_2(CH_2)_2$)	$C_{10}H_{17}NO$	71.81 (71.40	10.25 10.20	8.37 8.31)
 (**13b**)	76—78 (23)		Liquid	1630(C=O)	5.76 (1H, s, C=CH) 2.95 (6H, s, $N(CH_3)_2$) 1.93 (3H, s, $C(CH_3)_2$) 1.85 (3H, s, $C(CH_3)_2$)	$C_7H_{13}NO$	66.11 (66.33	10.30 10.30	11.01 10.88)
 (**14a**)	129—131 (3)		Liquid	1650(C=O)	4.18 (1H, d, J=8.0 Hz, >CHCl) 3.74—3.26 (4H, m, $N(CH_2)_2$) 2.56—2.07 (1H, m, $(CH_3)_2CH$) 1.12 (3H, d, J=7.0 Hz, $C(CH_3)_2$) 0.98 (3H, d, J=7.0 Hz, $C(CH_3)_2$)	$C_{10}H_{18}ClNO$	58.96 (59.26	8.91 8.84	6.88 6.90)
(**14b**)	102—103 (17)		Liquid	1665(C=O)	4.14 (1H, d, J=8.0 Hz, >CHCl) 3.09 (3H, s, $N(CH_3)_2$) 2.96 (3H, s, $N(CH_3)_2$) 2.68—2.01 (1H, m, $(CH_3)_2CH$) 1.14 (3H, d, J=7.0 Hz, $C(CH_3)_2$) 0.95 (3H, d, J=7.0 Hz, $C(CH_3)_2$)	$C_7H_{14}ClNO$	51.38 (51.40	8.62 8.58	8.56 8.46)

a) Melting points of the crystallized products are uncorrected.
b) IR spectra were obtained with a Hitachi EPI-G2 spectrophotometer.
c) NMR spectra were taken with a Hitachi R-24 spectrometer (at 60 MHz) using tetramethylsilane as an internal standard.

7d, **12a**) in 150 ml of *tert*-BuOH and 16.8 g (0.15 mol) of *tert*-BuOK was heated with stirring. The reaction mixture was worked up by the procedure described for **5a—c**. In the run with **6a**, the product, **9a**, was obtained by recrystallization of the resulting solid residue.

N-(α-Dichloromethylbenzylidene)amines (**10a—d**)——Amine Moiety: isopropylamine (**10a**), cyclohexylamine (**10b**), *sec*-butylamine (**10c**), *tert*-butylamine (**10d**). Procedure: A mixture of 0.05 mol of secondary 2,2,2-trichloroethylamine (**7a, b**,[2] **c, d**) in 150 ml of *tert*-BuOH and 16.8 g (0.15 mol) of *tert*-BuOK was heated with stirring. The reaction mixture was worked up by the procedure described for **5a—c**. In the runs with **7b** and **7c**, the products, **10b** and **10c**, were obtained by recrystallization of the resulting solid residues.

2,2-Dichloroaziridines (**11a—c**)——Amine Moiety: *p*-anisidine (**11a**), *p*-phenetidine (**11b**), *p*-toluidine (**11c**). Procedure: A mixture of 0.05 mol of secondary 2,2,2-trichloroethylamine (**8a, b**,[2] **c**) in 150 ml of *tert*-BuOH and 16.8 g (0.15 mol) of *tert*-BuOK was heated with stirring. The reaction mixture was worked up by the procedure described for **5a—c**. In the runs with **8a** and **8b**, the resulting residues were triturated with EtOH to give crystals of **11a** and **11b** which were recrystallized from an appropriate solvent. In the run with **8c**, hexane was added to the resulting residue and an insoluble resin was removed by decantation. The residue obtained by removal of the hexane was crystallized on standing in a refrigerator and was recrystallized from petr. ether to give **11c**.

Tertiary 1,2-Unsaturated and 1-Chloro-substituted Amines (**13a, b and 14a, b**)——Amine Moiety: piperidine (**13a, 14a**), dimethylamine (**13b, 14b**). Procedure: A mixture of 0.05 mol of tertiary 2,2,2-trichloroethylamine (**12b, c**) in 150 ml of *tert*-BuOH and 16.8 g (0.15 mol) of *tert*-BuOK was heated at 70—75° with stirring for 20 hr in the run with **12b** and for 12 hr in the run with **12c**. The reaction mixture was worked up by the procedure described for **5a—c**. The resulting residue was chromatographed on Al_2O_3 with benzene as an eluent to give the products (**13a, 14a** and **13b, 14b**).

N-Isobutylidenecyclohexylamine (**16**)——A mixture of 0.05 mol of secondary 2,2,2-trichloroethylamine (**15**)[10] in 150 ml of dry THF and 16.8 g (0.15 mol) of *tert*-BuOK was heated at 60° with stirring for 8 hr. The reaction mixture was worked up by the procedure described for **5a—c**. Distillation of the resulting residue under reduced pressure gave **16** in 46% yield; this product was identified as N-isobutylidenecyclohexylamine, bp 76—77° (18 mmHg), by comparison of its IR spectrum with that of an authentic specimen prepared by another route.

10) A Lukasiewicz and H. Czarnadola, *Rocz. Chem.*, **46**, 2321 (1972).