Photolytic hydration of cyanamides

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N-Cyanopiperidines (**1** and **2**) have been shown to possess a n → π* transition band in the vicinity of 260 mμ and, in the presence of a dilute acid, undergo photolytic reactions leading to hydration products (**3** and **4**). The fact that the reaction can be sensitized by acetophenone demonstrates that **1** reacts through a triplet state. E_T is about 76 kcal/mole. Increasing the water content in the photolysis medium reduced the yield of the hydration product.

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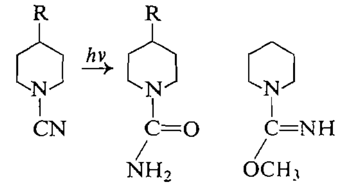
Introduction

There is some experimental evidence that the particular photolytic reactivities shown by nitrosamines are partially due to the extensive mixing of the n and π orbitals (1, 2). It has been argued that this extensive delocalization could raise the energy level of π* orbitals causing the observed difference in the electronic spectra of RNO, R_2NNO, and RONO systems (3). The observed differences in the photochemical reactions of nitrosamines and nitrites may be related to this argument.

In pursuing photochemical investigations of the related systems, we became interested in the cyanamide system. The π electrons of the carbon–nitrogen triple bond (—C≡N) differs considerably from those of the carbon–carbon triple bond in that the contribution of the polar form $(\text{—}\overset{+}{C}{=}N^{-})$ is as high as 70%, as indicated by the high dipole moment (ca. 4.0 D) of the simple nitrile (4). On the other hand the bond lengths of the carbon–carbon single bond in acetonitrile and acrylonitrile differ very slightly (1.458 Å and 1.426 Å respectively) (5) and the dipole moments of acrylonitrile and propionitrile are very close (3.8 D and 4.1 D respectively) (4). These figures strongly suggest that there is very little conjugative delocalization in acrylonitrile. In spite of this evidence it is surprising that a cyanamide shows a low intensity peak in 257 mμ region (vide infra) reminiscent of a n → π* transition band. Bearing in mind that the first transition band of acetonitrile occurs at 167 mμ (very weak) it is concluded that a sizable amount of electronic interaction may be present in the ground state of the cyanamide system. This electronic interaction apparently has shifted the first transition band to the ultraviolet region where irradiation experiments become feasible. Such considerations led us to examine the photochemical behavior of dialkylcyanamides.

Results and Discussion

The required compounds, N-cyanopiperidine (**1**) and N-cyano-4-methylpiperidine (**2**), were prepared from the parent amine via N-chloramine according to the method described by Berg (6). A dilute aqueous solution of **1** is distinctly basic and registers a value of 8–8.5 on pH paper. Thus in the 0.1 *N* hydrochloric acid solution the cyanamides are predominantly protonated and are difficult to extract into ether layers. In agreement with the required sp-hybridization of cyanamide group the geometry of N—C≡N group is linear, as is indicated from the magnetic equivalence of the α- and α′-proton chemical shifts in **1** and **2** at −40°.



1 (R = H) **3** **5**
2 (R = CH_3) **4**

In cyclohexane solution the cyanamides showed an absorption maximum at the region 260 mμ with the extinction coefficient of ca. 200. This peak, however, hypsochromically shifts to the 245 mμ region in methanol. In analogy to the similar hypsochromic shift of nitrosamines in more polar solvent (7) this band may be assigned to n → π* transition of the cyanamide group.

The irradiation was carried out with a Hanovia medium pressure mercury lamp through a

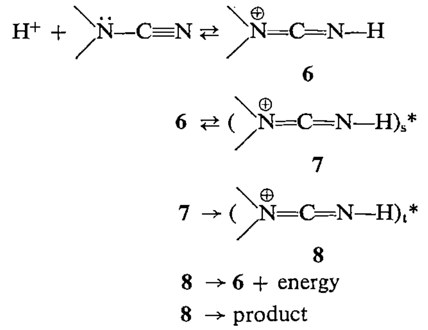
Vycor filter and the temperature was maintained at 15–20° with cold running water. While in a methanol or methanol–water solution **1** was stable to irradiation without showing any change at 233 mμ absorption, this peak slowly tapered off in 0.1 *N* methanolic hydrochloric acid solution. The decrease of the 233 mμ absorption became progressively slower as the irradiation proceeded and finally the residual absorption submerged into the tail of the new absorption centered at a lower wavelength. After 12 h of irradiation the reaction gave about 80% of crude piperidine-N-carboxamide (**3**) and 20% of unreacted **1**. In a similar manner N-cyano-4-methylpiperidine (**2**) was photolyzed to give 4-methylpiperidine-N-carboxamide (**4**) in 53% yields.

Since stoichiometrically the reaction portrays hydration of the nitrile group, the effect of water content in the reaction media should therefore be an important factor to investigate. In the presence of 10% water, other conditions being equal, the yield of **3** was 62% and the recovery of **1** 37% after 5 h irradiation. Instead of showing any improvement, the yield of **3**, however, varied erratically in the region of 45–55% regardless of prolonged irradiation (12 h period or longer) or use of a more powerful lamp (450 W Hanovia medium pressure mercury lamp). Progressive increases in water content to 15% and 25% brought down the yield of **3** to 22% and 6% respectively. The balance of the starting material was also recovered (75% and 82%). These results suggest that a photochemical equilibrium may exist between **1** and **2** and that the equilibrium is in favor of **1** in a medium of higher water content. This conclusion was shown to be incorrect since no **1** could be detected when **3** was photolyzed either alone under the same conditions or in the presence of a small amount of **1**.

Since moisture was excluded in the photolysis in methanol containing dry hydrochloric acid, it might be assumed that an intermediate was formed which reacted further with water to give **3** on working up. Unfortunately an attempt at trapping the presumed intermediate **5** with excess diethylamine after 12 h irradiation was not successful; **3** was obtained in 81% yield again. The failure to prove the presence of an intermediate and a photochemical equilibrium does not allow one to speculate on the primary process of the photoreaction. Neither does it offer an explanation of why the yield of **3** decreases at higher water concentration.

A control experiment in which the same reaction mixture (10% water) was worked up under the same conditions after leaving at room temperature for 12 h gave nearly a quantitative recovery of **1**. It was therefore concluded that hydration of the cyanamide is a genuine photolytic reaction. Experiments to determine the multiplicity of the excited electronic state responsible for the primary photoprocess was then in order. The photosensitized conversion of **1** and **2** could not be effected with 0.1 *M* benzophenone (E_T 69.2 kcal/mole) and acetophonone (E_T 76.3 kcal/mole) (8) in the absence of hydrochloric acid (pyrex filter). That no triplet energy transfer took place could be shown by the good recovery of the respective pinacols, the expected products from a photoreduction of the ketones (9). However, in 0.1 *N* hydrochloric acid, with acetophenone as a sensitizer, the hydration of **1** to **3** took place to an extent of 35% after 4 h irradiation. Since direct photolytic hydration of **1** does not occur in pyrex apparatus where energy is cut off at 280 mμ the triplet energy transfer from acetophenone to **1** must be taking place in the acidic medium to give the hydration product. In agreement with the mechanism of the triplet energy transfer, pinacol was formed only in small quantity and the majority of acetophenone was recovered (8). In contrast, benzophenone was ineffective in sensitizing this hydration reaction under similar conditions. It can be concluded that a part, if not all, of the direct hydration of **1** proceeds through the triplet state and that the E_T of **1** lies between 69 and 76 kcal/mole. In estimating the triplet energy of **1** by sensitization experiments, it was explicitly assumed that only the Franck–Condon type of energy transfer was involved (10). It should be pointed out that the E_T of **1** would be considerably higher than 76 kcal/mole should a nonvertical energy transfer take place (10).

A mechanistic consideration of this photolytic hydration is hampered by the obvious lack of knowledge of the role played by water in the reaction. The information available at the moment allows us to propose a reasonable mechanism for the direct photolysis as follows:



$$[1]\quad H^+ + {>}\ddot{N}{-}C{\equiv}N \rightleftarrows \underset{\mathbf{6}}{{>}\overset{\oplus}{N}{=}C{=}N{-}H}$$

$$[2]\quad \mathbf{6} \rightleftarrows \underset{\mathbf{7}}{({>}\overset{\oplus}{N}{=}C{=}N{-}H)_s^*}$$

$$[3]\quad \mathbf{7} \rightarrow \underset{\mathbf{8}}{({>}\overset{\oplus}{N}{=}C{=}N{-}H)_t^*}$$

$$[4]\quad \mathbf{8} \rightarrow \mathbf{6} + \text{energy}$$

$$[5]\quad \mathbf{8} \rightarrow \text{product}$$

The requirement of an acid in the photolytic hydration demonstrates that the protonated triplet state of **1** undergoes the reaction. Though the precise site of the protonation in the ground state of cyanamide is not known, the more resonance stabilized form, **6**, can be reasonably assigned to the protonated species. In the direct photolysis **6** is excited to the n → π* singlet state (**7**) which crosses over to the triplet excited state (**8**). Judging from the slow conversion of the cyanamides, the intersystem crossing, [3], may be very inefficient and the singlet excited state **7** may preferentially decay to the ground state by various routes (the reverse reaction of [2]). Alternatively, the triplet excited state **8** may preferentially decay to the ground state, as shown in [4], leaving only a small fraction to react via the hydration pathway [5]. No doubt [5] represents a multistep process, the nature of which remains to be clarified.

It has been further shown that under these photolytic conditions the addition of **1** to olefins did not take place, since no other product except **3** could be isolated when the irradiation was carried out in the presence of norbornylene or 1-hexene.

Experimental

Melting points were determined on a Fisher–Johns apparatus and were uncorrected. Infrared spectra were measured in a Unicam SP 200 as Nujol dispersions or liquid film. Ultraviolet (u.v.) spectra were taken with a Cary 14 and nuclear magnetic resonance (n.m.r.) spectra with Varian A 56/60 using tetramethylsilane as the internal standard.

Preparation of the Cyanamides

The preparations followed the procedures described by Berg (6). The amine was converted to N-chloramine which, in turn, was treated with potassium cyanide in methanol–water solution. N-Cyanopiperidine has b.p. 108–110° at 15 mm, λ_{max} 257 mμ (ε, 135) in cyclohexane and 244 mμ (ε, 142) in methanol, and ν (liquid) 2220 cm^{-1}, and the n.m.r. signals (CCl$_4$) at τ 6.87 and 8.39 have an intensity ratio of 4:6. N-Cyano-4-methylpiperidine has b.p. 105–107° at 5 mm, λ_{max} 260 mμ (ε, 224) in methanol, ν (liquid film) 2220, 1610, and 970 cm^{-1}, and n.m.r. signals (CCl$_4$) at τ 7.65 (broad doublet) and 8.06 (broad triplet).

Photolysis of the Cyanamides

Into the photolysis apparatus (equipped with a quartz cold finger carrying Vycor filter) a cyanamide (0.01 mole), 2 *N* hydrochloric acid (10 ml), and the required amount of water were placed and methanol was added to make up 200 ml. The solution was irradiated with a 200 W Hanovia medium pressure mercury lamp. At intervals, aliquots were withdrawn with a pipette and suitably diluted for u.v. scans. The zero hour sample was kept in the dark to serve as the control experiment.

The reaction mixture was evaporated. The aqueous solution of the residue was neutralized and extracted with ether. The ether solution gave the unreacted cyanamide after evaporation. The aqueous solution was evaporated in a rotatory evaporator at ca. 50° to dryness. The residue was then extracted with chloroform. The dry chloroform solution was evaporated to a small volume and a small amount of ether was added to induce crystallization. The crystals were recrystallized from the same solvent mixture to give the ureas.

Piperidine-N-carboxamide obtained from photolysis has m.p. 100–101°, which is not depressed in a mixture with an authentic sample prepared according to Cahour's method (lit. 105–106°) (11). 4-Methylpiperidine-N-carboxamide has m.p. 88–90° and ν_{max} (Nujol) 3380, 3180, 1650, and 1595 cm^{-1}. The mixed melting point with a sample prepared according to Cahour's method (11) is 88–91°.

The Control Experiment

The same constituent of the photolysis solution containing 10% of water and N-cyanopiperidine was prepared. This mixture was left at room temperature overnight and was worked up by the same procedure as that for the photolysis mixture. Only N-cyanopiperidine was recovered quantitatively.

Photosensitization Experiment

A pyrex cold finger was substituted in these runs. In the photolysis apparatus, N-cyanopiperidine (1.1 g), acetophenone (2.4 g), 2 *N* aqueous hydrochloric acid (10 ml), and methanol (185 ml) were placed and irradiated in the usual manner.

After the work-up acetophenone and its pinacol were found in the neutral fraction (2.51 g), as indicated by 1675 cm^{-1} absorption and τ 8.6 and 7.45 signals. The crude product of 2,3-diphenyl-2,3-butandiol crystallized from the light petroleum solution 650 mg, m.p. 95–120°, and showed the infrared peaks at 1335, 1130, 1111, 1355, and 1145 cm^{-1} and unresolved singlets at τ 8.6. This data indicated this fraction was a mixture of the *meso* and *dl* isomers (12). The basic extract (650 mg) contains mainly

N-cyanopiperidine as shown by the infrared spectrum. The urea **3** (450 mg) was isolated and purified in the usual manner.

Acknowledgments

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