January, 1973] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 303—306 (1973) 303

Studies on Nitrile Salts. III.[1] Dimerization of Nitriles Having No α-Hydrogen with Hydrogen Chloride

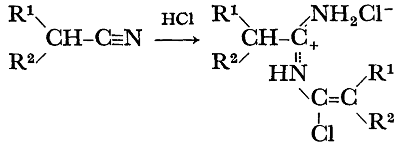
Shozo Yanagida, Tetsuo Fujita, Masataka Ohoka, Ichiro Katagiri,
Mikio Miyake, and Saburo Komori

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka

(Received May 1, 1972)

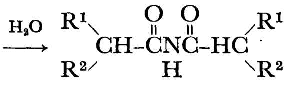
The reaction of nitriles having no α-hydrogen, such as aromatic nitriles and thiocyanates, with hydrogen chloride was investigated. Benzonitrile, *p*-tolunitrile, *m*-tolunitrile and some thiocyanates gave analytically pure 2:2 adducts in their reactions with HCl in a sealed glass tube at 30—60°C. The structure of the adducts was elucidated on the basis of NMR analysis and the mechanism of the generalized dimerization of nitriles was discussed.

In this laboratory,[2] it was shown that nitriles having α-hydrogen reacted with HCl to give *N*-(α-chloroalkenyl)alkylamidine hydrochlorides (**1**), and that the amidines (**1**) are readily hydrolyzed in water giving diacylamines (**2**) as follows:



$$\mathrm{R^1R^2CH{-}C{\equiv}N \xrightarrow{HCl} R^1R^2CH{-}\overset{+}{C}(NH_2Cl^-){-}NH{-}C(Cl){=}CR^1R^2}$$

1



$$\mathrm{\xrightarrow{H_2O} R^1R^2CH{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}HCR^1R^2}$$

2

Our interest not only in extending this dimerization reaction to other cyano compounds but also in seeking an explanation for the reaction mechanism, prompted us to investigate the reaction of nitriles having no α-hydrogen with HCl.

Attempts to dimerize trichloroacetonitrile[3] or pivalonitrile with HCl have failed. However, it has now been found that some aromatic nitriles and thiocyanates undergo dimerization.

This paper reports their dimerization reaction, the structure of the resulting 2:2 adducts and the mechanism of the dimerization of nitriles.

Results and Discussion

Reaction of Aromatic Nitriles with HCl. It was so far believed[4] that some aromatic nitriles react with HCl at a low temperature (below 0°C) to give arylimidoyl chloride hydrochlorides, which are stable only in the atmosphere of HCl but decompose to the starting materials in the air. It has now been found that the treatment of benzonitrile with dry HCl in a sealed glass tube at a higher temperature (30—60°C) leads to the isolation of the white addition product having the empirical formula C_7H_6NCl, which is stable in the air. When this salt-like adduct was dissolved in water and allowed to stand overnight at room temperature, dibenzoylamine was formed in 44% yield. The hydrolysis of the adduct with aqueous alkali unexpectedly gave *N*-benzoylbenzamidine contaminated with a small amount of 2,4,6-triphenyl-*s*-triazine. These facts indicate that the product is a 2:2 adduct. However, the mass spectrum and melting point of the adduct were found essentially identical with those of 2,4,6-triphenyl-*s*-triazine, suggesting that pyrolysis of the adduct produces 2,4,6-triphenyl-*s*-triazine.

Similarly, *m*- and *p*-tolunitrile gave the corresponding adducts (Table 1). In the case of *o*-tolunitrile, *p*-nitrobenzonitrile, and *p*-chlorobenzonitrile, ethyl ether was employed as a solvent to increase the solubility of HCl, since the nitriles dissolve less amount of HCl or the nitriles are solid in some cases. However, the reaction resulted in the formation of the corresponding amides.[5]

Reaction of Thiocyanates with HCl. Allenstein and Quis[8] reported that methyl thiocyanate reacted with HCl at 0°C giving methyl thioimidoyl chloride hydrochloride. However, the reaction at a higher temperature was not studied. We have found that the reaction of ethyl thiocyanate with excess HCl in a sealed glass tube at 60°C affords a dimeric 2:2 adducts, the structure of which was supported by the IR and mass spectra, and hydrolysis to bis(ethylthioformyl)amine.

The reaction was extended to methyl, propyl, butyl, octyl, and benzyl thiocyanates. Their IR spectra indicate the formation of the corresponding 2:2 adducts, but their mass spectra showed molecular and fragment ion peaks due to the corresponding 2,4,6-tris(alkylthio)-*s*-triazines. Hydrolysis of these adducts did not give the expected bis(alkylthioformyl)amines but unidentified oily or tarry substances. In addition, the isolation of analytically pure adducts was unsuccessful except for the case of octyl thiocyanate.

---

[1] Part II: S. Yanagida, T. Fujita, M. Ohoka, R. Kumagai, and S. Komori, This Bulletin, **46**, 299 (1973).

[2] S. Yanagida, T. Fujita, M. Ohoka, I. Katagiri, and S. Komori, This Bulletin, **46**, 292 (1973).

[3] Grundmann *et al.* reported the formation of the 2:1 adduct in the reaction of trichloroacetonitrile with HCl. C. Grundmann, G. Weisse, and S. Seide, *Ann. Chem.*, **577**, 77 (1952).

[4] E. N. Zil'berman, *Russ. Chem. Rev.*, **31**, 615 (1962).

[5] Especially *p*-chlorobenzamide was formed in 50% yield. The cleavage of ether linkage by hydrogen halides to an alcohol and a halide is well-known.[6] Thus the amide must be formed through imidates from nitriles, HCl and ethyl alcohol formed by the degradation of ethyl ether used as solvent.[7]

[6] E. Stande and F. Patat, "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience Publishers, New York, N. Y. (1967), p. 21.

[7] R. Roger and D. G. Neilson, *Chem. Rev.*, **61**, 179 (1961).

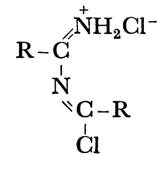
[8] E. Allenstein and P. Quis, *Chem. Ber.*, **97**, 3162 (1964).

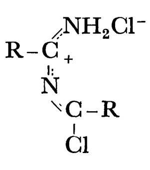
TABLE 1. PREPARATION AND ANALYSIS OF THE 2: 2 ADDUCTS FROM AROMATIC NITRILES AND THIOCYANATES

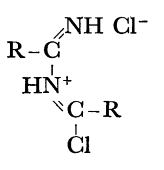
Starting nitrile RC≡N	Mol Ratio HCl/RC≡N	Reaction temp. (°C)	Reaction time (hr)	Yield (%)	Mp (°C)	IR (KBr) (cm^{-1})	Elemental analysis[a)] C%	H%	N%
$C_6H_5C≡N$	0.9	60	93	13	240—242[b)]	1663 1635	60.29 (60.23)	4.08 (4.33)	10.03 (10.04)
$C_6H_5C≡N$	0.9	30	192	23					
$C_6H_5C≡N$	1.1	30	75 days	57					
p-$CH_3C_6H_4C≡N$	1.0	60	286	27	293[c)]	1673 1635	63.12 (62.55)	5.38 (5.25)	9.32 (9.12)
p-$CH_3C_6H_4C≡N$	0.9	30	167	12					
m-$CH_3C_6H_4C≡N$	0.9	60	112	15	148—150[d)]	1665 1645	62.66 (62.55)	5.28 (5.25)	9.20 (9.12)
$C_2H_5SC≡N$[e)]	1.5	60	170	40	121.5—123.5	1617 1588	28.98 (29.15)	4.85 (4.89)	11.32 (11.33)
n-$C_8H_{17}SC≡N$	1.6	60	144	35	77—78	1620 1570	52.85 (52.03)	9.18 (8.73)	7.04 (6.74)

a) Values in parentheses are calculated ones. b) 2,4,6-triphenyl-*s*-triazine prepared melted at 242—243°C (lit,[22] 231—232°C). c) Melting point of 2,4,6-tirs(*p*-tolyl)-*s*-triazine: 278—279°C.[22] d) Melting point of 2,4,6-tris(*m*-tolyl)-*s*-tirazine: 152—153°C.[22] e) Mass spectrum shown in Experimental.

Structure of the 2: 2 Adducts. Taking into account the basicity of nitrogen atoms of the conjugate base, the dimeric adducts from aromatic nitriles or thiocyanates were expected to have structure A rather than B. In addition, in view of the possible resonance structures of A, the structure may well be expressed by the delocalized structure A′. In fact, the NMR spectra support structure A′ rather than A or B.


A


A′


B

In the NMR spectrum of the 2: 2 adduct from benzonitrile measured at −33°C in liquid SO_2, two distinct signals attributable to NH protons were observed (Fig. 1a).

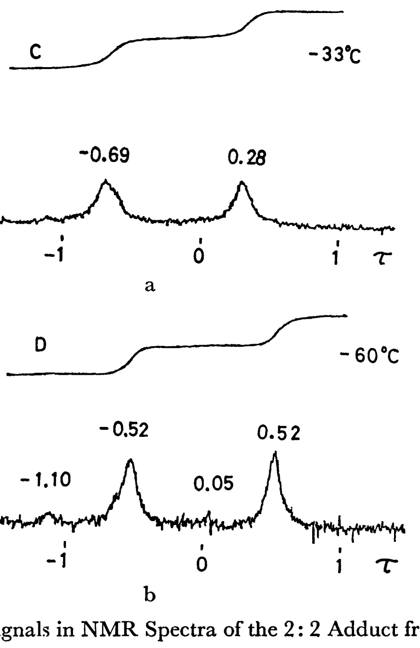
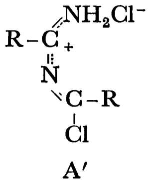
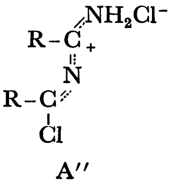


Fig. 1. NH_2 Signals in NMR Spectra of the 2: 2 Adduct from Benzonitrile.

An increase in temperature led to broadening and coalescence of the signals. The adduct from ethyl thiocyanate also exhibited a similar spectral change (see Experimental). These observations indicate the presence of NH_2 group in the adducts. The nonequivalence of the two amino protons may be accounted for by the hindered rotation about the CN bond owing to its partial double bond character. In addition, two pairs of phenyl ring protons and two pairs of methylene protons of the ethylthio groups have almost the same chemical shift. If the adducts took either structure A or B, one pair of the protons should have been greatly deshielded by the localized positive charge. The appearance of new small signals in Fig. 1b is probably ascribed to the presence of the following geometrical isomer A″:


A′


A″

Formation Mechanism of Dimeric Adducts. Some mechanisms for the dimerization of nitriles were proposed by several investigators[4,9,10] but they were still open to question.

von Braun *et al.*[11] and Prajsnar[12] reported that some *N*-substituted imidoyl chlorides having α-hydrogen, generated *in situ* from *N*-substituted amides, underwent dimerization, giving amidine derivatives as exemplified

---

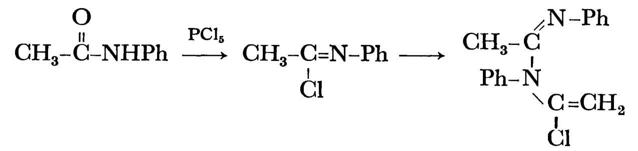
[9] W. Ruske, "Friedel-Crafts and Related Reactions," Vol. 3. Part 1. G. A. Olah, Ed., Interscience Publishers, New York, N. Y. (1964), p. 398.

[10] F. Johnson and R. Madronero, "Advances in Heterocyclic Chemistry," Vol. 6, A. R. Katrizky, Ed., Academic Press, New York, N. Y. (1966), p. 95.

[11] J. von Braun, F. Jostes, and H. Heymons, *Chem. Ber.*, **60**, 92 (1927).

[12] B. Prajsnar, *Roczniki Chem.*, **36**, 1449 (1962); *Chem. Abstr.*, **59**, 5139 (1963).

by the following equation:[13]



The reaction is quite comparable to the dimerization of nitriles in the presence of HCl.

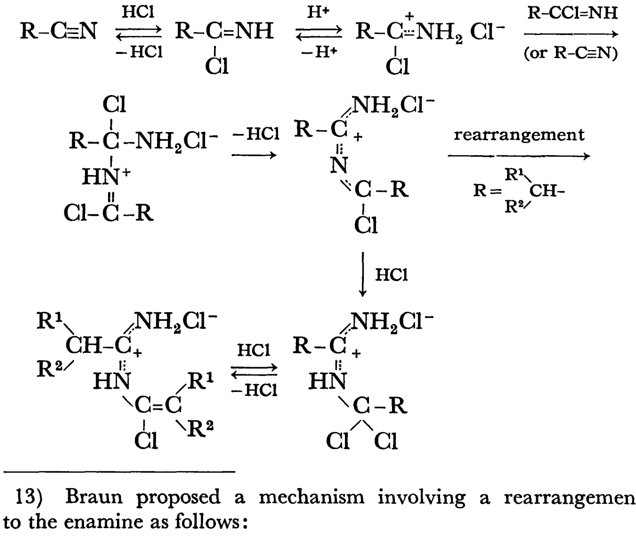
In order to get spectral evidence of the dimeric products and to seek an explanation for the mechanism of the dimerization of imidoyl chlorides, we reinvestigated the reaction of acetanilide with PCl_5 or phosgene.

The reaction of acetanilide with PCl_5, followed by neutralization with aqueous ammonia, gave *N,N'*-diphenyl-*N*-(α-chlorovinyl)amidine as reported, which was confirmed on the basis of NMR analysis.[14] Phosgene also gave the identical amidine. These facts suggest that HCl formed during the reaction plays an important role in the dimerization.[15] Accordingly it may be concluded that imidoyl chlorides, especially having at least one α-hydrogen and free from steric hindrance around α-carbon atom, readily dimerize giving *N*-(α-chloroalkenyl)amidine derivatives.[16]

Recently Speziale and Freeman[17] showed that *N,N*-diethyl-1,2,2-trichlorovinylamine reacts with an amine giving a *N,N*-diethyl-*N'*-substituted dichloroacetamidine through the addition-elimination mechanism rather than the usual S_N2 mechanism.

In addition, it is claimed by a U. S. patent[18] that dimethyl cyanamide reacts with HCl to give *N,N*-dimethylaminoimidoyl chloride hydrochloride and that, on heating to 100°C, the hydrochloride dimerizes giving the 2: 2 adduct.

In view of these considerations and the facts gained through a series of these studies,[2] we propose the following sequence as a mechanism of the dimerization of nitriles with HCl:



The dimerization of *N*-substituted imidoyl chlorides,[11,12] the Pinner synthesis of imidates and the intramolecular amination of nitriles in the presence of HCl[19] may be interpreted in a similar manner, that is, displacement of chloride ion from imidoyl chloride hydrochloride by the nucleophilic imidoyl chloride, alcohol or amine.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and were corrected. The NMR spectra were obtained using a Model JNM–G–60 spectrometer (Japan Electronic Optics Laboratory Co.) with tetramethylsilane as an internal reference. The IR spectra were recorded with a Japan Electroscopic IR–E spectrophotometer, and the mass spectra with a Hitachi mass spectrometer Model RMU–6E.

Dimerization of Aromatic Nitriles or Thiocyanates with HCl. A typical procedure is as follows: Dry HCl was bubbled into benzonitrile (3 g, 29.1 mmol) in 30 ml glass tube under cooling in an ice bath (1.02 g, 28.0 mmol of HCl was absorbed). The glass tube, after being sealed, was placed in a water bath maintained at 60°C for 93 hr. As the reaction proceeded, the reaction mixture became viscous. The tube was opened carefully and excess HCl was removed. Addition of dry ether into the reaction mixture caused precipitation of the 2: 2 adduct, which was filtered with suction, dried and analyzed (Table 1) (1.0 g, 12.8% yield).

The reaction conditions and yields for the other cases are shown in Table 1. It should be noted that the longer the reaction time, the higher the yield.

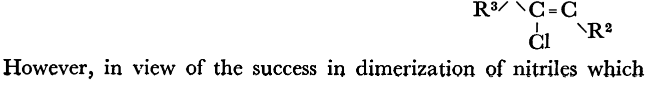
The mass spectrum of the adduct from ethyl thiocyanate shows the following fragment ion peaks (70 eV): *m/e* (rel intensity) 181 (19) [$C_2H_5SC(=NH)N=CClS^+$], 175 (10) [$C_2H_5SC(=NH)N=C^+-SC_2H_5$], 149 (100) [$C_2H_5SC(=NH)N=C^+-Cl$]. NMR ($SO_2$) at −30°, τ 0.43 (bs, 1H), 0.86 (bs, 1H), 6.81 (q, 4H, J=7.5 Hz), 8.54 (t, 3H, J=7.5 Hz), and 8.59 (t, 3H, J=7.5 Hz); at −62°C, τ 0.55 (bs, 1H), 1.10 (bs, 1H), 6.82 (q, 4H, J=7.5 Hz), 8.55 (t, 3H, J=7.5 Hz), and 8.60 (t, 3H, J=7.5 Hz).

Hydrolysis of the 2: 2 Adduct from Benzonitrile or Ethyl Thiocyanate. According to the procedure reported previously,[2] 4 g of the adduct from benzonitrile was dissolved in 50 ml of water and left standing at room temperature overnight. The resulting precipitate was filtered with suction, dried and identified as dibenzoylamine on the basis of the following analysis (1.58 g, 44%): mp 149—152°C (lit,[20] 147—148°C).

Analogous treatment of the adduct from ethyl thiocyanate

---

[13] Braun proposed a mechanism involving a rearrangement to the enamine as follows:



However, in view of the success in dimerization of nitriles which never undergo rearrangement to the enamine structure due to the absence of α-hydrogen, a similar mechanism for the dimerization of nitriles is unlikely.

[14] Braun determined the structure on the basis of elemental analysis and hydrogenation to *N,N'*-diphenyl-*N*-ethylacetamidine.

[15] S. Yanagida, M. Yokoe, I. Katagiri, M. Ohoka, and S. Komori, This Bulletin, **46**, 306 (1973).

[16] R. Bonnet, "The Chemistry of the Carbon-nitrogen Double Bond," S. Patai, Ed., Interscience Publishers, New York, N. Y. (1970), p. 597.

[17] A. J. Speziale and R. C. Freeman, *J. Amer. Chem. Soc.*, **82**, 909 (1969).

[18] I. Hechanbleikner, U. S. 2768204 (1956).

[19] F. F. Blicke, A. J. Zambite, and R. E. Stenseth, *J. Org. Chem.*, **26**, 1826 (1961).

[20] K. Brunner, *Chem. Ber.*, **47**, 2679 (1914).

with water gave a pale yellow crystalline precipitate, which was purified by recrystallization from acetone–water and identified as bis(ethylthioformyl)amine (40%): mp 104—105.5°C. IR (KBr) 3236, 3150 (NH), 1710 (C=O) cm^{-1}. Mass spectrum (70 eV) *m/e* (rel intensity) 193 [M$^+$], 131 (20) [$C_2H_5SCONCO^+$], 103 [$C_2H_5SCON^+$], 89 (20) [$C_2H_5SCO^+$], 70 (100) [$HCONCO^+$], 62 (39) [$C_2H_5SH^+$], 29 (80) [$C_2H_5^+$], 27 (45) [$C_2H_3^+$]. Found: C, 37.40; H, 5.89; N, 7.40%. Calcd for $C_6H_{11}NS_2O_2$: C, 37.28; H, 5.74; N, 7.25%.

Isolation of N-*Benzoylbenzamidine.* The aqueous solution of the adduct from benzonitrile (1 g in 20 ml of water) was made basic to litmus with aqueous Na_2CO_3, causing rapid precipitation of a brown crystal. The IR spectrum indicated that it was a mixture of *N*-benzoylbenzamidine and a small amount of triphenyl-*s*-triazine. The product was recrystallized from petroleum ether giving pure *N*-benzoylbenzamidine: mp 98°C (lit,[21] 98°C). IR (KBr) 1603 (C=O) 1563 (C=N) cm^{-1}. Mass spectrum (70 eV) *m/e* (rel intensity) 224 (46) [M$^+$], 208 (t) [M$^+$–NH_2], 147 (46) [M$^+$–C_6H_5], 105 (100) [$C_6H_5CO^+$], 77 (86)[$C_6H_5^+$], 51 (34).

Reaction of Acetanilide with PCl_5. According to the same procedure as that of Braun *et al.*,[9] powdered acetanilide (27 g) was allowed to react with powdered PCl_5 (43.5 g), followed by neutralization with aqueous ammonia, giving crude *N,N'*-diphenyl-*N*-(α-chlorovinyl)acetamidine (16 g). Extraction with petroleum ether using a Soxhlet extractor, concentration and recrystallization from hexane gave an analytically pure amidine: mp 106—108°C (lit,[9] 119°C), IR (KBr) 1650, 1630, 1595 cm^{-1}. Mass spectrum (70 eV) *m/e* (rel intensity) 270 (15) [M$^+$+1], 269 (15) [M$^+$], 118 (100) [CH_3C^+=N–C_6H_5], 93 (44) [$C_6H_5NH_2^+$], 77 (59) [$C_6H_5^+$]. NMR ($CDCl_3$) τ 8.12 (s, 3H), 4.68 (d, 1H) (*J*=3 Hz), 4.61 (d, 1H) (*J*=3 Hz), *ca.* 2.5—3.4 (m, 10H).

The NMR signals at τ 4.68 and τ 4.61, which are attributable to olefinic protons, support the *N*-(α-chlorovinyl)structure.

Reaction of Acetanilide with Phosgene. In a 200 ml four necked flask fitted with a thermometer, a condenser, a mechanical stirrer and a gas inlet tube, 27 g of acetanilide and 100 ml of benzene were placed and heated to 60—70°C. With stirring, phosgene was bubbled into the mixture. At first a yellow precipitate was formed. Upon continued heating and bubbling phosgene, the precipitate dissolved, giving a red brown transparent mixture which was cooled and left standing overnight. After filtration, the filtrate was concentrated with rotary evaporator, giving 18.5 g of a red brown oily substance. 5.1 g of this was dissolved in 300 ml of water and insoluble substance was removed by filtration. The filtrate was made basic by adding 28% aqueous ammonia, affording 2.68 g of red-yellow viscous material which gradually solidified on standing. Extraction with petroleum ether and concentration gave 0.6 g of *N,N'*-diphenyl-*N*-(α-chlorovinyl)actamidine.

The authors wish to thank Mr. H. Moriguchi for the mass spectrum measurement, Mrs. M. Sakurai for the NMR measurement, and Miss J. Maenaka and Mr. and Mrs. Muneishi for elemental analysis. This work was supported in part by a grant-in-aid from Kokusan Gijutsu Shinkokai. We wish to express our thanks to the founder, the late Mr. Chikara Kurata.

---

21) E. Beckmann and K. Sandel, *Ann. Chem.*, **296**, 285 (1897).

22) A. Cook and D. Jones, *J. Chem. Soc.*, **1941**, 278.