The amidine was identical with that prepared from N-phenyl-2,2-dichloroacetimidoyl chloride as follows: To a solution consisting of 10.62 g. (0.048 mole) of N-phenyl-2,2-dichloroacetimidoyl chloride[32] and 25 ml. of benzene there was added 7.02 g. (0.096 mole) of diethylamine which was dissolved in 15 ml. of benzene. The benzene–amine solution was added at such a rate that the temperature rose slowly from 25 to 67°. The reaction mixture was then refluxed for 1.5 hours. Diethylamine hydrochloride, m.p. 227–228° (5.26 g., 100% yield), was filtered and washed with benzene after the reaction mixture was cooled to about 30°. The filtrate and washings were mixed and the benzene distilled *in vacuo*. N,N-Diethyl-N′-phenyl-2,2-dichloroacetamidine, b.p. 92° (0.05 mm.), $n^{25}\mathrm{D}$ 1.5650, d^{25} 1.1605, was distilled through a 15 × 70 mm. Vigreux column. The yield was 10.68 g. (86.4%).

Anal. Calcd. for $C_{12}H_{16}Cl_2N_2$: C, 55.61; H, 6.22; Cl, 27.36; N, 10.81. Found: C, 55.52; H, 6.25; Cl, 27.37; N, 11.10.

N-Phenyl-2,2-dichloroacetimidoyl Chloride.[32]—A mixture of 61.23 g. (0.3 mole) of 2,2-dichloroacetanilide, 60 g. (0.288 mole) of phosphorus pentachloride and 100 ml. of benzene was heated at 45° for 0.5 hour and then refluxed 0.5 hour. The benzene and phosphorus oxychloride were co-distilled *in vacuo*. N-Phenyl-2,2-dichloro·acetimidoyl chloride, b.p. 115–117° (10 mm.), $n^{25}\mathrm{D}$ 1.5723, was distilled through a 15 × 70 mm. Vigreux column. The yield was 44.63 g. (69.4%).

ST. LOUIS 66, MO.

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[32] J. F. Braun, F. Jostes and W. Munch, *Ann.*, **453**, 133, 146 (1927).

[CONTRIBUTION FROM THE ST. LOUIS RESEARCH DEPARTMENT, ORGANIC CHEMICALS DIVISION, MONSANTO CHEMICAL CO.]

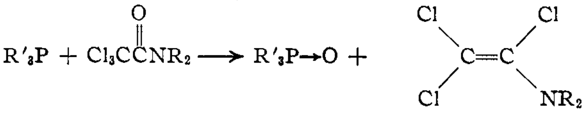
The Reactions of Enamines. I. N,N-Disubstituted-1,2,2-trichlorovinylamines

BY A. J. SPEZIALE AND R. C. FREEMAN

RECEIVED JULY 2, 1959

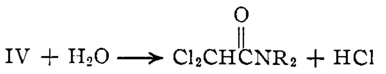
N,N-Diethyl-1,2,2-trichlorovinylamine (IVa) is an effective reagent for the replacement of hydroxyl groups by chloride. The yields are good in the cases of carboxylic acids and primary, secondary and tertiary alcohols. *d-sec*-Butyl alcohol is transformed to *l-sec*-butyl chloride in good yield and high optical purity. Amidines are formed from the reaction of IVa with amines. Stable salts are obtained from the reaction of IVa with halogen acids. The mechanisms for these reactions are discussed. The iminium ion $>\mathrm{CH}\overset{|}{\mathrm{C}}=\overset{+}{\mathrm{N}}\mathrm{H}-$ appears to be important in the reaction of IVa with acids, alcohols and amines.

Trivalent phosphorus compounds have been shown to undergo oxidation by trichloroacetamides to yield the corresponding phosphates or phosphine oxides and trichlorovinylamines.[1]



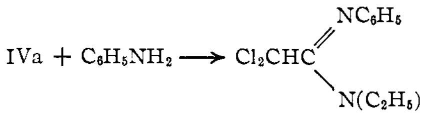
I II III IVa, R = C_2H_5

As part of the proof of structure of IVa, it was reported that upon reaction with water,[1,2] hydrogen chloride and the dichloroacetamide (Va) were formed. In addition, reaction of IVa with aniline yielded the amidine VIa.



$$\mathrm{IV} + H_2O \longrightarrow Cl_2CH\overset{\overset{\displaystyle O}{\|}}{C}NR_2 + HCl$$

Va, R = C_2H_5



VIa

The reactions of these trichlorovinylamines have now been extended to alcohols, acids and to aliphatic and aromatic amines and their hydrochlorides.

N,N-Diethyl-1,2,2-trichlorovinylamine (IVa) reacted rapidly with alcohols and carboxylic acids[3] (see Table I) to give good yields of the corresponding alkyl and acid chlorides, respectively. In these reactions N,N-diethyl-2,2-dichloroacetamide was isolated in yields ranging from 67–95%. The conversion of trichloroamides to dichloroamides

TABLE I

REACTION OF N,N-DIETHYL-1,2,2-TRICHLOROVINYLAMINE (IVa) WITH WATER, ALCOHOLS AND ACIDS

ROH R =	Yield, % RCl, R =	Yield, % $Cl_2CHCON(C_2H_5)_2$	Reacn. temp., °C.
H	H, 95.5	76.0	25
C_2H_5	C_2H_5[a]	79.6	35–38
C_2H_5	C_2H_5, 82	86.5	55–60
dl-s-C_4H_9	*dl-s*-C_4H_9, 81[b]	91.8	40–50
dl-s-C_4H_9	*dl-s*-C_4H_9, 68.7[c]	83.5	60–75
d-s-C_4H_9	*l-s*-C_4H_9, 83.8[b]	94.5	40–50
t-C_4H_9	*t*-C_4H_9, 50.8[d]	61.8[e]	20–25
t-C_4H_9	*t*-C_4H_9, 56.2[f]	87.0	60–75
t-C_4H_9	*t*-C_4H_9, 23.1[g]	78.7[h]	75–80
CH_3CO	CH_3CO, 72.1	75.1	50–60
C_6H_5CO	C_6H_5CO, 72.3	66.6	85
2,4,6-$(NO_2)_3C_6H_2$	O[i]	0	65–70

[a] Ether was used as solvent; ethyl chloride was not isolated. [b] About 1% of hydrogen chloride and 2-butene were formed. [c] The amount of hydrogen chloride and 2-butene were not determined. [d] The yield was 60.8% based on the recovery of 16.9% of *t*-butyl alcohol. Only a trace of hydrogen chloride was detected. [e] The yield was 77.9% based on the recovery of 21% of IVa. [f] Isobutylene was formed. [g] Benzene was used as a solvent. The yield was 32.8% based on the recovery of 29.4% of *t*-butyl alcohol. [h] The yield was 92.3% based on the recovery of 14.8% of IVa. [i] 85.6% of the picric acid was recovered and 89.3% of IVa.

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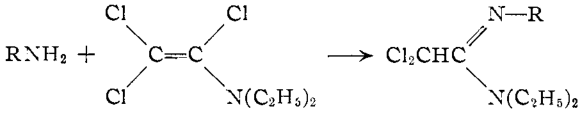
(1) A. J. Speziale and R. C. Freeman, THIS JOURNAL, **81**, 903 (1959).

(2) E. Ott, *et al.*, *Chem. Ber.*, **76B**, 80, 84, 88 (1943). These authors reported the reaction: $ClCH{=}C(Cl)N(C_2H_5)_2 + H_2O \rightarrow ClCH_2CON(C_2H_5)_2$.

(3) Th. R. Rix and J. F. Arens, *Proc. Koninkel. Ned. Akad. Wetenschap.*, **56B**, 368,372 (1953); *C.A.*, **44**, 2300 (1955), reported that 1-chloro-1-ethoxyethylene reacted with alcohols and carboxylic acids to yield ethyl acetate and the corresponding alkyl chlorides and acid chlorides. Also see I. A. Smith, *J. Chem. Soc.*, 1099 (1927), and H. Crompton and P. L. Vanderstichele, *ibid.*, 691 (1920), who obtained similar results with 1,2-dihalo-1-alkoxyethylene.

TABLE II

FORMATION OF AMIDINES



IVa VI

	Amine R	Reacn. time, hr.	HCl liberated,[a] %	Yield, %	B.p. (mm.) or m.p., °C.	$n^{25}\mathrm{D}$	Formula	Analysis							
								C		H		Cl		N	
								Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
VIa	C_6H_5	16	58[b]	77.7	88 (0.02)	1.5649	....	...	...	..	..	...	...	...	...
	C_6H_5[c]	22	69.4	81.8	....	....	....	...	...	..	..	...	...	...	...
VIb	$4\text{-}CH_3C_6H_4$	4.5	70	91.7	87 (0.02)	1.5606	$C_{13}H_{18}Cl_2N_2$	57.17	57.14	6.64	7.05	25.96	25.76	10.26	10.36
VIc	$4\text{-}ClC_6H_4$	22	67	65.6	95 (0.02)	1.5766	$C_{12}H_{15}Cl_3N_2$	49.08	50.41	5.15	4.54	36.23	36.51	9.54	9.62
VId	$4\text{-}O_2NC_6H_4$	2.5	..	87.2	104–105	....	$C_{12}H_{15}Cl_2N_3O_2$	47.38	47.61	4.97	4.92	23.31	23.41	13.81	14.05
VIe	$4\text{-}C_2H_5OC_6H_4$	4.5	0	18.9	118–119 (0.06)	1.5582	$C_{14}H_{20}Cl_2N_2O$	55.45	55.67	6.65	6.28	...	...	...	...
VIf	C_4H_9	20	0	22.6	102 (8.1)	1.4825	$C_{10}H_{20}Cl_2N_2$	50.21	49.78	8.43	8.23	29.64	30.06	...	...
	C_4H_9[d]	48	0	44.5	....	....	....	...	...	..	..	...	...	...	...
	C_4H_9[e]	24	47.8	68	....	....	....	...	...	..	..	...	...	...	...

[a] Hydrogen chloride liberated during reaction and collected in sodium bicarbonate solution. [b] Calculated from the amount of triethylamine hydrochloride isolated (42%); data taken from ref. 1. [c] Aniline hydrochloride. [d] There was used a 1:2 molar ratio of IVa to amine. [e] Butylamine hydrochloride.

via the reaction sequence II → IV → V appears to be of preparative value and represents a novel transformation. The reaction of IV with alcohols and acids occurs in neutral media under mild reaction conditions. Thus, hydroxyl-containing compounds which possess groups sensitive to the usual reagents ($SOCl_2$,PCl_5 etc.) may be converted to the corresponding halide by the action of IV.

The yields of alkyl halide obtained in the reaction of IVa with alcohols depend on the type of alcohol, the temperature at which the reactions are conducted and whether or not solvents are used. For example, N,N-diethyl-1,2,2-trichlorovinylamine (IVa), at 60–75° reacted with ethanol, *dl-s*-butyl alcohol and *t*-butyl alcohol to give 82, 69 and 56% yields, respectively, of the corresponding alkyl chlorides. The yields (84–87%) of N,N-diethyl-2,2-dichloroacetamide (Va) was not appreciably affected by the type of alcohol. In the case of *dl-sec*-butyl alcohol and *t*-butyl alcohol, however, hydrogen chloride and 2-butene and isobutylene, respectively, were isolated. The lower yields of *sec*-butyl chloride and *t*-butyl chloride (as compared to ethyl chloride) was, therefore, due to the dehydration of the alcohols. The dehydration reaction also occurred to a greater extent when the reaction was conducted in solvents. *t*-Butyl chloride was formed in only 33% yield in refluxing benzene and a larger amount of isobutylene was formed than in the case where no solvent was used. At 40–50°, *sec*-butyl alcohol reacted with IVa to give an 81% yield of *sec*-butyl chloride and only a 1% yield of hydrogen chloride. However, at 20–25° reaction of IVa with *t*-butyl alcohol was incomplete. The alcohol and vinylamine (IVa) were recovered in 16.9 and 21% yield, respectively.

Trichlorovinylamines are useful agents for the conversion of optically active alcohols to their corresponding chlorides with inversion of configuration. Treatment of one equivalent of *d-sec*-butyl alcohol ($[\alpha]^{20}\mathrm{D}$ + 13.89°) with an equivalent of IVa at 50° (no solvent) afforded an 83.8% yield of *l-sec*-butyl chloride $[\alpha]^{20}\mathrm{D}$ −27.94°. Material of high optical purity ($[\alpha]^{20}\mathrm{D}$ −31.05°) was obtained by one redistillation. The purity of *l-sec*-butyl chloride[4] indicated that racemization occurred only to a small extent. The ease of preparation and high yield of product with high optical purity make this an attractive method for the preparation of active alkyl halides. The relatively low reaction temperatures (20–25°) for this transformation may become important in the conversion of sensitive alcohols to active halides and in this respect this reaction may have some advantage over the iminoester pyrolysis method.[5]

Although the reaction of benzoic acid with IVa was less exothermic than acetic, good yields of both acid chlorides were isolated. Acetyl chloride was identified by conversion to its anilide and benzoyl chloride as its *p*-toluidide. Picric acid was completely inert toward IVa, under conditions in which benzoic and acetic acids were very reactive.

The reaction of IVa with aliphatic and aromatic amines and their hydrochlorides led to the formation of amidines VI. The data on their preparation are given in Table II. The yields of amidines ranged from 19 to 92%. The aromatic amines were more reactive toward IVa than aliphatic amines. The rate of reaction of IVa with aniline, butylamine and their hydrochlorides was based on the rate of hydrogen chloride evolution, heat of reaction and yields of amidine. Hydrogen chloride was evolved slowly from the reaction mixture of IVa and aniline and there was no heat of reaction. With aniline hydrochloride, hydrogen chloride was evolved rapidly from the exothermic reaction mixture. Similar results were obtained with butylamine and its hydrochloride. Other weak aromatic amines reacted rapidly to give the respective amidines with liberation of hydrogen chlo-

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[4] R. L. Letsinger, L. G. Maury and R. L. Burwell, Jr., THIS JOURNAL, **73**, 2373 (1951), calculated that the rotation of optically pure enantiomorph of *sec*-butyl chloride should lie between $[\alpha]^{25}\mathrm{D}$ 29.2° and 33.2°. If the higher rotation represents optically pure butyl chloride, racemization or reaction with retention of configuration could have occurred only to the extent of 6–7%.

[5] (a) C. L. Stevens, D. Morrow and J. Lawson, *ibid.*, **77**, 2341 (1955), reported a rotation of $[\alpha]^{20}\mathrm{D}$ −31.2° for *sec*-butyl chloride obtained from the pyrolysis of *d-sec*-butyl iminoacetate hydrochloride at 150°. (b) Also compares F. Cramer and H. J. Baldauf, *Ber.*, **92**, 370 (1959), who reported similar results from optically active *sec*-octyl alcohol and α-phenylethanol with trichloroacetonitrile and hydrogen chloride without isolation of the iminoester hydrochlorides.

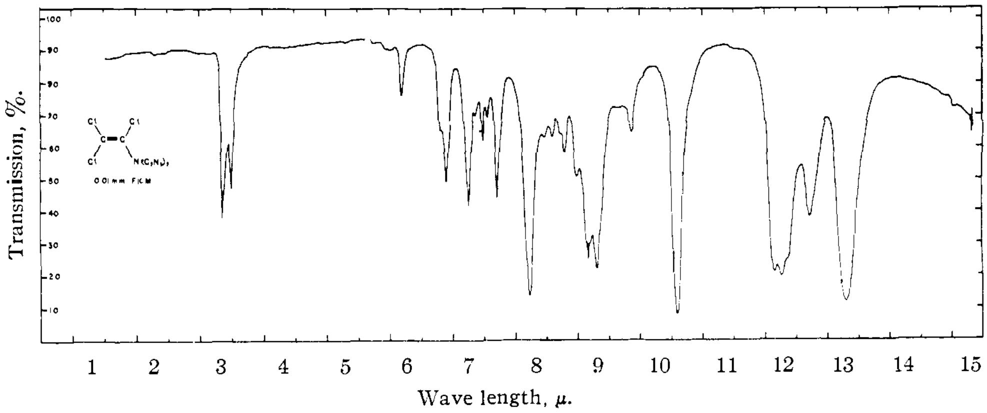
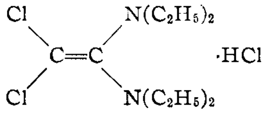


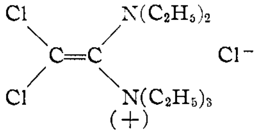
Fig. 1.—N,N-Diethyl-1,2,2-trichlorovinylamine.

ride. In Table III the amines are listed in the order of increasing pK_a values which qualitatively represents the order of reactivity with the vinylamine IVa.

Diethylamine or triethylamine were found to be unreactive toward IVa. The vinylamine was recovered unchanged (86.6 and 86.2%, respectively). There was no evidence for the formation of VII or VIII which could arise by an SN2 reaction at the C-1 atom.



VII



VIII

Butylamine and IVa afforded a 22.6% yield of amidine VIf, in 20 hours, and butylamine hydrochloride gave a 68% yield of VIf in 24 hours in refluxing benzene. Trichlorovinylamine (IVa) (51.6 and 27.9%, respectively) was recovered in both reactions. Aromatic amines such as aniline reacted with IVa more rapidly than butylamine. For example, a 77.7% yield of VIa was isolated from the reaction of IVa with aniline after 16 hours in refluxing benzene. Aniline hydrochloride gave an 82% yield of VIa under similar conditions.

TABLE III

ORDER OF ACTIVITY OF AMINES WITH N,N-DIETHYL-1,2,2-TRICHLOROVINYLAMINE (IVa)

Amine	pK_a
Aniline hydrochloride	. . .
4-Nitroaniline	1.17
4-Chloroaniline	4.05
Aniline	4.58
4-Methylaniline	5.10
Butylamine hydrochloride	. . .
4-Ethoxyaniline	5.25
Butylamine	10.59
Diethylamine	10.98
Triethylamine	10.65

In contrast to the reaction of carboxylic acids, mineral acids formed stable salts with the vinylamine IVa. The hydrochloride (m.p. 68–69.5°), the hydrobromide (m.p. 72–74°dec.) and perchlorate (m.p. 137.8–138°) salts of IVa were prepared. In addition to being very hygroscopic the hydrochloride salt gave off hydrogen chloride (the hydrobromide salt behaved similarly) to yield the vinylamine IVa. This process is accelerated in vacuum. All three salts (HCl, HBr and $HClO_4$) were more reactive with water (also with ethanol and aniline) than the free base. In the case of the hydrochloride salt, N,N-diethyl-2,2-dichloroacetamide was isolated in an 86.3% yield, thereby demonstrating that IVa and its hydrochloride react with water in the same manner.[1]

The infrared spectrum of IVa (see Table IV and Figs. 1, 2 and 3) showed absorption at 1612 cm.$^{-1}$

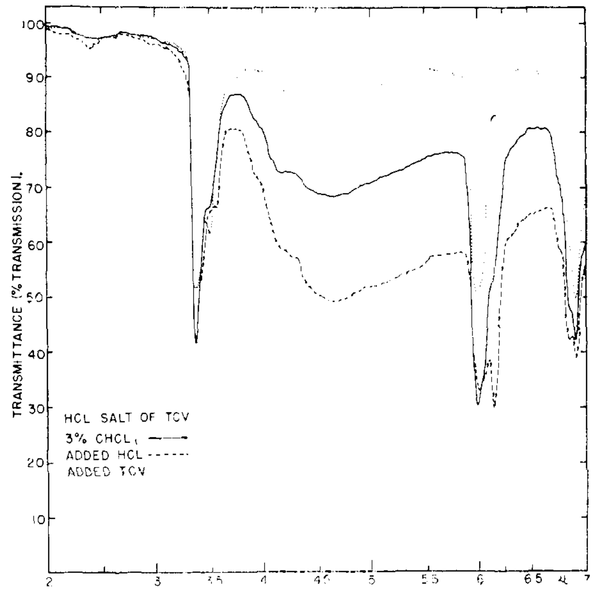
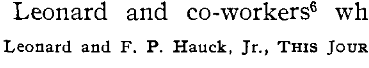


Fig. 2.—TCV = N,N-diethyl-1,2,2-trichlorovinylamine.

while the hydrochloride, hydrobromide and perchlorate salts absorbed intensely at 1669 cm.$^{-1}$. These shifts (57 cm.$^{-1}$) toward higher infrared frequency in going from the enamine (IVa) to its iminium salt correspond to the structural transformation



$$>C=\overset{|}{C}N< \xrightarrow{H^+} >CH\overset{|}{C}=\overset{+}{N}<$$

This interpretation is substantiated by the work of Leonard and co-workers[6] who investi-

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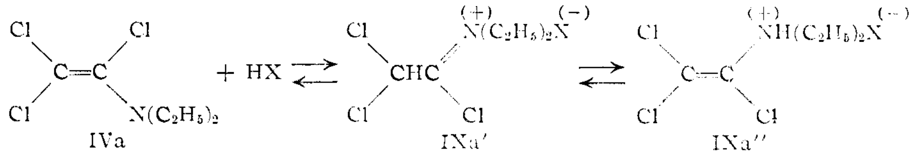
[6] N. J. Leonard and F. P. Hauck, Jr., THIS JOURNAL, **79**, 5279 (1957).

TABLE IV

INFRARED DATA OF SALTS OF N,N-DIETHYL-1,2,2-TRICHLOROVINYLAMINE



Salt[a] X =	H+ region 2150 cm.$^{-1}$	Absorbancy C=C and C=N region 1669 cm.$^{-1}$	1658 cm.$^{-1}$	1615 cm.$^{-1}$	1632 cm.$^{-1}$	1612 cm.$^{-1}$	C–N region 945 cm.$^{-1}$
Cl	0.13	0.41	Sh[b]	..	Sh	..	0.27
Cl[c]	.04	.27	Sh	Sh	Sh	0.05	0.72
Cl[d]	.30	.21	Sh	..	0.31	..	Very weak
Br	.04	.70	Sh	..	Sh	..	Very weak
Br[e]	.06	.37	Sh	..	0.25	..	Very weak
ClO$_4$	Very broad	.63	Sh	..	0.30	..	..
IVa, free base	....	..	..	..	..	0.09	1.05

[a] Taken in a 0.2-mm. sodium chloride cell using a Perkin–Elmer model 21 instrument. All spectra were taken in a 3% chloroform solution except the perchlorate salt which was taken in a 10% acetonitrile solution and IVa which was taken as a capillary film (0.01 mm.). [b] Shoulder or inflection on the 1669 cm.$^{-1}$ peak. [c] With excess IVa. [d] With excess HCl. [e] With excess HBr.

gated, rather thoroughly, the shifts in the infrared spectrum which took place when α,β-unsaturated cyclic amines were converted to their perchlorate salts. Although the infrared spectrum of the hydrochloride of IVa exhibited a characteristic broad maximum (weak) for $\overset{(+)}{N}$—H, the C=C peak at 1612 cm.$^{-1}$ observed in that of IVa was not present.

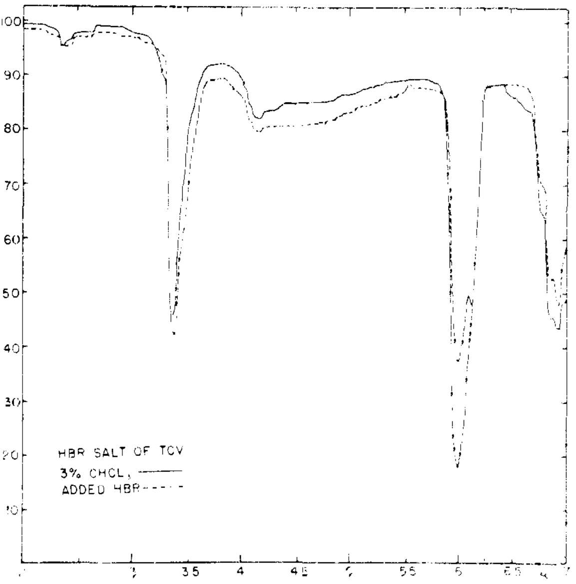


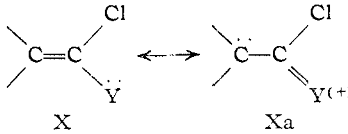
Fig. 3.—TCV = N,N-diethyl-1,2,2-trichlorovinylamine.

Interestingly, the intensity of the shoulder at 1632 cm.$^{-1}$, in the spectra of both the hydrochloride and hydrobromide salts of IVa, changed with the intensity of the broad band at 2150 cm.$^{-1}$ which is associated with the ammonium ion (H$^+$). The spectra of the two salts taken in a 3% chloroform solution were compared with those taken in a 3% chloroform solution which was previously saturated with the respective acids (HCl and HBr). The intensity of both bands (2150 and 1632 cm.$^{-1}$) were increased in the chloroform–acid spectra. The broad ammonium peak increased in absorbancy from 0.13 to 0.30 for the hydrochloride salt and from 0.04 to 0.06 for the hydrobromide salt. The 1632 cm.$^{-1}$ band which appeared as a shoulder (HCl salt, 0.13 absorbancy; HBr salt, 0.02 absorbancy) on the 1669 cm.$^{-1}$ band in the chloroform spectra became a separate definite peak, also at 1632 cm.$^{-1}$ (HCl salt, 0.31 absorbancy; HBr salt, 0.25 absorbancy), in the chloroform–acid spectra. In both chloroform–acid spectra there was a decrease in the intensity of the 1669 cm.$^{-1}$ band. The 1632 cm.$^{-1}$ could be due to either normal NH–deformation frequency or the $>C{=}\underset{\diagdown}{\overset{|\ \diagup}{C}}NH^+$ IXa″ grouping.

In either case both assignments would be evidence for the presence of the salt in form of IXa. If this is the case, then the intensity of 1632 cm.$^{-1}$ band should be lowest in the spectrum of the hydrochloride which contains excess IVa. The approximate absorbancies were 0.13 for the hydrochloride salt, 0.31 for the salt containing excess hydrogen chloride and 0.02 in the presence of excess vinylamine IVa. In the last case the ammonium ion band was exceedingly weak.

Discussion

1-Halovinyl compounds of the type X which bear an electronegative group Y can be stabilized by resonance hybridization and should react with electrophilic reagents in a similar manner.[7]



X Xa

Y = NR$_2$, SR, OR, F, Cl

The removal of the 1-halo atom by these reagents could proceed by one of three mechanisms;[8] (1) addition–elimination, (2) elimination–addition

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(7) See H. C. Volger and J. F. Arens, *Rec. trav. chim.*, **77**, 1170 (1958) for a similar polarization of ethoxyacetylene and ethylthioacetylene; also see L. F. Fieser and M. Fieser, "Organic Chemistry," second edition, D. C. Heath and Co., Boston, Mass., 1950.

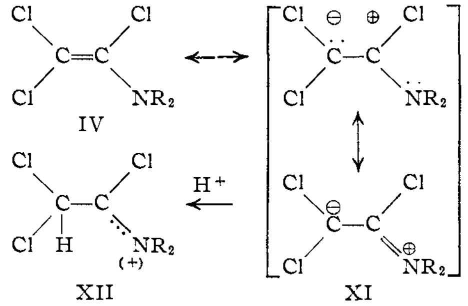
(8) S. I. Miller and P. K. Yonan, THIS JOURNAL, **78**, 5931 (1956).

and (3) nucleophilic displacement. Considering the conditions employed in the reactions of IVa, the second mechanism is not applicable. It is unlikely that water, alcohols, acids and amines would be capable of dechlorinating IVa to give an acetylenic intermediate. Furthermore, the products which would be formed *via* this mechanism were not detected.

The reagents mentioned above would not be expected to undergo a nucleophilic reaction with IVa. Evidence for this conclusion was obtained from a comparison of the rates of reaction of IVa with ethanol and sodium ethoxide at room temperature. Ethanol reacted with IVa exothermally and completely in two hours while the reaction with sodium ethoxide was 83.5% complete after 22 hours. This rate of reactivity is the reverse of what would be expected if the reaction proceeded by a nucleophilic displacement.

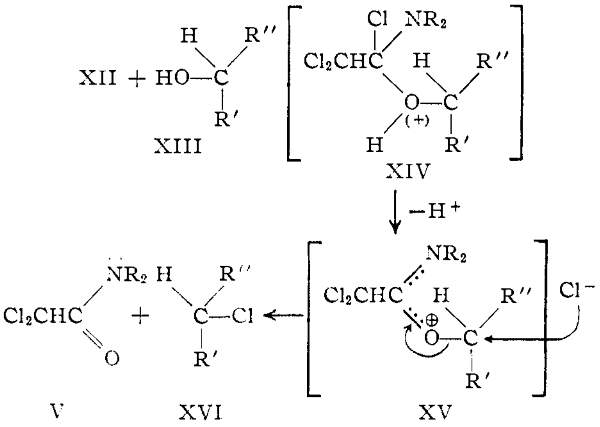
Reactions of alcohols and water with IVa occurred only in the presence of catalytic amounts of hydrogen chloride. Under these conditions a strong exothermic reaction took place at room temperature. If the trace amounts of hydrogen chloride, formed from IVa and atmospheric moisture, were neutralized with triethylamine, no reaction occurred on the addition of alcohol even at 80°. The vinylamine IVa was recovered unchanged.

To account for these transformations, an addition–elimination mechanism is proposed. The resonance forms XI can be written for the trichlorovinylamine IVa.



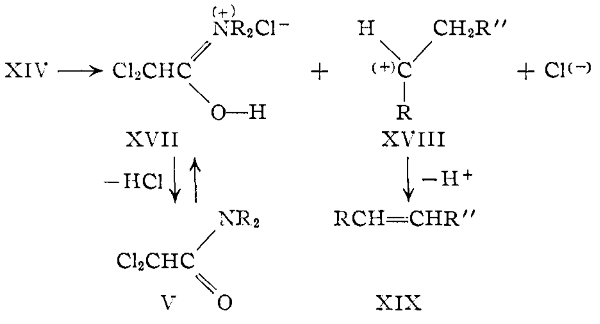
The catalytic amount of hydrogen chloride is necessary for β-protonation[9] of IV. The successful reaction of alcohols and amines with trichlorovinylamines is based on the presence of catalytic quantities of the iminium salt XII. When triethylamine is added initially, the iminium salt is reconverted to IV. Alcohols, water and amines are incapable of adding to the resonance forms IV and XI in the absence of a proton. The isolation and stability of the iminium salts IXa′ and the infrared spectral data of these salts clearly demonstrate that the proton prefers to become attached to the β-carbon atom instead of the nitrogen atom of IVa. Hence the iminium salt XII must be an intermediate in the reaction of N,N-disubstituted-1,2,2-trichlorovinylamines (IV), with protolytic reagents.

The following mechanism is postulated for the acid-catalyzed reaction of trichlorovinylamines IV with alcohols, water and carboxylic acids. The alcohol adds to the electrophilic carbon atom of the β-protonated iminium salt XII to give an oxonium intermediate XIV.



Abstraction of the proton from XIV by the basic trichlorovinylamine would regenerate the iminium intermediate XII and also give rise to the iminoether type compound XV. Attack by chloride ion at the ether carbon atom would afford the alkyl halide XVI and dichloroamide V. If the chloride[10] reacts with XV *via* a bimolecular displacement reaction, the resulting alkyl halide XVI should have a configuration opposite to that of the alcohol XIII. The experimental results mentioned earlier clearly show that *d*-*sec*-butyl alcohol reacted with IVa (without solvent) to yield *l*-*sec*-butyl chloride of high optical purity. The fact that inversion[11] occurred at the optically active center demonstrates that the proposed nucleophilic attack on XV by chloride ion is valid.

The formation of olefin and hydrogen halide from the reaction of alcohols with IVa in solvents and also at temperature of 60–75° may be due to the decomposition of XIV to amide salt XVII and carbonium ion XVIII. The carbonium ion could then react with chloride ion to give alkyl halide or lose a proton to give an olefin XIX and hydrogen halide.



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[9] See N. J. Leonard and R. R. Sauers, THIS JOURNAL, **79**, 6210 (1957). These investigators demonstrated that the iminium salt of $\Delta^{1(10)}$-dehydroquinolizidine was an important intermediate in the reduction of the free base with formic acid.

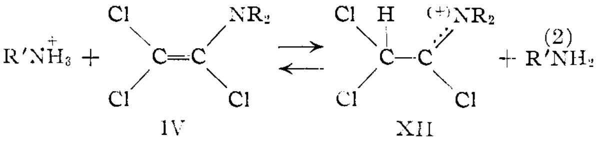
[10] The data presented do not allow for a clear differentiation as to which intermediate (XIV or XV) is attacked by chloride ion. Structure XIV is a protonated ether while XV is an iminoester salt. The vinylamine IVa could be protonated by either XIV or the amide salt XVII.

[11] *d*-*sec*-Butyl chloride has been shown to have the same configuration as *d*-*sec*-butyl alcohol; W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937). For a discussion of the relationship of configuration and sign of rotation also see H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, second ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 278; and C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 386.

This interpretation seems justified inasmuch as the amount of alkyl chlorides isolated decreases as the alcohols were changed from primary to secondary to tertiary, and the reaction of chloride with the carbonium ion or olefin would lead to racemization which occurred to a maximum of 6–7% at lower temperature.

Amines could react with IVa by an SN2 mechanism. The low yield of amidine in the case of butylamine and no reaction with diethyl and triethylamines could be accounted for on the basis that displacement reactions at an unsaturated carbon atom are difficult.[8] To account for the difference in reactivity of aliphatic and aromatic amines with trichlorovinylamines an addition–elimination mechanism is also proposed. The same intermediate which was important in the reaction of IV with protolytic reagents is involved in the reaction with amines. The first step in this mechanism is the neutralization of catalytic amounts of hydrogen chloride by the amine. The following equilibrium condition would be created

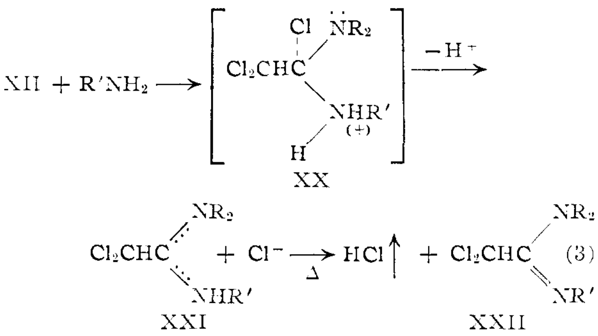
$$R'NH_2 + H^+ \rightleftarrows R'\overset{+}{N}H_3 \qquad (1)$$



The role of the catalytic amount of amine salt would be to protonate IV to give the iminium intermediate XII. The more acidic aromatic ammonium ion should effect this protonation much easier than the less acidic aliphatic ammonium ion. The results from the reactions of IVa with aniline, butylamine and their hydrochlorides substantiate this postulation. Furthermore, the reaction of IVa and *p*-nitroaniline produced a better yield (87%) of amidine in 2.5 hours than either aniline (78%) or butylamine (23%) in 16 and 20 hours, respectively. These data are interpreted to mean that the ammonium ion derived from *p*-nitroaniline is more effective in the protonation of IVa than that derived from either aniline or butylamine. Thus it is clear that in equation 2 the equilibrium would be displaced more to the left for the aliphatic amines studied and more to the right for the aromatic amines.

Once a catalytic amount of XII is formed (equation 2) the free amine which is liberated could react with this intermediate XII in two ways. The amine could abstract hydrogen chloride from XII to form the corresponding ammonium salt and IV or react with the intermediate to form, irreversibly, the amidine (equation 3). Based on our experimental data, butylamine, diethylamine and triethylamine were quite effective in abstracting hydrogen ion from XII while *p*-nitroaniline and aniline easily converted XII to the amidine.

The reaction sequence as depicted by equation 3 would explain the amidine formation. The reaction of amines with XII would give XX which would lose a proton to yield the amidine hydrochlorides XXI. The proton which would be liberated from XX would be neutralized by the unreacted amine to give the ammonium salt. This salt would



then be available for protonation of IV to give XII (equation 2). When amine hydrochlorides, such as butylamine hydrochloride and aniline hydrochloride, were used initially, a rapid evolution of hydrogen chloride occurred. The slower evolution of hydrogen chloride when aromatic amines were used was probably due to the pyrolysis of the amidine hydrochlorides XXI.

A comparison of the data from the reaction of IVa with amines, water, alcohols and acids clearly demonstrates that these reactions are acid catalyzed and that the data obtained are consistent with the rationalization presented.

Acknowledgment.—We are indebted to Dr. B. Katlafsky and Messrs. O. Kinast and E. E. Bieber for the infrared spectra, and to Messrs. J. L. O'Sullivan and O. S. Kring for the analytical data. We are indebted to Professors N. J. Leonard and E. E. van Tamelen for their stimulating discussions and interest.

Experimental[12]

Reaction of N,N-Diethyl-1,2,2-trichlorovinylamine (IVa). A. Ethanol. 1. With Absolute Ethanol.—Absolute ethanol (4.61 g., 0.1 mole) was added to 20.25 g. (0.1 mole) of IVa at such a rate that the exothermic reaction was kept between 55–60°. The temperature was raised to 75° for 40 minutes after the addition (20 minutes) was completed. Ethyl chloride, 5.28 g. (82%), was collected during this time. Distillation of the residue yielded 15.93 g. (86.5%) of N,N-diethyl-2,2-dichloroacetamide,[13] b.p. 80–80.5° (1.1 mm.), $n^{25}D$ 1.4830. The amide was identified by infrared analysis and the ethyl chloride was converted to propionanilide,[14] m.p. 104–105°, *via* the Grignard reagent and phenyl isocyanate. A mixture melting point determination with an authentic sample[15] was not depressed, m.p. 104–105.6°.

2. With Absolute Ethanol in the Presence of Triethylamine. a. In Ether.—To a refluxing (45°) solution of 0.1 mole of IVa and 10.1 g. (0.1 mole) of triethylamine in 50 ml. of ether was added dropwise 4.61 g. (0.1 mole) of absolute ethanol in 25 ml. of ether. Refluxing was continued for two hours, after which time the ether and ethanol were distilled *in vacuo*. The residue was distilled through a short Vigreux column; b.p. 89° (28 mm.), $n^{25}D$ 1.4819, 18.09 g. (89.2% recovery) of IVa. A small sample of the recovered IVa reacted violently with water which contained a very small amount of hydrochloric acid.

b. In Benzene.—The preceding experiment was repeated employing benzene as a solvent. The refluxing temperature was 76° for two hours. There was obtained an 88.3% recovery of IVa, b.p. 85–86° (28 mm.), $n^{25}D$ 1.4848.

B. *dl-sec*-Butyl Alcohol.—1. A 100-ml. three-necked round-bottomed flask was fitted with a dropping funnel, stirrer and a reflux condenser to which was connected

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(12) The boiling points and melting points reported are uncorrected.

(13) A. D. Swenson and W. E. Weaver, THIS JOURNAL, **70**, 4060 (1948).

(14) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1949, p. 229.

(15) Eastman Kodak Co. white label sample, m.p. 105–106°, was recrystallized from ethanol.

through a calcium chloride tube, a bubbler and three traps. Two traps each contained 0.1 mole of sodium hydroxide (100 ml.) and one trap, last in line, contained 50 ml. of 5% solution of bromine in carbon tetrachloride. The *dl-sec*-butyl alcohol was added to IVa dropwise until the temperature of the reaction mixture rose to 72°. The rate was then adjusted such that the temperature remained between 60–72°. Only a small amount of gases was evolved initially but the rate increased considerably toward the end. The bromine solution was completely decolorized near the end. After the addition was completed (1 hour) the temperature was slowly raised in order to distil the *dl-sec*-butyl chloride, b.p. 66–69°, n^{25}D 1.3939, yield 12.7 g. (68.7%). The butyl chloride[5a] was redistilled, b.p. 66–69°, n^{25}D 1.3945. N,N-Diethyl-2,2-dichloroacetamide distilled at 111–112° (9.4 mm.), n^{25}D 1.4831, yield 30.7 g. (83.5%). The contents of traps were not worked up.

2. **With *dl-sec*-Butyl Alcohol at 40–50°.**—The above reaction was repeated using the same set-up with a few changes. The bromine trap was filled with 50 ml. of carbon tetrachloride and 8 g. of bromine. Only 20.25 g. (0.1 mole) of IVa and 7.41 g. (0.1 mole) of *dl-sec*-butyl alcohol was used. The reaction temperature was kept between 40–50° during the addition by intermittently cooling with a cold water-bath. Stirring was continued for 40 additional minutes during which time the temperature of the mixture dropped to 25°. At this time the sodium hydroxide and bromine traps were replaced with two clean Dry Ice–acetone traps and the *dl-sec*-butyl chloride was distilled *in vacuo*. There was obtained from the first trap 7.5 g. (81%), n^{25}D 1.3930, *dl-sec*-butyl chloride. Distillation of the residue through a 15 × 150 mm. Vigreux column afforded 16.9 g. (91.8%) of N,N-diethyl-2,2-dichloroacetamide, b.p. 99–101° (2,4–2.6 mm.), n^{25}D 1.4833. Butyl chloride was redistilled, b.p. 67–68°, n^{25}D 1.3941. The first sodium hydroxide trap contained only 0.001 mole of chloride (1%). The bromine solution was not decolorized during the reaction and gas evolution was very slow.

C. ***d-sec*-Butyl Alcohol.**—The above procedure (experiment B-2) was followed except that 40.5 g. (0.2 mole) of vinylamine IVa and 14.8 g. (0.2 mole) of *d-sec*-butyl alcohol, $[\alpha]^{20}$D +13.89 ± 0.01°, were used. There was obtained 34.8 g. (94.5%) of N,N-diethyl-2,2-dichloroacetamide, b.p. 94–99° (1.2–1.8 mm.), n^{25}D 1.4833, and 15.5 g. (83.8%) of *l-sec*-butyl chloride, n^{25}D 1.3925, $[\alpha]^{20}$D −27.94°. The *l-sec*-butyl chloride[5a] was redistilled, b.p. 67–68°, n^{25}D 1.3937, $[\alpha]^{20}$D −31.05 ± 0.01° (pure liquid 2 dm.). The sodium hydroxide solution contained 0.002 mole of chloride ion (1%). The contents of the bromine trap were discarded.

D. **With *t*-Butyl Alcohol.** 1. **In Benzene.**—A solution of 40.5 g. (0.2 mole) of IVa, 14.8 g. (0.2 mole) of *t*-butyl alcohol and 150 ml. of benzene were heated at the refluxing temperature for three hours. During the refluxing period two sodium hydroxide traps (8 g., 0.2 mole, each) and one bromine (16 g.) were set up in the previously described manner (experiment B-2). After the refluxing period the reflux condenser was replaced with a 15 × 150 mm. Vigreux column and about one-half the benzene, all of the unreacted *t*-butyl alcohol and *t*-butyl chloride were distilled (b.p. 60–79°) at atmospheric pressure. The benzene fraction contained by infrared analysis 4.35 g. (29.4% recovery) of unreacted *t*-butyl alcohol (10.99 μ) and 4.27 g. (23.1% conversion, 32.8% yield) of *t*-butyl chloride (12.38 μ). At this time the sodium hydroxide and bromine traps were replaced with two Dry Ice–acetone traps and the remainder of the benzene was distilled at room temperature *in vacuo*. All of the benzene was caught in the first trap and did not contain any *t*-butyl chloride or *t*-butyl alcohol.

Unreacted IVa (b.p. 65–70° (7 mm.), n^{25}D 1.4840) was then distilled followed by the amide. There was recovered 6 g. (14.8%) of unreacted IVa. N,N-Diethyl-2,2-dichloroacetamide, b.p. 60–61° (0.08 mm.), n^{25}D 1.4843, was isolated in 92.3% yield (28.9 g., 78.7% conversion). The two sodium hydroxide traps contained 0.402 mole of chloride. This high value must be due to the entrainment of some of the vinylamine IVa. The excess bromine was destroyed by shaking the contents of the trap with aqueous sodium thiosulfate. The dried (magnesium sulfate) carbon tetrachloride solution yielded 8.2 g., n^{25}D 1.5247, of a mixture of bromoalkanes. This mixture[16] was separated into two major fractions: (a) 1,2-dibromo-2-methyl propane,[16a] b.p. 63–64° (44 mm.), n^{25}D 1.5070, yield 4.3 g. (11.2%); and (b) 1,2,3-tribromo-2-methylpropane,[16b,c] b.p. 124–125° (44 mm.), n^{25}D 1.5587, yield 2.1 g. The presence of these bromoalkanes proves that isobutylene was formed in the reaction mixture. The low yield of *t*-butyl chloride indicates that *t*-butyl alcohol was converted predominantly to isobutylene in the reaction with IVa in benzene.

2. **Without Solvent.**—*t*-Butyl alcohol (14.8 g., 0.2 mole) was allowed to react with 40.5 g. (0.2 mole) of IVa under the conditions described in experiment B-1 at 60–75°. The sodium hydroxide (8 g.) and bromine (16 g.) traps were set up as previously described in B-2. The reaction products were fractionated through a 15 × 150 mm. Vigreux column: (a) b.p. 45–49° atmospheric pressure, n^{25}D 1.3820, 10.4 g.; (b) b.p. 115–121° (8–10 mm.), n^{25}D 1.4827, 32.0 g. Fraction a represented a 56.2% yield of *t*-butyl chloride (b.p. 50–50.5°, n^{25}D 1.3846) and (b) an 87% yield of N,N-diethyl-2,2-dichloroacetamide. The sodium hydroxide trap was acidified with dilute sulfuric acid and titrated potentiometrically for chloride. There was found 0.02 mole (10%) yield of chloride ion. The bromine trap was worked up in the usual manner (see experiment D-1 above) distillation of which afforded the following fractions: (a) 2.6 g., b.p. 67–68° (46 mm.), n^{25}D 1.5345; (b) 1.2 g. b.p. 68–69° (46 mm.), n^{25}D 1.4970; and (c) the residue, 0.94 g., n^{25}D 1.5738. Fractions a and b were 1,2-dibromo-2-methylpropane[16a] based on physical data and the infrared spectra. Splitting of the band assigned to the methyl group was observed at 7.24 and 7.32 μ in the infrared of fractions a and b while that of fraction c possessed only one peak at 7.28 μ. Fraction c was 1,2,3-tribromo-2-methylpropane.[16b,c]

The above experiment D-2 was repeated exactly, except that the temperature of the reaction mixture was maintained between 20–25° with the aid of a cold water-bath. After stirring 3 hours, the unreacted *t*-butyl alcohol and *t*-butyl chloride were distilled *in vacuo* (see experiment B-2 above) at room temperature, fraction a. The unreacted vinylamine IVa, fraction b, distilled at 66–68° (6.8 mm.) n^{25}D 1.4850, yield 8.5 g. (21% recovery). Fraction c was the N,N-diethyl-2,2-dichloroacetamide, b.p. 106–107° (7.0 mm.), n^{25}D 1.4840, yield 22.7 g. (61.8% conversion, 77.9% yield). Fractionation of the alcohol–chloride mixture, fraction a, through a 7 × 300 mm. spiral wire-packed column yielded 9.4 g. (50.8% conversion, 60.8% yield) of *t*-butyl chloride, b.p. 49–52°, n^{25}D 1.3828, and 2.5 g. (16.9% recovery) of *t*-butyl alcohol, b.p. 79–80°, n^{25}D 1.3953.

E. **With Acetic Acid.**—Glacial acetic acid (6.01 g., 0.1 mole) was added dropwise to 20.25 g. (0.1 mole) of IVa. The temperature of the reaction mixture quickly rose to 50°. The rate of addition was then adjusted such that the temperature of the reaction was maintained between 50–60°. The addition required about 20 minutes and heating was continued for an additional 1.5 hours. Distillation of the reaction mixture afforded 5.66 g. (72.1%) of acetyl chloride, b.p. 48.5–51°, and 13.83 g. (75.1%) of N,N-diethyl-2,2-dichloroacetamide, b.p. 75–76° (1.0 mm.), n^{25}D 1.4830. A small fraction of forerun to the amide was collected and discarded: 1.93 g., b.p. 57–75° (1.0 mm.), n^{25}D 1.4720. The amide was identified by infrared analysis while the acetyl chloride was identified by conversion to acetanilide, m.p. 115.4–116.2°. The admixture with an authentic sample[17] of acetanilide was not depressed, m.p. 115.8–116.2°.

F. **With Benzoic Acid.**—A slurry of benzoic acid (12.21 g., 0.1 mole) and 50 ml.of benzene was added to 20.25 g. (0.1 mole) of IVa in 50 ml. of benzene which was previously heated to 85°. The addition required 15 minutes, and heating was continued for 3 hours. After that time, the benzene was distilled *in vacuo* and the residue was fractionated through a 15 × 150 mm. column which was packed with glass helices. The following fractions were collected: (a) 10.15 g., b.p. 75.5–76° (9.5 mm.), n^{25}D 1.5494; (b) 2.19 g., b.p. 76–87° (9.5 mm.); (c) 5.01 g., b.p. 87–114° (9.5 mm.); (d) 12.27 g., b.p. 114° (9.5 mm.), n^{25}D 1.4835.

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(16) Several investigators have reported mixtures of these bromo compounds from the bromination of isobutylene under various conditions: (a) C. M. Suter and H. D. Zook, THIS JOURNAL, **66**, 738 (1944), reported b.p. 61° (40 mm.), n^{25}D 1.5070; (b) B. K. Mereschowski, *J. Russian Phys-Chem. Gesellschaft*, **46**, 113 (1923); "Beilstein," Vol. 1, p. 128, reported b.p. 108–109° (18 mm)., n^{14}D 1.57012; (c) C. M. Suter, J. D. Malkemus and S. Archer, THIS JOURNAL, **63**, 1594 (1941), reported b.p. 75.5° (5 mm.), n^{20}D 1.5652.

(17) Dow Chemical Co., sample m.p. 115–116°.

Fraction a represented a 72.3% yield of benzoyl chloride. Fractions b and c were mixtures of benzoyl chloride and N,N-diethyl-2,2-dichloroacetamide. Fraction d represented a 66.6% yield of N,N-diethyl-2,2-dichloroacetamide. The amide was identified by infrared analysis while benzoyl chloride was identified as its *p*-benzotoluidide,[18] m.p. 157.8–158.6°.

G. With Picric Acid.—To a solution of 10.12 g. (0.05 mole) of N,N-diethyl-1,2,2-trichlorovinylamine (IVa) in 50 ml. of benzene, heated to 65°, there was added slowly a solution of 11.5 g. (0.05 mole) of picric acid in 75 ml. of benzene. The reaction mixture was heated two hours after the addition was completed. At this time the benzene was distilled *in vacuo*. The solid–oily residue was treated with ether and filtered. The solid was shown by infrared analysis to be picric acid. The infrared spectrum of the recovered picric acid was identical with that of an authentic sample. The ethereal filtrate was concentrated to an oil-solid mixture which was shaken with petroleum ether (b.p. 38–48°). There was obtained by filtration 3.82 g. of picric acid (total amount 9.87 g., 85.6% recovery). Evaporation of the petroleum ether filtrate yielded 9.01 g. (89.3% recovery) of the starting vinylamine which was identified by infrared analysis.

H. With Inorganic Acids. 1. N,N-Diethyl-1,2,2-trichlorovinylamine Hydrochloride.—An ethereal solution (100 ml.) of IVa (20.25 g., 0.1 mole) was saturated with hydrogen chloride. The resulting solid was filtered and washed with ether. The hydrochloride, m.p. 65–68°, was dried *in vacuo* and weighed 11.2 g. The filtrate, by concentration *in vacuo*, yielded an additional 12.63 g., m.p. 68–69.5°. The total yield of the hydrochloride was 23.83 g. (100%). The entire sample was mixed with ether and again saturated with hydrogen chloride. The melting point of the extremely hygroscopic salt was 68–69.5° (sealed capillary). The infrared spectrum showed a strong peak at 1669 cm.$^{-1}$, a shift of 57 cm.$^{-1}$ toward higher frequency from the peak observed in the spectrum of the parent compound (IVa, 1612 cm.$^{-1}$). A broad maximum for the ammonium ion at 2150 cm.$^{-1}$ was also present in the spectra.

Anal. Calcd. for $C_6H_{11}Cl_4N$: C, 30.15; H, 4.64; Cl, 59.35; N, 5.86. Found: C, 29.68; H, 4.78; Cl, 58.87; N, 5.96.

2. N,N-Diethyl-1,2,2-trichlorovinylamine Hydrobromide.—From 20.2 g. (0.1 mole) of N,N-diethyl-1,2,2-trichlorovinylamine dissolved in 50 ml. of ether there was obtained, according to the procedure described above, 22.9 g. (71.5%), m.p. 72–74° dec. (sealed capillary), of the desired compound. *Anal.* Calcd.[19] for $C_6H_{11}BrCl_3N$: C, 25.42; H, 3.91; Br, 28.20; Cl, 37.53; N, 4.94. Found: C, 23.32; H, 3.72; Br, 36.24; Cl, 30.00; N, 4.57.

3. N,N-Diethyl-1,2,2-trichlorovinylamine Perchlorate.—An ether solution of perchloric acid was prepared by shaking ether with 70–72% perchloric acid. The top ethereal layer was added cautiously to an ether solution of 5 g. (0.025 mole) of IVa at room temperature until there was no further precipitation of solids. The precipitated perchlorate salt was filtered and dried; m.p. 137.6–138°, yield 1.75 g. (23.1% yield). The infrared spectrum of the perchlorate salt (1669 cm.$^{-1}$) showed a shift of 57 cm.$^{-1}$ toward a higher frequency from that of the patent compound (IVa, 1612 cm.$^{-1}$). The low yield of the perchlorate salt was probably due to hydrolysis of the reactive chlorine atom in IVa by the wet ether.

Anal. Calcd. for $C_6H_{11}Cl_4NO_4$: C, 23.78; H, 3.66; Cl, 46.81; N, 4.62. Found: C, 24.42; H, 4.11; Cl, 46.80; N, 4.99.

I. With Amines. 1. Triethylamine.—A mixture of 10.12 g. (0.1 mole) of triethylamine, 20.25 g. (0.1 mole) of N,N-diethyl-1,2,2-trichlorovinylamine (IVa) and 75 ml. of benzene was refluxed 4 hours. About 0.05 g. of triethylamine hydrochloride was formed during the refluxing period. The benzene and triethylamine were distilled at 25° *in vacuo*. The residue was distilled at 69–70° (11.0 mm.). There was obtained 17.41 g. (86.2%), $n^{25}D$ 1.4848, of the starting compound IVa. A 94.6% (12.89 g.) recovery of triethylamine as its hydrochloride (m.p. 258–259°) was obtained by saturation of the benzene distillate with hydrogen chloride.

2. Diethylamine.—A benzene (75 ml.) solution of IVa (20.25 g., 0.1 mole) and 7.31 g. (0.1 mole) of diethylamine was refluxed 24 hours. After this time, diethylamine and *ca.* 50 ml. of benzene were distilled through a short Vigreux column. The amine–benzene distillate was saturated with hydrogen chloride after which the benzene was distilled (20–30°) *in vacuo*. The residue of diethylamine hydrochloride (9.36 g., 85.5%) was washed with ether, filtered, dried and melted at 229.4–230.4°. The remainder of the benzene in the reaction mixture was distilled *in vacuo*. Distillation of the residue afforded 17.61 g. (87% recovery) of the starting trichlorovinylamine IVa, b.p. 71° (8 mm.), $n^{25}D$ 1.4850. The recovered IVa (17.3 g., 0.9856 mole) was treated with water and the aqueous layer was titrated potentiometrically for chloride ion. There was found 0.0793 mole (93.6%) of chloride ion. There was isolated from the organic phase 13.85 g. (88%) of N,N-diethyl-2,2-dichloroacetamide, b.p. 57° (0.1 mm.), $n^{25}D$ 1.4830. The amide and trichlorovinylamine were further identified by infrared analysis.

3. N,N-Diethyl-N'-*n*-butyl-2,2-dichloroacetamidine (VIf).—(a) A solution consisting of 75 ml. of benzene, 7.31 g. (0.1 mole) of *n*-butylamine and 20.25 g. (0.1 mole) of IVa was heated at the reflux temperature (84°) for 20 hours. Hydrogen chloride was not evolved during the reaction period. After this time the reaction mixture was cooled to 25° and filtered. The dried solid weighed 3.13 g. (30%), m.p. 208–209°, and was shown to be impure *n*-butylamine hydrochloride. A mixed melting point determination with an authentic sample of *n*-butylamine hydrochloride, m.p. 213–214°, was not depressed. The filtrate was concentrated *in vacuo* and the residue was fractionated through a 15 × 150 mm. glass helices packed column. There was obtained 10.47 g. (51.6%) recovery of the trichlorovinylamine IVa, b.p. 83–86° (20–22 mm.), $n^{25}D$ 1.4846, and 5.4 g. (22.6% yield), of the desired amidine, b.p. 102° (8.1 mm.), $n^{25}D$ 1.4825.

(b) There was obtained from 20.25 g. (0.1 mole) of IVa and 14.62 g. (0.2 mole) of butylamine after 48 hours at reflux a 44.5% yield of the desired amidine, b.p. 85–87° (1.4 mm.), $n^{25}D$ 1.4831.

4. N,N-Diethyl-N'-*p*-tolyl-2,2-dichloroacetamidine (VIb).—To a benzene (50 ml.) solution of 20.25 g. (0.1 mole) of N,N-diethyl-1,2,2-trichlorovinylamine at 60° there was added dropwise 10.71 g. (0.1 mole) of *p*-toluidine in 25 ml. of benzene. The temperature rose to 80° during the addition (10 minutes). A trap of sodium bicarbonate was connected to the reflux condenser in order to trap the hydrogen chloride evolved. The clear reaction mixture was refluxed 4.5 hours. At this time the bicarbonate solution was acidified with concd. nitric acid and then diluted to 100 ml. There was present in the carbonate solution 0.07 mole (theory, 0.1 mole) of chloride ion. The benzene was distilled *in vacuo*. Part of the residue was ether soluble and therefore was dissolved in 50 ml. of ether. The ether-insoluble residue was dissolved in 25 ml. of water and the free amidine base liberated with sodium hydroxide pellets. The aqueous solution was extracted with ether and the two ethereal solutions were mixed. After drying with calcium oxide, the ether was removed *in vacuo* and the amidine was distilled. N,N-Diethyl-N'-*p*-tolyl-2,2-dichloroacetamidine distilled at 87° (0.02 mm.), $n^{25}D$ 1.5606, yield 25.06 g. (91.7%).

5. N,N-Diethyl-N'-*p*-chlorophenyl-2,2-dichloroacetamidine (VIc).—This reaction was carried out in a manner similar to that of IVa and *p*-toluidine. From 30.38 g. (0.15 mole) of IVa and 19.14 g. (0.15 mole) of *p*-chloroaniline there was obtained 31.25 g. (65.6%) of N,N-diethyl-N'-*p*-chlorophenyl-2,2-dichloroacetamidine, b.p. 95° (0.02 mm.), $n^{25}D$ 1.5766, d^{25} 1.2319. The amine and IVa were refluxed 22 hours in benzene during which time 0.1 mole (0.15 mole possible) of hydrogen chloride was evolved.

6. N,N-Diethyl-N'-*p*-ethoxyphenyl-2,2-dichloroacetamidine (VIe).—A mixture of 20.25 g. (0.1 mole) of IVa, 13.72 g. (0.1 mole) of *p*-phenetidine and 25 ml. of benzene were heated at the reflux temperature (88°) for 4.5 hours. The reaction mixture was allowed to cool to 25° and then 20 g. of triethylamine was added and stirred for 1 hour. The

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(18) See ref. 14, p. 207.

(19) The individual percentages of bromine and chlorine deviated considerably from the calculated values. The carbon, hydrogen and nitrogen analyses were lower than theory. The total halogen percentage was in the acceptable range (theory 65.73, found 66.24). These differences are compatible with the formation of $Cl_2CH\underset{\underset{Br}{|}}{C}=N(C_2H_5)_2Br^-$. The analyses agree with the formula $C_6H_{11}Br_{1.4}Cl_{1.6}N$. This compound would result by displacement of the 1-chlorine atom by bromide.

reaction mixture was filtered, the residue was washed with benzene, filtered, dried and weighed. There was obtained 1.34 g. (0.1 mole) of triethylamine hydrochloride, m.p. 156–157°. The benzene and excess triethylamine were removed *in vacuo* and then unreacted IVa was distilled. There was recovered 12.66 g. (0.063 mole) (62.5%) of unreacted trichlorovinylamine (IVa), b.p. 20–25° (0.5 mm.), n^{25}D 1.4872. To the semi-solid pot residue was added 25 ml. of water and then the aqueous solution was made strongly basic with sodium hydroxide pellets. The *p*-phenetidine–amidine mixture was extracted from the aqueous solution with ether. The ethereal solution was dried with magnesium sulfate, and filtered. The filtrate was evaporated to an oily residue. The oily residue was distilled through a 15 × 150 mm. Vigreux column. Two major fractions were collected: (a) b.p. 63–65° (0.15 mm.), n^{25}D 1.5579, weight 10.75 g.; (b) b.p. 118–119° (0.06 mm.), n^{25}D 1.5582, weight 5.72 g. Fraction a represents a 78.4% recovery of the *p*-phenetidine. This amine was identified by infrared analysis and conversion to the known *p*-acetophenetidine,[18] m.p. 134.7–135.8°. A mixture melting point with an authentic sample was not depressed. Fraction b represents an 18.9% yield of N,N-diethyl-N′-*p*-ethoxyphenyl-2,2-dichloroacetamidine.

The sodium bicarbonate trap which was connected to the reflux condenser during the refluxing period contained only a trace of chloride ion.

7. **N,N-Diethyl-N′-*p*-nitrophenyl-2,2-dichloroacetamidine (VId).**—Solid *p*-nitroaniline (13.8 g., 0.1 mole) was mixed with 100 ml. of benzene and added in small portions to 20.25 g. (0.1 mole) of IVa which was preheated to 80° in 50 ml. of benzene. The addition required one hour but heating was continued 1.5 hours. The reaction mixture was cooled to 25° and filtered. The residue was discarded and the filtrate was evaporated to dryness *in vacuo*. From the solid residue (28.9 g., m.p. 104–110°) there was obtained, on recrystallizing from hexane, 26.5 g. (87.2%) of N,N-diethyl-N′-*p*-nitrophenyl-2,2-dichloroacetamidine, m.p. 104.2–104.8°. Hydrogen chloride was evolved rapidly during the entire heating period.

J. With Amine Hydrochlorides. 1. **Butylamine Hydrochloride.**—Solid butylamine hydrochloride (10.96 g., 0.1 mole) was added to 20.25 g. (0.1 mole) of IVa dissolved in 50 ml. of benzene at room temperature. Since the reaction was not exothermic, the temperature was slowly raised to 84° and maintained for 24 hours. During this time, hydrogen chloride was evolved at the average rate of 1.99 meq. per hour. The total amount of acid evolved was 47.82 millimoles (calcd. 100 millimoles). The solvent was decanted from the viscous oily residue. The residue was washed with more benzene which was added to the decanted fraction. From the benzene fractions there was isolated 5.5 g. (0.0279 mole, 27.9% recovery) of IVa, b.p. 80° (20 mm.), n^{25}D 1.4848. The benzene-insoluble residue was slurried with 25 ml. of triethylamine and 100 ml. of ether. A mixture of triethylamine and butylamine hydrochlorides (12.7 g., m.p. 197–245°) was isolated. The ethereal amidine filtrate was concentrated. Distillation of this residue through a 15 × 150 mm. Vigreux column afforded 16.01 g. (67%) of N,N-diethyl-N′-butyl-2,2-dichloroacetamidine (VIf), b.p. 73–74° (0.75 mm.), n^{25}D 1.4832. The infrared spectrum of VIf prepared by this method was identical with that prepared from the reaction of *n*-butylamine with IVa.

2. **Aniline Hydrochloride.**—To a refluxing (86°) solution of IVa (20.25 g., 0.1 mole) and 50 ml. of benzene there was cautiously added in small amounts, 12.96 g. (0.1 mole) of solid aniline hydrochloride. About 15 minutes were required for the addition of the amine salt. Hydrogen chloride was evolved rapidly from the beginning (total 0.15 mole, theory 0.2 mole) and was trapped in a solution of sodium bicarbonate. The amount of chloride present was determined potentiometrically. The reaction mixture was concentrated to an oil, *in vacuo*, which was treated with 15 ml. of triethylamine and 50 ml. of ether. Only a very small amount of triethylamine hydrochloride was obtained by filtration. The filtrate was concentrated *in vacuo* and the oily residue was distilled through a 15 × 150 mm. Vigreux column. N,N-Diethyl-N′-phenyl-2,2-dichloroacetamidine[1] distilled at 92–95° (0.13 mm.), n^{25}D 1.5647, yield 21.20 g. (81.8%). The infrared spectrum of the amidine prepared by this method was identical with that prepared by the other methods.[1]

Reaction of N,N-Diethyl-1,2,2-trichlorovinylamine Hydrochloride with Water.—Ten grams (0.0433 mole) of the solid hydrochloride of IVa was added to 100 g. of ice. The solid became an oily mixture which solidified immediately. The reaction mixture was allowed to warm up to room temperature and 30 ml. of 95% ethanol was added. The homogeneous mixture was then heated 2 hours on the steam-bath. After this time, solid sodium carbonate was added until the mixture was slightly basic. The reaction mixture was extracted with ether from which 6.81 g. (85.7%) of N,N-diethyl-2,2-dichloroacetamide, n^{25}D 1.4833, was isolated. The aqueous layer was acidified with dilute sulfuric acid, diluted to 200 ml. and a 2-ml. aliquot was titrated potentiometrically for chloride. There was required 8.35 ml. of 0.1005 *N* silver nitrate for complete precipitation. Therefore 35.6% of chloride (0.1043 mole) was liberated in the reaction. Theory for one chloride was 29.67% (0.0866 mole).

The above experiment was repeated except that 30 ml. of 2,4-dinitrophenylhydrazine[20] solution was added during the heating period. The solution was then heated an additional two hours. To the cooled reaction mixture 400 ml. of water was added. The dark red solid which precipitated was washed several times with water, dried and weighed. There was obtained 1.26 g. (100% recovery, m.p. 199–200°) of the solid which was shown to be 2,4-dinitrophenylhydrazine by a mixture melting point determination and infrared analysis. The aqueous phase was extracted with ether from which was isolated 4.21 g. (47.7%) of N,N-diethyl-2,2-dichloroacetamide, b.p. 64° (0.35 mm.), n^{25}D 1.4833. Since all of the unreacted 2,4-dinitrophenylhydrazine was recovered, the 2-chlorine atoms were not hydrolyzed to N,N-diethylglyoxamide aldehyde.

***d-sec*-Butyl Alcohol.**[21]—*dl-s*-Butyl hydrogen phthalate m.p. 59–60°, was prepared in an 88.3% yield according to the procedure of Pickard and Kenyon.[22] The acid phthalate ester was resolved by the procedure of Kantor and Hauser[23] in which case 311.4 g. (41.7%) of the *d-sec*-butyl hydrogen phthalate-*l*-brucine salt, m.p. 157.8–159.2°, $[\alpha]^{20}$D −2.81 to −2.94 ± 0.01° (*c* 4, 95% ethanol), was obtained from 535 g. (2.41 moles) of acid phthalate ester and 956 g. (2.44 moles) of brucine.[24] Following the procedure of Stevens and co-workers,[5a] *d-sec*-butyl alcohol, b.p. 98–98.5°, n^{25}D 1.3950, $[\alpha]^{20}$D +13.89 ± 0.01° (pure liquid, 2 dm.) was obtained in a 79.5% yield (27.8 g.).

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(20) G. D. Johnson, THIS JOURNAL, **73**, 5888 (1951); prepared according to described procedure.

(21) We are indebted to H. W. Frazier for the resolution of *d-sec*-butyl alcohol.

(22) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

(23) S. W. Kantor and C. R. Hauser, THIS JOURNAL, **75**, 1744 (1953).

(24) Fisher Scientific Co. purified crystalline brucine alkaloid.