# Synthetic Studies Starting from β-Cyanopropionaldehyde. VI.[*1] The Synthesis of α-Cyanomethylacrolein

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(Received March 22, 1968)

As a part of synthetic studies starting from β-cyanopropionaldehyde (β-CPA) (I), the synthesis of a new vinyl compound, α-cyanomethylacrolein (VI) containing an aldehyde group and a nitrile group, will be presented in this paper. Two synthetic methods illustrated in Fig. 1 have been used.

The reaction of the diethyl acetal of β-CPA (II) with acetyl chloride caused an exchange of ethoxy group for chlorine leading to obtain α-ethoxy-γ-cyanopropyl chloride (III). This reaction was carried out at room temperature, but the reaction was difficult to control and a large amount of tar was formed above 60°C. Treatment of this chloride (III) in dry diethyl ether with an excess of anhydrous pyridine gave ethyl γ-cyanopropenyl ether (IV), which was also obtained by heating II with phthalic anhydride with loss of ethyl alcohol from II. As the boiling point of this product was not so different from that of II, several times of fractional distillation were required. When dibutyl acetal was used in place of II, the corresponding butyl derivative was obtained. A reaction of IV with diethyl formal in the presence of boron trifluoride etherate as a catalyst was carried out, and the reaction mixture obtained was directly hydrolyzed with hydrochloric acid to give α-cyanomethylacrolein (VI). In these successive reactions, V was regarded as an intermediate,1) but it was not really isolated.

Some examples of the reaction of acetals with vinyl ethers were reported by Hoaglin,1) but formaldehyde acetal was not used for this reaction. As stated above, however, it was found that formaldehyde diethyl acetal undergoes the same reaction with vinyl ether as diethyl acetal of other aldehydes containing more than two carbon atoms does.

The IR spectrum of the product (VI) showed the characteristic absorptions of unconjugated nitrile at 2250 cm$^{-1}$, of α,β-unsaturated aldehyde at 1693 cm$^{-1}$ and of the carbon-carbon double bond at 1640 cm$^{-1}$. Moreover, the structure of VI was confirmed by the NMR spectrum, as illustrated in Fig. 2.

On the other hand, the labile hydrogen at the α-position of the aldehyde group of β-CPA was readily removed by condensation with both formaldehyde and an amine as in the Mannich reaction. When morpholine or piperidine was used as the amine component, a Mannich base was obtained and subsequent thermal decomposition of the base gave VI. When dimethylamine was used, however, no Mannich base was obtained.

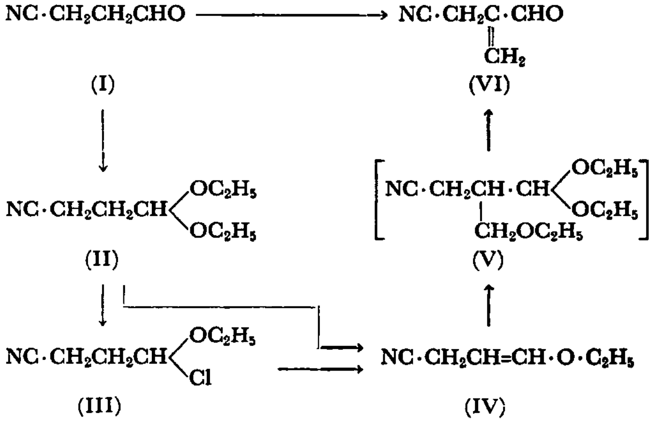

Fig. 1.

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[*1] Part V: S. Motoki, S. Satsumabayashi and F. Minemura, *J. Org. Chem.* **33**, 3667 (1968).

1) R. I. Hoaglin and D. H. Hirsh, *J. Am. Chem. Soc.*, **71**, 3468 (1949).

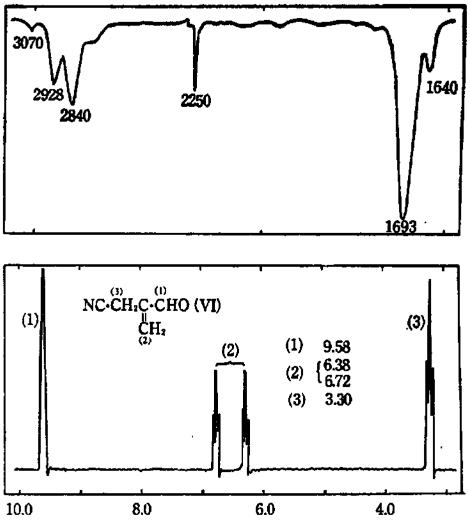

Fig. 2. The IR and NMR spectra of VI.
A Varian A-60 NMR spectrometer was employed using tetramethylsilane as an internal standard.

## Experimental

**α-Ethoxy-γ-cyanopropyl Chloride (III).** To 31.4 g (0.2 mol) of β-CPA diethyl acetal, 23.6 g (0.3 mol) of acetyl chloride was added slowly at about 20°C, and the mixture was stirred for 5 hr at room temperature. By fractional distillation, 23.0 g of III was obtained, bp 68—70°C/3 mmHg, yield 78.0%. Found: C, 48.65; H, 7.07; N, 9.73%. Calcd for $C_6H_{10}ONCl$: C, 48.82; H, 6.83; N, 9.49%.

**Ethyl γ-Cyanopropenyl Ether (IV).** Under an anhydrous condition, 29.5 g (0.2 mol) of III was added slowly to 39.5 g (0.5 mol) of pyridine at room temperature. After the solution was stirred for 6 hr, the reaction mixture was extracted with ether, washed with water and dried. Distillation of the extract gave 9.4 g of IV, bp 60—61°C/4 mmHg, yield 42.3%. Found: C, 64.92; H, 8.33; N, 12.74%. Calcd for $C_6H_9ON$: C, 64.84; H, 8.16; N, 12.60%.

A mixture of 157 g (1 mol) of II and 177.6 g (1.2 mol) of phthalic anhydride was heated at 150°C for 8 hr, and filtered. The filtrate was then distilled and the fraction boiling at 55—75°C/4 mmHg was collected. When this fraction was redistilled two more times, 31.4 g of IV was obtained, bp 60—62°C/4 mmHg, yield 28.5%. Found: C, 64.55; H, 8.11; N, 12.89%. Calcd for $C_6H_9ON$: C, 64.84; H, 8.16; N, 12.60%.

Similarly, 26.8 g of *n*-butyl γ-cyanopropenyl ether was obtained from 106.5 g (0.5 mol) of β-CPA dibutyl acetal, bp 83—85°C/4 mmHg, yield 38.5%. Found: C, 68.81; H, 9.60; N, 10.14%. Calcd for $C_8H_{13}ON$: C, 69.03; H, 9.41; N, 10.06%.

**α-Cyanomethylacrolein (VI) from IV.** A mixture of 22.2 g (0.2 mol) of IV and 31.2 g (0.3 mol) of diethyl formal was stirred. To this mixture was added 1.0 g of boron trifluoride etherate in 10 m*l* of diethyl ether, with the internal temperature kept at about 20°C. After 10 hours' stirring, the catalyst was neutralized with good agitation by 4 g of anhydrous sodium carbonate during a period of 4 hr. The reaction mixture thus obtained was refluxed with 100 m*l* of 5% hydrochloric acid for 8 hr. The product was extracted with ether, washed with water and dried. Distillation gave 3.5 g of VI, bp 96—98°C/20 mmHg, yield 18.4%. Found: C, 63.02; H, 5.25; N, 14.61%. Calcd for $C_5H_5ON$: C, 63.15; H, 5.30; N, 14.73%.

**α-Cyanomethylacrolein (VI) from I.** Into a solution of 41.5 g (0.5 mol) of β-CPA (I) dissolved in 50 m*l* of water, a solution of 61.8 g (0.5 mol) of morpholine hydrochloride and 50 g of 37% formaline was added over a two-hours' period, the temperature being maintained at about 65°C. After another 8 hours' stirring, the solution was neutralized with potassium carbonate, extracted with chloroform and the extract was dried. Dry hydrogen chloride was run into the extract, then the yellowish white Mannich base was precipitated as its hydrochloride. This crude Mannich base was placed in a Claisen flask and heated gently for half an hour using an oil bath, the temperature of which was maintained at about 150°C. At the end of this period, the system was placed under a reduced pressure of about 20 mmHg. The fraction which boiled at 70—110°C/20 mmHg was collected, washed with water, extracted with ether and the extract was dried. After redistillation, 7.5 g of VI was obtained, bp 96—97°C/21 mmHg, yield 15.8% based on I. Found: C, 62.96; H, 5.47; N, 14.75%. Calcd for $C_5H_5ON$: C, 63.15; H, 5.30; N, 14.73%.

Mannich reaction was also carried out with piperidine instead of morpholine. Yield 18.0%.

The authors wish to thank Professor Yojiro Tsuzuki for his helfpul advice and encouragement.