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THE CHEMISTRY OF CYANOACETYLENES VII THE REACTION OF HYDROGEN CHLORIDE WITH DIETHYLAMINOCYANOACETYLENE

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The cyclobutene ring formation by the cycloaddition of alkenes with alkynes or alkynes with chlorine is documented, but the yields are generally too low to be a preparative method for that purpose (1). Recently, cyclobutanecyanine has been prepared by the protonation of alkylynamine with hydrogen chloride but in 44% yield (2). In the previous paper, we reported the direct synthesis of cyanoynamines from chlorocyanoacetylene and several secondary amines for the first time, in which we impressed their characteristic reactivity different from that of alkylynamines, presumably because of their strongly polar structures (3). This paper deals with the result of the reaction of diethylaminocyanoacetylene (I), one of the cyanoynamines, with hydrogen chloride.

Dry hydrogen chloride gas was introduced into a dichloromethane solution of I at 0 ∿ -5° for 2 ∿ 3 hr until I had completely disappeared on TLC. After removing the solvent and surplus hydrogen chloride under reduced pressure, the residual oil was distilled under vacuum to give 85% yield of a colorless, viscous oil (II) at bp 93 ∿ 95°/0.01 mmHg; the analysis and the mass spectrum showed a chemical formula of $C_{14}H_{21}N_4Cl$ (M.W. 280). It seems noteworthy that the chlorine was bound to skeletal carbon instead of being involved as a part of the hydrochloride in the reaction product of alkylynamine with hydrogen chloride (2), which was demonstrated by the mass spectrum (no removal of hydrogen chloride) and the chemical evidence (no change on the treatment with aqueous alkali under cooling). Characteristic spectral data of II are given in Table 1.

Similar reaction in the presence of a small amount of water led to the exclusive formation of N-diethylcyanoacetamide (III).

II was dissolved in methanol and hydrogenated with atmospheric pressure of hydrogen in the presence of a catalytic amount of palladium on charcoal at room temperature. The worked up product (IV) was a colorless crystal of mp 154 ∿ 156° (from chloroform-ether) in 80% yield; it showed a chemical formula $C_{14}H_{22}N_4 \cdot HCl$ (salt form) on the basis of the analysis and the mass spectrum. Some characteristic spectral data are given in Table 1.

An ethanolic solution of II was refluxed with potassium hydroxide for 11 hr and the worked up product was a colorless oil, which was purified by silica-gel chromatography to give compound V; it showed a chemical formula of $C_{16}H_{28}N_4O$ on the basis of the analysis and the mass spectrum. The other spectral features are given in Table 1.

From the spectral similarities in Table 1, compounds II, IV and V are concluded to have common structure either of cyclobutene-ring or the ring-opened butadiene structure (2). It seems practically impossible to discriminate these two structures from the spectral data (2,3,4,5), but the presence of two methine protons in a cis-configuration (J=7.8 c.p.s.) in the NMR spectrum of IV (Table 1) let us conclude that all II, IV and V should have cyclobutene structure. The mechanism for the formation of such a cyclobutene ring system from I and hydrogen chloride might be explained by the initial protonation of I to form an electrophilic intermediate (VI) which reacted with nucleophilic I to give an intermediate (VII). The mechanism so far is similar to that for the reaction of alkynylamine with hydrogen chloride (2). This intermediate VII was readily attacked by chlorine ion because of the presence of strongly negative cyano group and subsequent intramolecular cyclization afforded a product II. Addition of hydroxide ion to VI led to the formation of III. These are visualized in the following scheme.

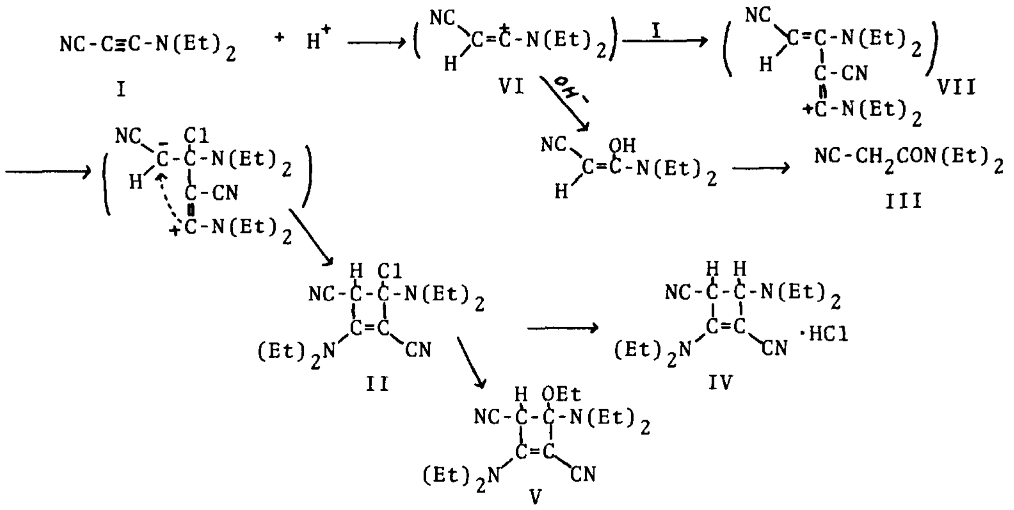

Table 1. Spectral Data of II, IV and V

	IR $(cm^{-1})^*$	UV (EtOH) mμ (ε)	NMR $(CDCl_3)$ τ
II	2220 (CN) 1555 v.s.** 1545	336 (9.91 x 10^3)# 256 (3.34 x 10^4) 212 (2.39 x 10^4)	8.74 t (12 H) 6.44 q (8 H) 3.90 s (1 H)
IV	3100∿2660 (-N·HCl) 2220 (CN) 1638 1581	310 (7.73 x 10^3)# 258 (4.02 x 10^4)	8.62 t (12 H) 6.27 q (4 H) 6.16 q (4 H) 3.47 d (1 H) } J=7.8 c.p.s. 2.02 d (1 H) } -4.58 ∿ -3.50 (1 H)
V	2220 (CN) ** 1564 v.s.	318 (1.35 x 10^4)# 256 (4.02 x 10^4) 217 (2.98 x 10^4)	8.78 } 8.73 } (15 H) 8.66 } 6.58 } (8 H) 6.39 } 5.70 (2 H) 4.51 s (1 H)

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* IR spectra were taken in chloroform solution for II and V and as a KBr pellet for IV.

** Strong IR-absorption at 1600±10 cm^{-1} is a characteristic in the cyano-ynamines, which might be atributable to polarized $-\bar{C}=\overset{+}{C}=N$ linkage (3).

\# The bathochromic shift compared with cyclobutanecyanine(290 cm^{-1}) suggests strong resonance-contribution of nitrile group to the cyclobutene ring, which causes the ring stabilization.

The facile formation of such a cyclobutene ring system with better yields and relatively higher stability of the ring-system compared with the similar reactions of methyl and phenylynamines with hydrogen chloride (2,5) might provide another characteristic feature in the reactivity of the cyanoynamine series in addition to the previous paper (3).

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