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COMMUNICATION

Dimerization of an *N*-Alkylformimidoyl Cyanide

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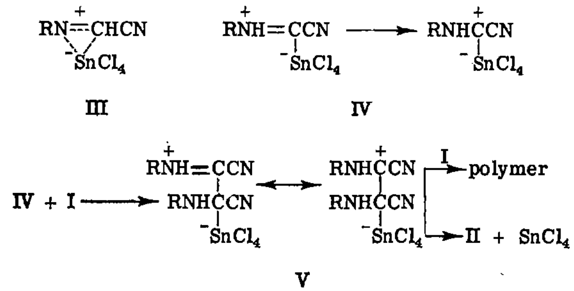
A Lewis acid-catalyzed dimerization of an *N*-alkylformimidoyl cyanide into an *N,N'*-dialkyldiaminomaleonitrile, **I** → **II**, complements a proposed scheme for a prebiotic chemical evolution from an oligomerization of hydrogen cyanide (4HCN → **II**, R = H) (*1*). This new reaction was carried out in anhydrous benzene stirred for 12 hr at room temperature with equimolar amounts of **I** and stannic chloride (best), or another Lewis acid, and gave good yields of **II**: b, 35%; c, 74%; d, 96%. *N*-Methyl-formimidoyl cyanide **Ia** gave extensive polymerization and **IIa** was not directly detected. Each new compound gave satisfactory elemental analysis and its structure was established by nmr, ir, and mass spectroscopic analysis.

$$\underset{\mathrm{I}}{\mathrm{RN{=}CHCN}} \qquad \underset{\mathrm{II}}{\begin{array}{c}\mathrm{RNHCCN}\\ \| \\ \mathrm{RNHCCN}\end{array}} \rightleftharpoons \begin{array}{c}\mathrm{RN{=}CCN}\\ | \\ \mathrm{RNHCHCN}\end{array}$$

a, $R = CH_3$; b, $R = C_2H_5$; c, $R = (CH_3)_2CH$; d, $R = (CH_3)_3C$.

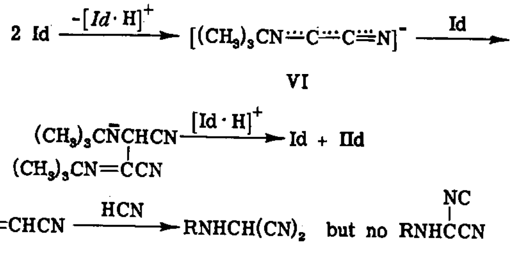
The overall transformation **I** → **II** is reminiscent of the dimerization of benzaldehyde into benzoin (compare with the tautomeric form of **II**) and of the anil of benzaldehyde into dianilinostilbene (*2*), each catalyzed by the cyanide anion. Neither benzaldehyde nor its *N*-*t*-butylimine was changed on treatment with stannic chloride in benzene. On the other hand the dimerization **I** → **II** was not detected when hydrogen cyanide and **I** in an alkaline environment gave several products (*3*).

Through polarization by the electron-withdrawing cyano group, the aldimine carbon atom is electron enriched relative to the aldimine nitrogen atom in **I** (*4*). This facilitates stabilization of an intermediate adduct **III** between stannic chloride and the azomethine linkage of **I** by the development of a bond between tin and the aldimine carbon as (after) the aldimine proton migrates to nitrogen. For a similar reason the combination of zwitterion **IV** and **I** leads to a new CC bond in the adduct V which dissociates into **II** and stannic chloride. A Lewis acid did not dimerize *N*-*t*-butylacetimidoyl cyanide ($(CH_3)_3CN{=}C(CH_3)CN$), which was recovered after similar treatment with stannic chloride.



The substitution of anhydrous hydrogen chloride for stannic chloride was unsuccessful in bringing about dimerization of **Id**. Since the hydrolysis of **Id** into *N*-*t*-butylformamide (*3*) was not accompanied by a detectable amount of dimerization into **IId**, it appears that the claim for **Id** to have been an intermediate for the formation of **IId** when $(CH_3)_3CN{=}CHC(CN){=}NC(CH_3)_3$ as the hydrochloride salt was hydrolyzed (*5*) is erroneous.

The improbability that a carbene tautomer of **I** (R = H) may participate in the aqueous base catalyzed tetramerization of hydrogen cyanide into diaminomaleonitrile **II** (R = H) can be extended to the *N*-alkyl homologs in the present work. A base accelerated dissociation of an aldimine proton, proposed for certain heterocyclic aromatic (*6*) and linear (*7*) aldimines, can account for the thermal dimerization (*8*) **Id** → **IId** at 130°C as an autocatalytic process in which the anion **VI** may participate in resonance with both an imine linkage and with an adjacent cyano group. In an alternative explanation, the intermediacy of a carbene tautomer of **Id** was proposed (*9*). The reactivity of an *N*-alkylformimidoyl cyanide as a carbene is, however, not consistent with other known reactions, e.g., a carbene reacts with hydrogen cyanide to give both an organic cyanide and an isocyanide (*10*), but **I** gives a cyanide with no trace of the isomeric isocyanide (*1*, *3*).



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