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Reaction of Isocyanogen (CNCN) with Hydrogen Chloride

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Introduction

The history of C_2N_2 isomers already started in 1815 when Gay-Lussac synthesized cyanogen (NCCN) from mercury(II) cyanide.[1] The search for other linear isomers was fruitless until 1988, when the second isomer isocyanogen (CNCN) was synthesized, which was initially believed to be diisocyanogen (CNNC).[2] It was, however, positively identified as isocyanogen by means of infrared spectroscopy,[3] microwave spectroscopy,[3] photoelectron spectroscopy,[4] NMR spectroscopy,[5] X-ray crystallography,[6] and gas-phase electron diffraction.[7] Very recently, diisocyanogen, too, has been prepared in low yield by several methods.[8]

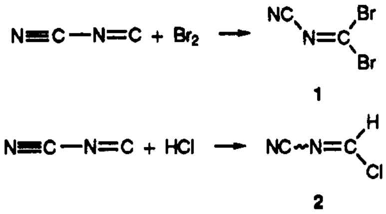
Isocyanogen is extremely unstable. In solution, polymerization takes place above −80 °C so that in most attempted derivatization reactions, polymerization prevailed. The structure of this polymer paraisocyanogen has been investigated and compared to the structure of paracyanogen.[9] So far, only two reactions have produced identifiable low molecular weight products. The first one was the complexation reaction with $(CO)_5Cr(2\text{-}Me\text{-}THF)$[10a] giving the known compound $(CO)_5CrCNCN$.[10b] The second successful reaction of isocyanogen was that with bromine.[5]

We now wish to report the reaction of isocyanogen with hydrogen chloride both in the gas phase and in the condensed phase; for comparison, two other reactions are briefly mentioned: the reaction with bromine in the gas phase and the attempted reaction with lithiating agents (*n*-butyllithium and phenyllithium).

Results and Discussion

1,1-Addition of organolithium compounds to isocyanides takes place at carbon to give 1-lithium aldimides.[11] With *n*-butyllithium and phenyllithium, this reaction did not work in the case of isocyanogen in the temperature range from −60 °C to room temperature; only polymerization of isocyanogen was observed.[12] Apparently, this addition cannot compete with polymerization.

Scheme I



The reaction of isocyanogen with hydrogen chloride was performed in the condensed phase and in the gas phase. For reasons of comparison, the reaction of isocyanogen with bromine, already investigated in the condensed phase at low temperature (−80 °C),[5] was performed in the gas phase, too. When the gases of isocyanogen and bromine were mixed at −20 °C, immediate decolorization took place; also in solution (diethyl ether, −80 °C), bromine was decolorized nearly instantaneously to give 1 (Scheme I).[5]

The reaction of isocyanogen with hydrogen chloride was performed under the same conditions, i.e. at −20 °C in the gas phase and at −80 °C in solution, and gave 2. The expected[5] products 1 and 2 (Scheme I) were too unstable to be isolated in pure form and were only characterized by ^1H, ^{13}C, and ^{14}N NMR spectroscopy and by high resolution mass spectroscopy.

Both 1 and 2 have ^{14}N and ^{13}C NMR chemical shifts in the regions characteristic for imino and cyano functionalities,[13] respectively (1: $\delta\ ^{14}N = -95, -135$ ppm; $\delta\ ^{13}C = 127, 110$ ppm; 2: $\delta\ ^{14}N = -103, -121$ ppm; $\delta\ ^{13}C = 160, 109$ ppm, respectively), indicating their structural analogy. The ^{13}C nucleus of the imino carbon ($C{=}N$) in 1 is rather shielded; analogous effects have been reported for $Mes^*P{=}CBr_2$ ($\delta\ ^{13}C = 128$ ppm) and $Mes^*P{=}CI_2$ ($\delta\ ^{13}C = 64$ ppm)[14] and are presumably caused by an anisotropy effect of the halogen atoms.[15b]

The ^{14}N chemical shift ranges of cyanides and imines are close to each other ($C{\equiv}N$ −100 to −120 ppm; $C{=}N$ −20 to −80 ppm[13]): however, the nitrogen nucleus of cyanides is usually a little more shielded than that of imines. Presumably, the more shielded signals (2: −121 ppm; 1: −135 ppm) must be assigned to the cyano group, and the others (2: −103 ppm; 1: −95 ppm) to the imine functionalities. The ^1H NMR spectrum of 2 showed one signal ($\delta\ ^1H = 8.92$ ppm), characteristic for aldimino protons.

In the ^1H NMR spectrum of 2, ^{13}C satellites were observed [$^1J(H^{13}C) = 244$ Hz]. This was confirmed by the proton coupling on carbon in the ^{13}C NMR spectrum. The value of the coupling constant is very large for a sp^2 hybridized carbon, nearly as large as the $^1J(CH)$ coupling in the sp-hybridized acetylene, which is 250 Hz. This large coupling constant is, however, similar to that of certain substituted aldehydes $XC({=}O)H$ (Table I). Differences in coupling constants are usually ascribed to the inductive effect of the substituent, which primarily affects the electron density on the carbon nucleus.[15a,b] This, in turn,

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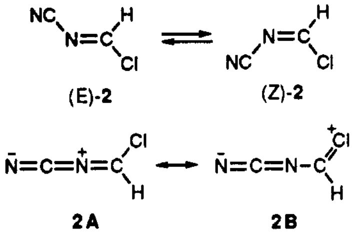
Table I. Coupling Constants ^{1}J(CH) of Formyl Derivatives $XC(=O)H$[15a,b]

X	^{1}J(CH), Hz	X	^{1}J(CH), Hz
H	172	O^-	194.8
CH_3	172	OH	222.0
t-Bu	168.8	OCH_3	226.2
C_6H_5	173.7	F	267.0
$N(CH_3)_2$	191.2		

Scheme II



causes a rehybridization of carbon resulting in more s character in the C–H bond. (Note, however, that it has been suggested that the change in nuclear charge makes a *direct* contribution to the large coupling constant, too[15c]).

In the ^{1}H NMR spectrum of 2, only one signal was observed at a temperature of −35 °C; even cooling to −85 °C did not result in splitting of this signal as one would have expected for two stereoisomers (*E*)-2 and (*Z*)-2 (Scheme II). Similarly, the ^{13}C NMR spectrum showed one set of signals only (*vide supra*). According to MNDO/PM3[16] calculations, the heat of formation at 298 K of (*Z*)-2 (H_f^0 = 54.7 kcal/mol) is 0.7 kcal/mol lower than that of the *E* isomer (H_f^0 = 55.4 kcal/mol). Assuming comparable entropies of formation for the two isomers, this small enthalpy difference implies that both should be present in detectable amounts (roughly *Z*/*E* = 7:3).

In principle, several situations might apply. In the first place, even though imines normally are bent, 2 may have a linear structure **2A** (Scheme II). This could be facilitated by the particular substitution pattern of the imino function in **2**: the cyano substituent will favor the allenic type structure **2A**, and the chlorine may be expected to furnish additional stabilization as indicated in **2B**.[17] We consider this possibility as less likely, because one would expect to find the allenic ^{13}C NMR signal at a much more deshielded position (below 200 ppm); moreover, the heat of formation of **2A** was calculated to be about 23 kcal/mol above that of **2** (MNDO/PM3).

A second possibility would be an accidental coincidence of the signals of (*E*)-**2** and (*Z*)-**2**, or a very small difference between them. While this cannot completely be excluded for the ^{1}H signals, it is rather unlikely to apply simultaneously for the ^{13}C NMR spectrum.

Therefore, we favor the third alternative, an equilibrium between (*E*)-**2** and (*Z*)-**2** which is rapid on the NMR time scale, even at −85 °C. Most likely, this is established via an inversion mechanism involving a transition state such as **2A,B**. In most cases, inversion is the lowest energy pathway for the cis–trans isomerization of imines, and for **2**, this is supported by MNDO/PM3 calculations predicting the perpendicular transition state of rotation, i.e. with the fixed C=N–C angle of *Z*-(**2**) (124.7°), to be higher by 10 kcal/mol than for **2A,B**. It should be pointed out that the barrier of 23 kcal/mol via **2A,B** is insufficient to prevent (at least slow) establishment of the equilibrium between (*E*)-**2** and (*Z*)-**2**; this excludes the possibility that one isomer is formed stereospecifically and preserved by a high isomerization barrier. On the other hand, if the calculated barrier of 23 kcal/mol is realistic, it means that the NMR signals of the two stereoisomers must be very close (see second possibility).

Unfortunately the IR spectrum (resolution 1 cm^{-1}) does not help to clarify the situation; in particular, it cannot be decided from the relatively broad signals whether they are due to one isomer or to two isomers with closely spaced vibrational frequencies.

Experimental Section

NMR spectra were recorded on a Bruker WM 250 spectrometer (^{1}H: 250 MHz, ^{13}C: 62.9 MHz, ^{14}N: 18.07 MHz). High resolution mass spectra were recorded on a Finnigan MAT 90 spectrometer. Isocyanogen was prepared according to ref 5. The IR spectrum of **2** was recorded on a Nicolet 7199B FTIR interferometer with a liquid-nitrogen-cooled MCT detector (resolution 1 cm^{-1}).

N-Cyanodibromoformaldimine (1). A. See ref 5 for [$^{15}N_2$]-**1**. B. Isocyanogen (1 mmol) and Br_2 (1 mmol) were evaporated into a reaction vessel (100 mL) in high vacuum[18] at −20 °C. Immediate decoloration was observed. The products were not isolated, because polymerization to a colorless insoluble polymer occurred:[5] ^{13}C NMR ($CDCl_3$; −30 °C); δ 127.3 (s, *C*=N), 109.7 (s, *C*≡N);[5] ^{14}N NMR ($CDCl_3$; −30 °C) δ −95, −135, HRMS calcd for $C_2N_2{}^{79}Br_2$ 209.8427, found 209.843.

***N*-Cyanochloroformaldimine (2).** A. Isocyanogen (1 mmol) and HCl were dissolved in an NMR tube (10 mm) in Et_2O at −100 °C. The reaction was monitored by ^{13}C NMR spectroscopy at −80 °C. B. Isocyanogen (1 mmol) and HCl (1 mmol) were evaporated into a reaction vessel (100 mL) in high vacuum at −20 °C.[18] After standing at −20 °C for 2 h, the products were partly distilled into an NMR tube (10 mm) and dissolved in Et_2O-d_{10}; another part was distilled into a vessel which was subsequently connected to the direct inlet of a mass spectrometer: IR (room temperature, gas phase) 3120, 2220, 1625, 949, 889, 801 cm^{-1}; ^{1}H NMR (Et_2O-d_{10}; −35 °C) δ 8.92 ($^{1}J(H^{13}C)$ = 244 Hz); ^{13}C NMR (Et_2O-d_{10}; −35 °C) δ 160 (d, ^{1}J(CH) = 244.5 Hz, *C*=N), 109 (d, ^{3}J(CH) = 17 Hz, *C*≡N); ^{14}N NMR (Et_2O-d_{10}; −35 °C) δ −103, −121; MS for C_2HN_2Cl *m*/*z* (rel inten) 88 (M^+, 40), 53 (100), 27 (14); HRMS calcd for $C_2HN_2{}^{35}Cl$ 87.9828, found 87.982.

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Supplementary Material Available: Copies of ^{1}H, ^{13}C, and ^{14}N NMR spectra of **2** including MNDO optimized structures including heats of formation of (*E*/*Z*)-**2** and **2A** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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