

Preparation of Mono-¹⁵N-Cyanogen and Mono-¹³C-Cyanogen

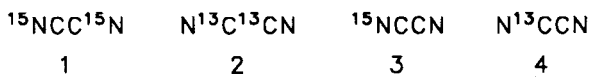
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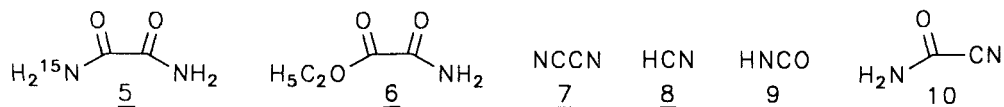
Keywords: ¹⁵N- and ¹³C-labelled oxamide; cyanogen

Summary: The preparation of the unsymmetrically isotope-labelled title compounds was achieved in pure form for the first time. While mono-¹⁵N-cyanogen is available in a two-step-synthesis, the preparation of mono-¹³C-cyanogen requires five steps, the last step in both cases being the dehydration of mono-¹⁵N- e.g. mono-¹³C-oxamide with phosphorus pentoxide.

In 1980 cyanogen, NCCN, was detected by the space probe Voyager I in the atmosphere of the Saturn moon Titan via the emission spectrum of its lowest lying fundamental band ν_5 (1). Furthermore the discovery and identification of two new C₂N₂-isomers, namely CNCN (2–4) and CNNC (5), renewed the chemical, spectroscopic and theoretical (6–8) interest in the most stable isomer. For these reasons we have embarked on a research project to determine the molecular structure of NCCN via high resolution infrared spectroscopy. This effort requires the chemical synthesis of isotopically labelled NCCN compounds. The two symmetrically labelled isotopomers of cyanogen ¹⁵NCC¹⁵N 1 and N¹³C¹³CN 2 have been prepared in our laboratory by thermolysis of ¹⁵N- or ¹³C- silver cyanide. This method together with all other methods to prepare cyanogen found in the literature (9) do not offer any direct access to unsymmetrically ¹⁵N- or ¹³C-labelled cyanogen [¹⁵NCCN 3 and N¹³CCN 4]. Since we were interested in undertaking infrared spectral investigations of both compounds 3 and 4, we decided to look for alternative routes for their synthesis.

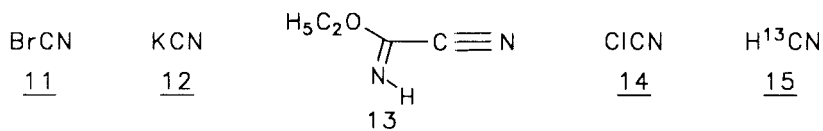


In the case of ¹⁵NCCN 3 it seemed promising to choose mono-¹⁵N-oxamide 5 as the precursor, since the latter is easily accessible by reaction of commercially available oxamic acid ethyl ester 6 with ¹⁵N-ammonia. Experiments carried out with unlabelled material revealed, however, that the reaction of oxamide with phosphorus pentoxide does not solely produce cyanogen, as claimed in the literature (10). The infrared spectral analysis of the reaction products showed that cyanogen 7 was present, accompanied by comparable amounts of hydrogen cyanide 8 and isocyanic acid 9. Compounds 8 and 9 arise from the thermal decomposition of the intermediate cyanofornamide 10, which under certain reaction conditions can also be isolated as a sublimate in up to 30% yield. Both the impurities 8 and 9 could be removed by passing the reaction mixture over dry NaOH-pellets, yielding pure cyanogen 7. Mono-¹⁵N-cyanogen 3 could then indeed be prepared by dehydration of mono-¹⁵N-oxamide 5 with phosphorus pentoxide followed by the purification process just mentioned.

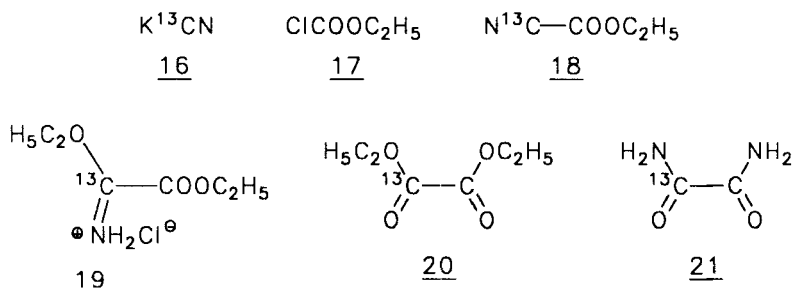


In order to synthesize mono- ^{13}C -cyanogen 4 one has to connect a ^{12}C -unit with a ^{13}C -unit. The coupling reaction of a metal cyanide with a cyanogen halide seemed to be a straightforward approach. The reaction of cyanogen bromide 11 with potassium cyanide 12 in aqueous/ethanolic solution is known to produce the imido-ester 13 (11). It seems most likely that cyanogen 7 is being formed first as an intermediate which then undergoes addition with one molecule of ethanol to yield the ester 13. However, all our attempts to produce cyanogen by direct reaction of potassium cyanide or cuprous cyanide with cyanogen bromide in solution only led to the formation of dark coloured polymeric material.

Cyanogen also forms in a one-step reaction when cyanogen chloride 14 and hydrogen cyanide 8 are passed over an activated-charcoal catalyst at 680 - 800 °C (9). This reaction was done on a small scale employing ^{13}C -hydrogen cyanide 15 instead of 8. The infrared spectral analysis of the reaction products showed that not only the desired compound 4 was present but also the isotopomers 2 and 7. In addition unreacted ^{13}C -hydrogen cyanide 15 was observed accompanied by equal amounts of unlabelled hydrogen cyanide 8, the latter being formed during the reaction. These findings indicate that scrambling processes must have occurred in the above reaction leading to the observed product distribution.



A successful synthesis of mono- ^{13}C -cyanogen (4) was finally carried out in a five-step reaction. The ^{12}C - ^{13}C -carbon-bond was linked already in the first step by reacting ^{13}C -potassium cyanide 16 and ethyl chloroformate 17 together with catalytic amounts of crown-ether (12) to produce the cyano-ester 18. Treatment of the latter with gaseous hydrogen chloride in the presence of ethanol following Nef's procedure (11) led to the precipitation of the imidoester-hydrogen-chloride-adduct 19, which upon contact with water yielded the oxalic ester 20. The latter was converted with aqueous ammonia to the oxalic amide 21, which was dehydrated with phosphorus pentoxide producing mono- ^{13}C -cyanogen 4.



Experimental Section

1.1 *Mono- ^{15}N -oxamide* 5: 1.305 g (23.95 mmol) $^{15}\text{NH}_4\text{Cl}$ were dissolved in 12 ml water, then 0.958 g NaOH added at 0 °C and stirred until everything was dissolved. Dropwise addition of 2.805 g (23.95 mmol) oxamic acid ethyl ester 6 led to the immediate precipitation of a white solid, which after a few hours of stirring was filtered by suction. The solid was washed once with ice water, twice with ethanol and then dried under high vacuum to give 1.428 g (66.9%) of compound 5.

1.2 Mono-¹⁵N-cyanogen 3: All of the above material (16.03 mmol), 18.6 g P₂O₅ and 8.5 g sand were mixed thoroughly and this mixture poured in a pyrex reaction tube. Then a 1"-layer of P₂O₅ was placed on top of it and everything fixed with glass wool. After evacuation to 10⁻³ Torr the tube was heated 2 h to 180 °C, then 2 h to 200 °C, 2 h to 220 °C and 3 h to 250 °C. The reaction products were frozen at -195 °C and then recondensed into a storage vessel at 10⁻³ Torr after the reaction was finished. The vessel was subsequently warmed up to -100 °C and the developing gas expanded into the vacuum system and pumped off several times, until the vapour pressure stayed constant at approximately 1 Torr. This procedure is necessary to remove CO₂, which forms in considerable amounts as a side product during the reaction. The residual material was then thawed to room temperature and passed through a glass tube filled with NaOH-pellets (surface-moisture having been removed under high vacuum) employing a weak nitrogen flow. After passing a layer of P₂O₅ the product was trapped at -195 °C and then recondensed at 10⁻³ Torr into a storage vessel to yield 200 mg (23.5 %) 1-¹⁵N-cyanogen 3. The infrared spectrum showed absorptions at 2638 (ν₃+ν₄), 2548 (ν₁+ν₅), 2139 (ν₃), 2087 (ν₁-ν₅), 732 (ν₄+ν₅) and 603 cm⁻¹ (ν₂-ν₅) (BRUKER IFS 25).

2.1 2-¹³C-cyanoformic acid ethyl ester 18: 3.306 g (50 mmol) K¹³CN 16 were added to a solution of 4.992 g (46 mmol) ethyl chloroformate 17 and 100 mg Dibenzo-18-crown-6 in 20 ml absolute CH₂Cl₂. The mixture was stirred for 4 days, while the progress of the reaction was monitored by gas chromatography. The solids were filtered and the solvent carefully removed from the filtrate. The remaining yellow liquid developed a white precipitate (crown-ether), which was filtered by suction and washed with a small amount of absolute ether. The filtrate contained the crude reaction product 18 together with ether. It was used directly without purification.

2.2 1-¹³C-oxalic acid diethyl ester 20: All the material from above was dissolved in 20 ml absolute ether and 4 ml absolute ethanol. Hydrogen chloride gas was now added in a modest flow rate for 30 min under exclusion of water; the imidoester-hydrochloride 19 started to precipitate already after a few seconds. The solvents were removed at 50 °C at 20 Torr and the solid white residue treated with 50 ml ether and 20 ml water. The organic layer was separated and dried with MgSO₄. Removal of the ether yielded 2.137 g of a pale yellow liquid which contained the oxalic ester 20 in 90.6% purity (GC) and approximately 7% of ether. The overall yield of the last three steps was 32% (based on compound 17).

2.3 Mono-¹³C-oxamide 21: The material from above was dissolved in 10 ml of absolute ethanol. This solution was slowly added to 10 ml of concentrated aqueous ammonia at room temperature. After stirring for 2 h the precipitated white solid was filtered, washed with ethanol and dried under high vacuum to yield 1.024 g (79.2%) amide 21.

2.4 Mono-¹³C-cyanogen 4: The material from above was mixed thoroughly with 15.44 g P₂O₅ and 8.36 g sand, then treated as described in section 1.2 to yield 129 mg (21.2%) of the product 4. It showed infrared spectral absorptions at 2621 (ν₃+ν₄), 2530 (ν₁+ν₅), 2129 (ν₃), 2070 (ν₁-ν₅), 724 (ν₄+ν₅) and 618 cm⁻¹ (ν₂-ν₅) (BRUKER IFS 25).

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