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Studies on Nitrile Salts. I. Dimerization of Nitriles Having α-Hydrogen in the Presence of Hydrogen Chloride

Shozo Yanagida, Tetsuo Fujita, Masataka Ohoka, Ichiro Katagiri, and Saburo Komori
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka

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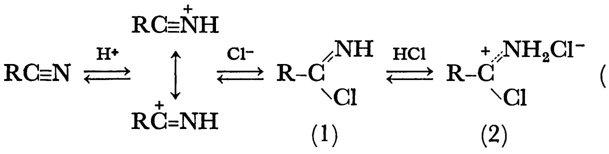
The compositions and structures of several stable nitrile-HCl salts previously reported were reinvestigated. Most of them have been found to have the composition of 2RC≡N·2HCl and have been identified as *N*-(α-chloroalkenyl)alkylamidine hydrochlorides (**3**) by mass and NMR spectra analyses. However, the 2:3 adduct from chloroacetonitrile was confirmed to be *N*-(α,α,β-trichloroethyl)chloroacetamidine hydrochloride. The scope and limitations of the dimerization reaction of nitriles having α-hydrogen with HCl were studied. Most nitriles having α-hydrogen react with HCl to give *N*-(α-chloroalkenyl)alkylamidine hydrochlorides (**3**). Their hydrolysis to diacylamines (**4**) was also investigated.

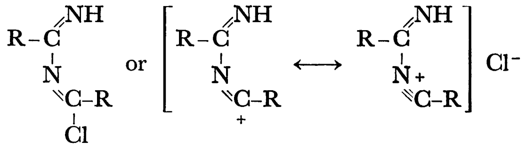
Since Gautier[1] first reported the reaction of propionitrile with hydrogen chloride in 1866, the reactions of nitriles with hydrogen halides have been well documented.[2-6]

It is now believed that nitriles react with HCl at a low temperature to form various salt-like species which are in equilibrium with each other, as is shown in Eq.1:

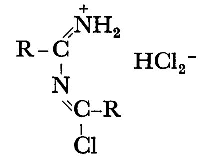

(1)

In addition, it has recently been ascertained,[7] on the basis of neutron-diffraction analysis, that the addition product prepared from acetonitrile and HCl at a low temperature has the structure of **2**($R=CH_3$), as was proposed by Allainstein and Schmidt.[8] On the other hand, there have been some reports concerning the addition products assigned to Structure **1**; Michael and Wing[9] assigned the nitrile salt prepared from propionitrile and HCl according to the method of Gautier[1] to propionimidoyl chloride (**1**, $R=C_2H_5$–) on the basis of the reaction with aniline. Similarly, a U. S. Patent[10] has claimed that 2-chloropropionitrile and 2-chlorobutyronitrile react with HCl in ether to give the corresponding imidoyl chloride (**1**, $R=CH_3CHCl$–, CH_3CH_2CHCl–).

In addition to the simple imidoyl chloride salts (**1** or **2**), some nitriles are known to form isolable dimeric hydrochlorides. Grudmann *et al.*[11] reported that some α-chloronitriles reacted with HCl in ether to give dimeric salts with the composition of 2RC≡N·HCl and proposed the following structures on the basis of their salt-like properties:



Zil'berman *et al.*,[12] however, reported that α-haloacetonitriles gave dimeric salts with the composition of 2RC≡N·3HCl under the same conditions and assumed the following dihydrochloride structure:



Recently we reported that the reaction of chloroacetonitrile with HCl gave the 2:2 adduct.[13] Hinkel and Treharne.[14] has also reported that, on standing, the unstable acetimidoyl chloride (**2**, $R=CH_3$–) changed slowly to *N*-(α-chloroethylidene)acetamidine hydrochloride, which has the composition of $2CH_3C{\equiv}N\cdot 2HCl$.

Similar dimeric salts of nitriles have also been postulated as intermediates in the reactions of nitriles in the presence of HCl.[2,4,13,15,16]

In view of the uncertainties surrounding the composition of stable nitrile-HCl salts, we have now undertaken a complete reinvestigation of the reactions of nitriles with HCl.

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1) A. Gautier, *Compt. Rend.*, **63**, 920 (1866); see also *Ann. chem.*, **142**, 289 (1867).

2) E. N. Zil'berman, *Russian Chem. Rev.*, **31**, 615 (1962).

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6) F. C. Schaefer, "The Chemistry of the Cyano Group," Z. Rapport, Ed., Interscience, New York (1970), pp. 239—306.

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10) E. W. Shand, U. S. 2411064 (1946).

11) C. Grundmann, G. Weisse, and S, Seide. *Ann. Chem.*, **577**, 77 (1952).

12) a) E. N. Zil'berman and A. Y. Lazaris, *J. Gen. Chem. USSR.*, **31**, 1224 (1961). b) A. Y. Lazaris, E. N. Zil'berman, and D. D. Strizhakov, *ibid.*, **32**, 890 (1962).

13) S. Yanagida, M. Ohoka, M. Okahara, and S. Komori, *J. Org. Chem.*, **34**, 2972 (1969).

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15) J. Houben, *Chem. Ber.*, **60**, 1759 (1927).

16) E. N. Zil'berman and P. S. Pyryalova, *J. Gen. Chem. USSR.*, **33**, 3348 (1963).

Table 1. Mass spectra of some dimer salts (**3**)

3	Dimer Salts		Fragment ion peaks (relative intensity)[a)]								
	R^1	R_2	$[M^+-HCl]$	$[M^+-HCl-Cl]$	$[R^1R^2CH-C{=}NH]$	$[R^1R^2CH-C{\equiv}N]$	Other peaks.				
3b	CH_3-	H	148(3) 146(8)	111(11)	56(74)	55(26)	54(42)	38(26)	36(79)	29(29)	28(100)[b)]
3g	Cl–	H	190(5) 188(15) 186(15)	153(18) 151(27)	78(25) 76(77)	77(31) 75(90)	51(8)	49(24)	42(58)	38(33)	36(100)
3m	CH_3-	CH_3-	176(8) 174(24)	139(32)	70(95)	69(100)	58(58) 41(66)	56(34) 38(29)	54(45) 36(84)	43(98)	42(79)
3n	C_2H_5-	CH_3-	204(t) 202(2)	167(3)	84(33)	83(40)	68(49) 38(22)	57(52) 36(63)	55(100) 29(59)	54(46) 28(38)	41(43) 27(35)
3t	Cl–	Cl–	260(8) 258(18) 256(25) 254(18)	221(5) 219(3)	114(4) 112(23) 110(37)	113(3) 111(17) 109(25)	185(10) 78(18)	183(10) 76(57)	175(32) 38(9)	173(100) 36(28)	171(100)
3u	CH_3-	Cl–	218(14) 216(41) 214(41)	181(46) 179(68)	92(23) 90(68)	91(39) 89(92)	153(16) 63(38)	151(24) 56(54)	145(9) 54(86)	143(27) 38(35)	65(12) 36(100)
3v	$ClCH_2-$	Cl–		249(t)[c)] 247(t) 245(t)	126(4) 124(5)		213(t) 149(13)	211(t) 38(33)	209(t) 36(100)	177(t)	151(8)
3w	n-C_4H_7-	Cl–	302(6) 300(19) 298(19)	267(5) 265(26) 263(40)	134(30) 132(90)		259(16) 242(24) 54(73)	257(46) 209(65) 38(17)	255(46) 207(100) 36(50)	246(9) 96(40)	244(24) 69(68)
3x	C_6H_5-	Cl–				153(7) 151(21)	116(100)	89(23)	38(28)	36(86)	

a) 70 eV.
b) Molecular ion peaks corresponding 2,4,6-triethyl-*s*-triazine was also observed.
c) Ratio 8: 10: 5.

Results and Discussion

Reinvestigation of Stable Nitrile Salts Previously Reported. In order to clarify the discrepancies in the results of the reaction of chloroacetonitrile and HCl, we first undertook a careful reinvestigation of the addition product.

As was reported previously,[13] the melting point of the adduct varied in several repeated experiments. It has now been found, on the basis of analyses of the chlorine content and the IR spectra, that the adduct freshly prepared in ether below 0°C is quite different from that prepared by heating in a sealed tube using a solvent such as chlorobenzene, and that, on standing, the former gradually changes to the latter. The analysis of the chlorine content indicated that the former has the composition of $2ClCH_2C{\equiv}N\cdot 3HCl$, and the latter, the composition of $2ClCH_2C{\equiv}N\cdot 2HCl$. The hydrolysis of the both adducts gave bis(chloroacetyl)-amine (**4g**), indicating that both have a dimeric structure. The mass spectrum of the latter salt also supported the dimeric structure (Table 1). In their IR spectra (Nujol), the absorptions in the region of 1500 to 1700 cm^{-1} are quite similar, but only the former has the characteristic absorption at 1750 cm^{-1}.[17]

However, when the latter salt was left standing in drying pistol at 50°C under reduced pressure, the chlorine content decreased to 59.0%; this corresponds to the composition of $2ClCH_2C{\equiv}N\cdot HCl$, as was analyzed by Grundmann *et al.*[11] The mass spectrum showed not only the fragment ion peaks due to the dimer salt with the composition of $2ClCH_2C{\equiv}N\cdot 2HCl$, but also the molecular ion and fragment ion peaks due to 2,4,6-tris(chloromethyl)-*s*-triazine, suggesting that the salt suffered from degradation.[18]

In view of the above facts, we concluded that the initially-formed salt, $2ClCH_2C{\equiv}N\cdot 3HCl$ is gradually transformed to a more stable dimer salt, $2ClCH_2C{\equiv}N\cdot 2HCl$ (**3g**), which is then further transformed to 2,4,6-tris(chloromethyl)-*s*-triazine with a loss of HCl.[19]

The reinvestigation has now been extended to the addition products prepared by the reactions of dichloroacetonitrile, 2-chloropropionitrile, or propionitrile with HCl.

An analogous treatment of dichloroacetonitrile and 2-chloropropionitrile with HCl in ether readily gave the white addition products, as were previously reported.[10,11] The elemental analyses of these adducts (**3t** and **3u** in Table 2) indicated that they all had the empirical formula $R^1R^2CHC{\equiv}N\cdot HCl$. Their IR spectra in the region from 1500 to 1700 cm^{-1} were similar

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[17] We assumed that this absorption might be assigned to the cation $\rangle C{=}N^+H-$, although the imminium bands were not observed clearly. B. Witkop, *Experientia.*, **10**, 420 (1954).

[18] In its IR spectrum, the characteristic absorption was observed at 1760 cm^{-1}.

[19] The formation of the *s*-triazines is under study in our group.

Table 2. Preparation and analysis of *N*-(α-chloroalkenyl)alkylamidine hydrochlorides (dimer salts) (**3**)

	Dimer salts (**3**)		Reaction conditions[a]		Yield[b] (%)	Mp (°C)	IR (Nujol) (cm^{-1})	Mass[c] (M$^+$−HCl)	Elemental analysis[d]		
	R^1	R^2	Molar ratio nitrile/HCl	Reaction time (hr)					C%	H%	N%
a)	H	H	1:1.12	136	67	—	1710	dec[e]			
b)	CH_3	H	1:1.72	136	86	125.0— 127.5	1673 1588	146	38.88 (39.36)	6.63 (6.61)	15.05 (15.30)
c)	C_2H_5	H	1:1.38	114	63	102.0— 104.0	1700 1600 1530	dec[e]	45.63 (45.51)	7.87 (7.64)	13.31 (13.27)
d)	*n*-C_4H_9	H	1:1.13	165	34	87.0— 90.0	1695 1600 1540	dec[e]	54.05 (53.93)	9.30 (9.05)	10.50 (10.48)
e)	*n*-C_6H_{13}	H	1:1.33	171	37	115.0— 116.5	1695 1600 1530	dec[e]	59.24 (59.43)	10.22 (9.98)	8.27 (8.66)
f)	Ph	H	1:1.23	46	53	135.0— 138.0	1686 1606[f]	dec[e]	62.21 (62.55)	5.23 (5.25)	9.01 (9.12)
g)	Cl	H	g)	—	90	122.0— 123.0	1695 1615	186	21.20 (21.45)	3.03 (2.70)	12.57 (12.51)
h)	$ClCH_2$	H	1:1.28	72	71 (90)[h]	93.0— 95.0	1685 1600[f]	—	30.44 (28.06)	4.90 (4.00)	12.09 (11.12)
i)	$PhCH_2$	H	1:1.22	168	52 (81)[h]	178.0— 180.0	1700 1670 1605	—	63.84 (64.48)	7.57 (6.01)	10.85 (8.36)
j)	CH_3O	H	1:1.49	2	i)						
k)	CH_3OCH_2	H	1:1.40	144	i)						
l)	$COOC_2H_5$	H	1:0.97	j)	i)						
m)	CH_3	CH_3	1:1.49 1:1.12[k]	48 72[k]	76 43[k]	193.0— 194.0(dec)	1695 1585 1530	174	45.26 (45.21)	8.46 (7.64)	13.31 (13.27)
n)	C_2H_5	CH_3	1:1.93	288	75	162.5— 164.0(dec)	1690 1585 1530	202	50.35 (50.21)	8.52 (8.42)	11.83 (11.71)
o)	*n*-C_3H_7	CH_3	1:1.43	260	48 (90)[h]	135.0— 137.0	1693 1590	—	53.44 (53.93)	9.07 (9.05)	10.39 (10.48)
p)	*n*-C_4H_9	CH_3	1:1.82	600	57 (93)[h]	123.0— 126.0	1690 1600	—	55.55 (56.94)	9.69 (9.56)	9.81 (9.49)
q)	Ph	CH_3	1:1.70	307	64	168.0— 170.0	1693 1603	—	65.08 (64.48)	6.15 (6.01)	8.76 (8.36)
r)	$ClCH_2$	CH_3	1:1.40	240	82 (95)[h]	98.0— 100.0	1690 1600 1530	dec[e]	35.28 (34.31)	5.36 (5.04)	10.40 (10.01)
s)	C_2H_5	C_2H_5	1:1.11	282	45 (75)[h]	147.0— 148.0	1682 1592	—	53.73 (53.93)	8.94 (9.05)	10.51 (10.48)
t)	Cl	Cl	g)	g)	l)	119.0— 121.0(dec)[m]	1698 1618 1520	254	16.15 (16.41)	1.43 (1.38)	9.59 (9.57)
u)	CH_3	Cl	n)	n)	l)	175.0— 176.0(dec)[o]	1700 1615 1530	214	28.29 (28.60)	4.21 (4.00)	11.22 (11.12)
v)	$ClCH_2$	Cl	1:1.13	168[p]	97 (100)[i]	>110(dec)	1690 1615 1520[f]	q)	23.43 (22.46)	2.73 (2.51)	9.00 (8.73)
w)	*n*-C_4H_7	Cl	1:0.50	67	38[r]	145.0— 148.0(dec)	1693 1610 1515	298	42.67 (42.88)	6.71 (6.60)	8.67 (8.34)
x)	Ph	Cl	1:0.57	70	46[r]	163.0(dec)	1650	q)	50.87 (51.09)	3.68 (3.75)	
y)	C_2H_5	Br	s)	76	51	130.0— 133.0	1690 1605 1515	dec[e]	24.81 (26.04)	3.95 (3.83)	7.73 (7.59)
z)	Ph	Ph	1:4.63	432	t)						

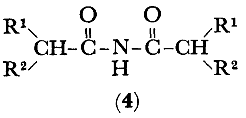
a) Reaction temp., 60—65°C. b) Based on nitrile. c) 70 eV. d) Values in parentheses are calculated ones. e) The molecular ion and fragment ions probably due to the *s*-triazine having the composition of $(R^1R^2CHC{\equiv}N)_3$ were obserbed f) KBr disk. g) According to the method of Grundmann *et al.*,[11] ethyl ether was used as solvent. h) Based on reacted nitrile. i) See experimental section. j) For 20 days at room temp. k) Reaction temp., 100°C. l) Almost quantitatively. m) Lit,[11] 140°C. n) According to the method of U. S. Patent.[10] o) Lit,[10] 175°C. p) Reaction temp., room temp. q) See Table 1. r) Based on HCl used. s) Ethyl ether was used as solvent and heated to 60—65°C. t) Diphenylacetamide was formed in 20% yield.

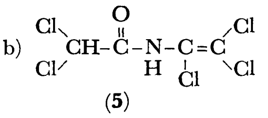
enough for us to assume that they all had the same structure as the dimer salt, $2ClCH_2C{\equiv}N\cdot 2HCl$ (**3g**), although sometimes their IR spectra showed a weak absorption around 1750 cm^{-1} as well as the precursor of **3g** described above.

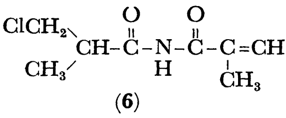
On the other hand, the addition product from propionitrile was prepared by reacting propionitrile with excess HCl in a sealed glass tube at 60—65°C. The resulting addition product (**3b**) was found, on the basis of elemental analysis and the melting point, to be

Table 3. Preparation and analyses of **4**[a], **5**[b], and **6**[c]

	Products		Yield (%)	Mp (°C)	IR(KBr) (cm^{-1})	Mass[d] (M$^+$)	Elemental analysis[e]		
	R^1	R^2					C%	H%	N%
4b)	CH_3	H	55[f](25)[g]	155.0—157.0[h]	3280 3180 1740				
4d)	n-C_4H_9	H	72	88.0— 90.0[i]	3280 3200 1740	213	66.11 (67.56)	10.23 (10.87)	6.29 (6.57)
4e)	n-C_6H_{13}	H	73	90.0— 91.0	3280 3190 1740	269	71.09 (71.32)	11.71 (11.60)	5.38 (5.20)
4f)	Ph	H	—	201.5—202.5	3280 3180 1730	253	76.39 (75.87)	5.93 (5.97)	5.62 (5.53)
4h)	$ClCH_2$	H	59	157.5—158.0	3285 3195[j] 1745	197	36.83 (36.39)	4.94 (4.58)	7.17 (7.07)
4i)	$PhCH_2$	H	81	108.0—109.0	3220 3140[j] 1740	281	77.05 (76.84)	6.99 (6.81)	5.18 (4.98)
4m)	CH_3	CH_3	50[g]	177.0—178.0[l]	3305 3215 1735	157	60.73 (61.12)	10.03 (9.62)	8.96 (8.91)
4o)	n-C_3H_7	CH_3	46	98.0— 99.0	3280 3195 1730	213	67.45 (67.56)	11.15 (10.87)	6.59 (6.57)
4p)	n-C_4H_9	CH_3	—	65.5— 67.0	3290 3200 1740	241	69.54 (69.67)	11.34 (11.27)	5.81 (5.80)
5)[b]	Cl	Cl	86	108.0—109.0	3222 2930 1704 1620 1524	255	18.80 (18.67)	0.76 (0.78)	5.11[n] (5.44)
4s)	C_2H_5	C_2H_5	30	84.5— 85.0	3280 3180 1732[j]	213	67.28 (67.56)	11.13 (10.87)	6.47 (6.57)
6)[c]	$ClCH_2$	CH_3	39	91.0— 91.5	3300 3180 1730 1690 1635 950	189	50.49 (50.67)	6.55 (6.38)	7.67[m] (7.39)
4u)	CH_3	Cl	65[g]	119.0—121.0	3330 3240[j] 1760	197	36.43 (36.38)	4.51 (4.58)	7.08 (7.07)
4v)	$ClCH_2$	Cl	27[k]	94.0— 96.0	3265 3190 1760	265	27.95 (27.00)	2.72 (2.64)	5.38 (5.25)
4y)	C_2H_5	Br	47	80.0— 83.0	3280 3200[j] 1750	313			4.97 (4.45)

a)

$(R^1)(R^2)CH-C(=O)-NH-C(=O)-CH(R^1)(R^2)$
(**4**)

b)

$Cl_2CH-C(=O)-NH-C(Cl)=CCl_2$
(**5**)

c)

$(ClCH_2)(CH_3)CH-C(=O)-NH-C(=O)-C(CH_3)=CH_2$
(**6**)

d) 70 eV. e) Values in parentheses are calculated ones. f) Hydrolysis using aq. Na_2CO_3. g) Yields in hydrolysis of the freshly prepared salts with water. h) Lit,[23] 153—154°C. i) Lit,[23] 174°C. j) Nujol. k) Acetone was used as solvent. l) Lit,[24] 92.5°C. m) NMR($CDCl_3$) (τ): 8.68(3H, doublet(J=6 Hz)), 7.98(3H, sharp singlet with fine structure), 6.0—6.5(3H, complex lines), 4.35(1H, complex lines), 4.10(1H, complex lines), 1.13(1H, broad line). n) NMR($CDCl_3$)(τ): 4.00(1H, singlet), 2.08(1H, broad line).

identical with a substance which had already been obtained by Gautier[1] and Michael.[9] Its IR spectrum did not show the absorption around 1750 cm^{-1} and indicated the same structure as the other adducts, **3g**, **3t**, and **3u**. Generally, the adducts obtained by heating in a sealed tube did not show the IR absorption around 1750 cm^{-1}.

As is shown in Table 1, their mass spectra exhibited the fragment ion peaks corresponding to M^+–HCl, M^+–HCl–Cl, $R^1R^2CHC{\equiv}\overset{+}{N}H$, and $R^1R^2CHC{\equiv}N$. Thus, all the addition products (**3b**, **3t**, and **3u**) have been confirmed to be dimer salts with the composition of $2R^1R^2CHC{\equiv}N{\cdot}2HCl$. Further proof was obtained by the hydrolysis of the addition products to diacylamine **4** or **5**, as will be discussed below.

Dimerization of Other Nitriles Having α-Hydrogen with HCl. Nitriles were generally allowed to react with an excess of dry HCl in a sealed glass tube at 60—65°C until the reaction mixture became viscous enough (Table 2). In two cases, those of isobutyronitrile and 2,3-dichloropropionitrile, the whole reaction mixture solidified at the end of the reaction. In the other cases, when the viscous product was treated with dry ether or was left standing with ether in a refrigerator, the white or pale yellow product crystallized or solidified. Most of the adducts thus obtained were analytically pure, as is shown in Table 2. The addition product from acetonitrile was very hygroscopic, as was the dimeric product reported by Hinkel and Treharne.[14] On the basis of the data in Tables 1 and 2, and the hydrolysis to the corresponding diacylamines (**4**) (see next section), all of the addition products were identified as dimer salts with the composition of $2R^1R^2CHC{\equiv}N{\cdot}2HCl$. It is worth pointing out that, in some of their mass

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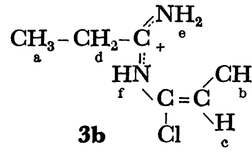
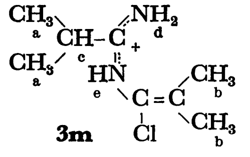
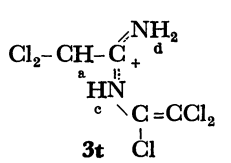
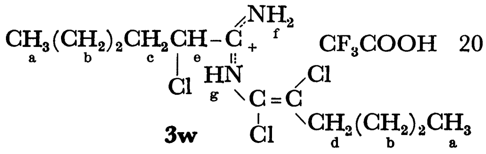
[21] Shand[10] reported that water converted the salt from 2-chloropropionitrile to 2-chloropropionamide.

[22] Grundmann *et al.*[2] reported that the treatment of the dimeric salt having the formula $(CHCl_2C{\equiv}N)_2HCl$, with water gave bis(dichloroacetyl)amine (**4t**).

[23] K. Brunner, R. Grunner, and Z. Benes, *Monatsh.*, **48**, 123 (1927).

[24] C. Norstedt and H. A. Wahlforss, *Chem. Ber.*, **25**, Ref. 637 (1892).

TABLE 4. NMR SPECTRA OF SOME DIMER SALTS (**3**)

Dimer salts (**3**)	Solvent	Temp.(°C)	Signal assignment (τ)					
 **3b**			(a) [3H]	(b) [3H]	(c) [1H]	(d) [2H]	(e) [2H]	(f) [1H]
	Liq. SO$_2$	20	8.67(t) (J=7.5Hz)	8.11(d) (J=6.7Hz) 8.08(d) (J=6.7Hz)	7.20(q)[a] (J=7.5Hz)	3.81(q) (J=6.7Hz) 3.79(q) (J=6.7Hz)	2.85(bs)[b] 1.75(bs)	−0.25(bs)[b]
	Liq. SO$_2$	0	8.60(t)	8.10(d) 8.07(d)	7.21(q)	3.80(q) 3.78(q)	2.84(bs) 1.84(bs)	−0.06(bs)
	Liq. SO$_2$	−35	8.60(t)	8.11(d) 8.08(d)	7.23(q)	3.79(q) 3.77(q)	2.80(bs) (2.44(bs)) 1.96(bs) (1.77(bs))	0.12(s)
	Liq. SO$_2$	−65	8.63(t)	8.12(d)	7.27(q)	3.82(q) 3.80(q)	2.81(s) (2.47(bs)) 2.12(s) (1.93(bs))	0.30(s)
	CF$_3$COOH	20	8.57(t) (J=7.5Hz)	8.08(d) (J=6.7Hz) 8.06(d) (J=6.7Hz)	7.21(q) (J=7.5Hz)	3.80(q) (J=6.7Hz) 3.78(q) (J=6.7Hz)	2.40(bs) 1.85(bs)	0.75(bs)
	d_6-DMSO	20	Decomposition					
 **3m**			(a) [6H]	(b) [6H]	(c) [1H]	(d) [2H]	(e) [1H]	
	Liq. SO$_2$	−28	8.59(d) (J=6.7Hz)	8.18(s) 8.05(s)	6.94(qui)[c] (J=6.7Hz)	2.95(b) 2.12(b)	0.50(b)	
	Liq. SO$_2$	−60	8.59(d)	8.17(s) 8.04(s)	6.98(qui)	2.92(b) 2.22(b)	0.64(b)	
	CF$_3$COOH	20	8.52(d) (J=6.7Hz)	8.14(s) 7.99(s)	6.94(qui)	2.44(b) 1.97(b)	1.04(b)	
	d_6-DMSO	20	8.72(d) (J=6.7Hz)	8.32(s) 8.14(s)	6.95(qui) (J=6.7Hz)	0.77(b) −0.11(b)	−1.71(b)	
 **3t**			(a) [1H]	(b) [2H]	(c)			
	CF$_3$COOH	20	3.06(s)	0.92(b) 0.73(b)	d)			
 **3w**			(a) [3H]	(b) [8H]	(c) [2H]	(d) [2H]	(e) [1H]	(f) [2H]
	CF$_3$COOH	20	9.00[e]	*ca.* 8.46(m)	*ca.* 7.81(m)	7.27(t)	5.08[f]	1.10(bs) 0.48(bs)
			(g) [1H]					
			−0.30(bs)					

a) (q)=quartet with fine line structure. b) (bs)=very broad. c) (qui)=quintet. d) The NH signal appears to be under the trifluoroacetic acid signal. e) Triplet with some distorted. f) Triplet with fine line structure.

spectra, the molecular-ion and degradation-ion peaks due to the *s*-triazine with the composition of $(R^1R^2CHC{\equiv}N)_3$ were observed instead of the degradation peaks due to the dimer salts (**3**).[19]

The reaction seems to proceed quantitatively. Especially, an excess of HCl and a prolonged reaction time seem to be beneficial for the reaction. Heating is not always necessary. Some α-chloronitriles quantitatively dimerize in ether under cooling, and isobutyronitrile reacts with a large excess of HCl at room temperature, although slowly, giving a quantitative yield of the salt (**3m**). A higher reaction temperature (100°C) did not favor the reaction (see **3m** in Table 2).

All attempts to prepare the solid dimer salts from methoxyacetonitrile, 3-alkoxypropionitriles, ethyl cyanoacetate, and diphenylacetonitrile were in vain (see Experimental Section).

Hydrolysis of the Dimer Salts (3) to Diacylamines (4). When most of the dimer salts (**3**) thus obtained were treated with water or with aqueous acetone or methanol, the corresponding diacylamines (**4**) were formed without being contaminated with other products (see Eq. 3). The yields and analytical data of the diacylamines (**4**) thus obtained are summarized in Table 3.[20]

It should be noted, however, that these dimer salts, **3b**, **3m**, and **3u**, were unreactive to water; they were recovered unchanged after the removal of water under reduced pressure. They were readily hydrolyzed by aqueous alkali to give these diacylamines, **4b**, **4m**, and **4u** respectively, as had been expected. However, the freshly-prepared ones were in part readily hydrolyzed by only cold water to give the corresponding diacylamines; this may be ascribed to the initial formation of unstable salts, such as 2: 3 adducts (see next section).

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[20] Diacylamines (**4**) were reported obtainable by the reaction of nitriles with carboxylic acids or acid chlorides. But the reaction conditions were very drastic (reaction temp. 100—250°C) and probably the yields may be low. (R. Otto and J. Troger, *Chem. Ber.*, **23**, 760 (1890)). This reaction provides a facile one-step synthesis of diacylamines (**4**).

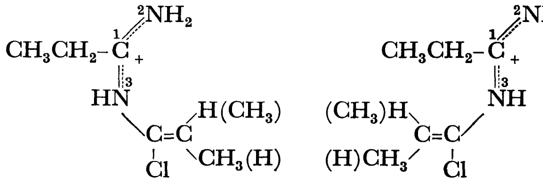
As is shown in Table 3, the similar treatment of the dimer salts **3r** and **3t** with water gave anomalous products. The former afforded *N*-(3-chloro-2-methylpropionyl)-*N*-methacryloylamine (**6**), which must be formed by the further but partial dehydrochlorination of bis(3-chloro-2-methylpropionyl)amine (**4r**) during work-up, while the latter gave a partially-hydrolyzed product, *N*-(1, 2, 2-trichlorovinyl) dichloroacetamide (**5**).[25]

Structure of the Dimer Salts (3). The mass spectra of the dimer salts (**3**) indicated that one mole of HCl in the salts was intrinsically bonded and that another mole of HCl was present in the ionic form. The analysis of the ionic chlorine content also supported this fact.

The most interesting problem was to determine the structure of the protonated amidine function in these dimer salts (**3**). In view of the above interest, we undertook an NMR investigation of their structures.

The NMR spectra of **3b** measured in the range from −60 to 20°C using liquid SO_2 as the solvent show two sets of quartets for the vinyl proton at τ 3.79 and 3.81 in almost the same ratio, and two sets of doublets for the methyl protons attached to the vinyl group at τ 8.08 and 8.11 in the same ratio; both the quartets and the doublets are coupled to each other ($J=6.7$ Hz), suggesting the presence of a propenyl group as a mixture of *cis* and *trans* in almost equal proportions.

The NH protons give rise to three broad signals at 20°C. As the temperature is lowered, a narrowing of the signals and slight shift to higher magnetic fields are observed. Below −35°C, the two upfield peaks were split, giving new, small, broad signals at τ *ca.* 1.77—1.93 and *ca.* 2.44—2.47 respectively. The simplest interpretation of these data is that the upfield signals are due to $>C^1{=}N^2H_2$, with a hindered rotation about the C^1N^2 bond because of its partial double-bond character, and that the low-field signal is due to a highly acidic proton on the nitrogen, N^3. The behavior of the upfield N^2H_2 protons at low temperatures may unambiguously be ascribed to the internal rotation of the α-chloroalkenyl group about the C^1N^3 bond with the partial double-bond character, as is shown in Eq. (2):

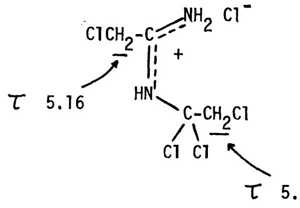


(2)

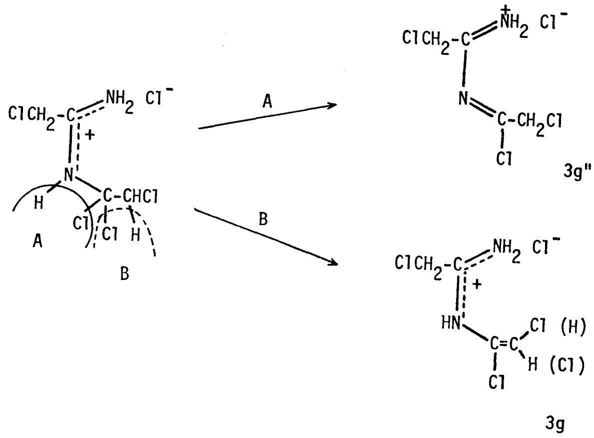
3b **3b′**

However, no splitting of the low-field N^3H signal was observed. The IR absorption patterns of **3b** in the region from 1500 to 1700 cm^{-1} are absolutely identical both in the solid state and in solution (in methanol).

The NMR spectrum of the 1 : 1 adduct from chloroacetonitrile, however, was not reproducible in any solvent such as DMSO-d_6, CF_3COOH, and liquid SO_2. Taking into account its instability, the freshly-isolated adduct, $2ClCH_2C{\equiv}N{\cdot}3HCl$, was analyzed instantly with a 100 MHz NMR spectrometer. The NMR spectrum (Fig. 1) suggests that the adduct has the following structure:



On the other hand, when the adduct was left standing under reduced pressure overnight, signals due to two pairs of methylene protons were deformed and signals attributable to the olefinic proton (*cis* and *trans*) appeared in its NMR spectrum (Fig. 2). These changes in the spectrum indicate the occurrence of partial dehydrochlorination, which may follow both A and B paths as follows:



3g″

3g

Accordingly, the lack of reproducibility of the NMR spectrum of the 2 : 2 adduct from chloroacetonitrile was ascertained to be attributable to the indefinite contamination with **3g″** or the 2 : 3 adduct.

Table 3 summarizes the NMR spectra of the 2 : 2 adducts measured in this investigation. The data

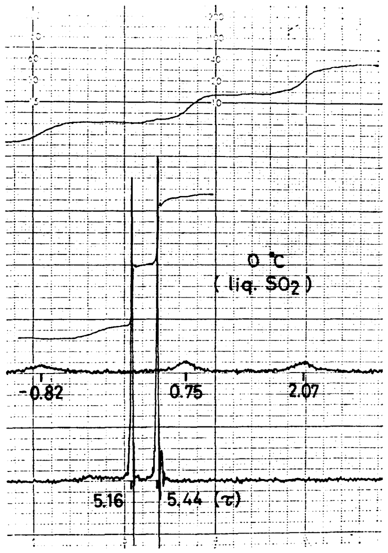


Fig. 1.

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[25] L. Hellerman, M. L. Cohn, and R. E. Hoen, *J. Amer. Chem. Soc.*, **50**, 1725 (1928).

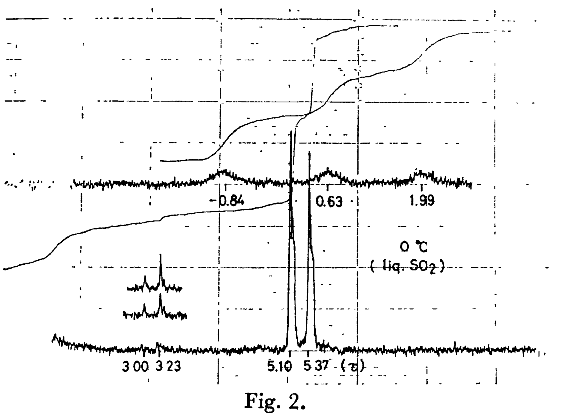
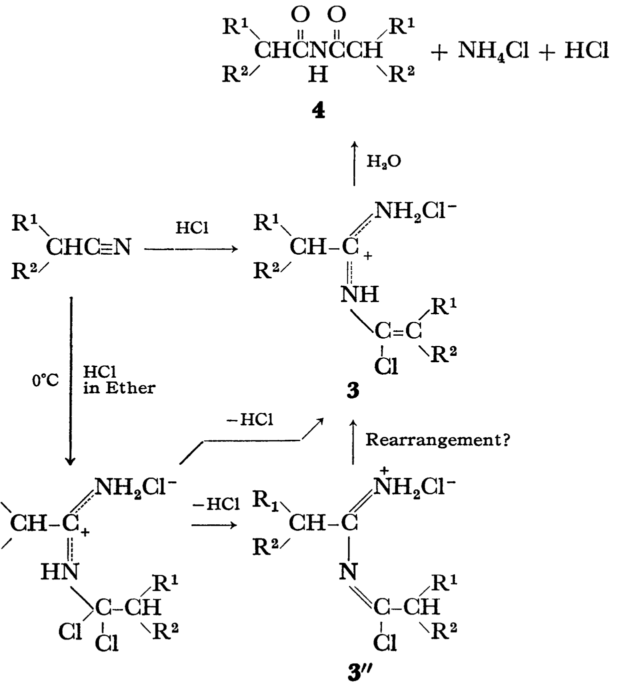


Fig. 2.

supported the general formula **3** as the structure of the dimer salts.

The reaction described above can now be presented as follows:



Extensive chemistry based on nitrile salts is now in progress in our group and will be described elsewhere.

Experimental

All the melting points were determined on a Yanagimoto micro-melting point apparatus and were corrected. The IR spectra were measured on a JASCO IR-E spectrometer; the NMR spectra, on JEOL JNM-G-60 and JNM-PS-100 spectrometers, with tetramethylsilane as the internal standard, and the mass spectra, on a Hitachi RMU-6E spectrometer.

General Procedure. In a 30 ml glass tube we placed 2—5 g of nitrile. The tube was then immersed in a mixture of ice and water, and dry HCl was allowed to be absorbed in it as much as possible. During that time, a white, crystalline solid, probably imidoyl chloride hydrochloride (**2**), was precipitated in some cases. The tube was stoppered, cooled in Dry Ice-acetone, sealed carefully, and heated to 60—65°C in a water bath until the reaction mixture was judged viscous enough. Table 2 lists the molar ratio of HCl to nitrile and the length of time. After the end of the reaction, the reaction tube was chilled in Dry Ice-acetone and opened carefully. After the removal of the HCl by warming, the stirring-in of dry ether caused the dimer salt to precipitate. When no solid precipitate appeared by this procedure, the mixture was then stored in a refrigerator for 24 hr or more, during which time the product was slowly crystallized and precipitated. Scratching the flask was sometimes beneficial for the solidification. The solid product was filtered, washed with dry ether, and dried under reduced pressure. In this manner, analytically-pure dimer salts were obtained and analyzed (Table 1). However, some salts (**3h, 3i, 3u,** and **3y**) required further purification. No attempt to find a good purification method was made.

Some reactions using ether as a solvent under cooling were carried out according to the methods previously reported.

The reaction of methoxyacetonitrile with HCl according to the general procedure, however, gave a black, hygroscopic substance. Ethyl cyanoacetate also gave a black, hygroscopic substance. The analogous treatment of 3-methoxypropionitrile or 3-butoxypropionitrile with HCl did not give the expected viscous reaction mixtures, and the starting nitriles were recovered. A small amount of the precipitated product consisted of ammonium chloride.

In the case of diphenylacetonitrile, di-*n*-butyl ether was employed as the solvent since the nitrile is solid. However, the resulting precipitate was identified as diphenylacetamide on the basis of following analytical results; mp 172—174°C (lit,[25] 167.5—168.5°C). Mass (M^+) 211. IR(KBr) 3380, 3180, 1650 cm^{-1}. Found: C, 79.59; H, 6.03; N, 6.67%. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.21; N, 6.63%. The formation of the amide is probably due to the degradation of di-*n*-butyl ether by HCl.

Preparation of the 2: 3 Adduct from Chloroacetonitrile. According to the method of Grundmann *et al.*,[11] chloroacetonitrile was allowed to react with HCl in ether under cooling. The resulting crystalline product was filtered by suction, left standing under reduced pressure for about 1 hr, and stored in a desiccator. Within 12 hr the white powder thus obtained was subjected to analysis. Found: Cl, 68.17%. Calcd for $C_4H_7N_2Cl_5$: Cl, 68.02%. Ionic chlorine content: Found: 40.56%. Calcd: 40.85%. The NMR tube containing the sample dissolved in liquid SO_2 was stored in a Dry Ice-acetone bath before measurement.

Hydrolysis of Dimer Salts (3). The dimer salt (**3**) (0.2—0.5 g) was dissolved in water (2—20 g). When the salt did not dissolve readily in cold water, the mixture was heated slightly, or methanol or acetone was added until the amidine salt dissolved. After a while, the diacylamine (**4**) was precipitated without being contaminated by other compounds, but in most cases several hours were required to observe the precipitation of diacylamines (**4**). Then, after the mixture had been allowed to stand overnight at room temperature, the diacylamine (**4**) formed was filtered with suction and dried. The diacylamines (**4**) thus obtained have a sufficient purity for synthetic use, but were further purified by sublimation and analyzed (Table 3).

When the amidines are resistant to hydrolysis in water, aqueous Na_2CO_3 was added until the mixture became alkali enough. Diacylamines **4** thus formed were treated in the same way.

In the hydrolysis of salt **3t**, after the filtration of **5**, the filtrate was extracted with ether. On evaporation, **5** was also obtained, but the further hydrolyzed product, bis(dichloroacetyl)amine (**4t**), was not isolated.

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