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Synthetic Studies starting from β-Cyanopropionaldehyde. III.* The Synthesis of β-Cyanoacrolein

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β-Cyanopropionaldehyde dimethyl acetal was brominated in the presence of calcium carbonate to give α-bromo-β-cyanopropionaldehyde dimethyl acetal. This was then dehydrobrominated with 10% alcoholic potash at −5 to 0°C, β-cyanoacrolein dimethyl acetal was thus obtained in a high yield. Free aldehyde of a light green liquid was given by the hydrolysis of the acetal. A similar procedure using α-chloro-β-cyanopropionaldehyde dimethyl acetal was also examined. On the other hand, β-cyanoacrolein was prepared by the direct dehydrogenation of β-cyanopropionaldehyde with selenium dioxide.

In the present paper, we wish to report the synthesis of β-cyanoacrolein (VI) starting from β-cyanopropionaldehyde (β-CPA) (I) through the process illustrated in Fig. 1.

The synthesis of VI by the oxidation of β-methyl acrylonitrile with selenium dioxide has been reported by Rambaud and others.[1] However, β-cyanoacrolein was not isolated by them, and the 2, 4-dinitrophenylhydrazone and semicarbazone of VI gave low *N*-analytical values.

In the present study, two methods of the synthesis of VI will be described. First, β-cyanopropionaldehyde dimethyl acetal (II) was brominated in carbon tetrachloride. Calcium carbonate had previously been added to the solution in order to remove any hydrogen bromide produced in this

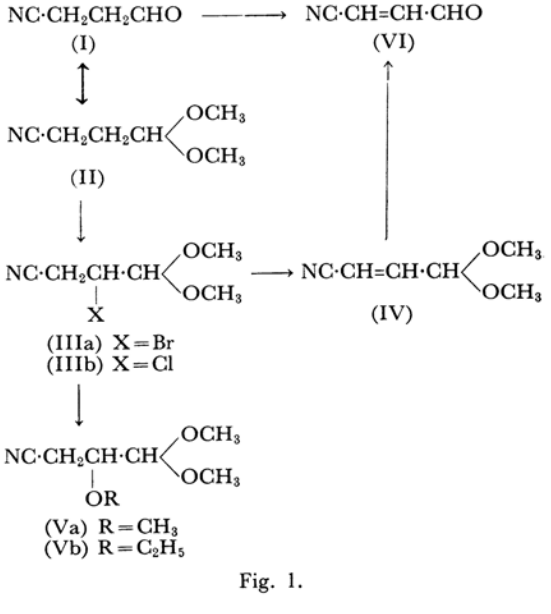

Fig. 1.

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* Part II: S. Motoki, S. Satsumabayashi and H. Kusano, This Bulletin, **38**, 922 (1965).

[1] R. Rambaud and M. Vessiere, *Bull. soc. chim. France*, **1961**, 1567.

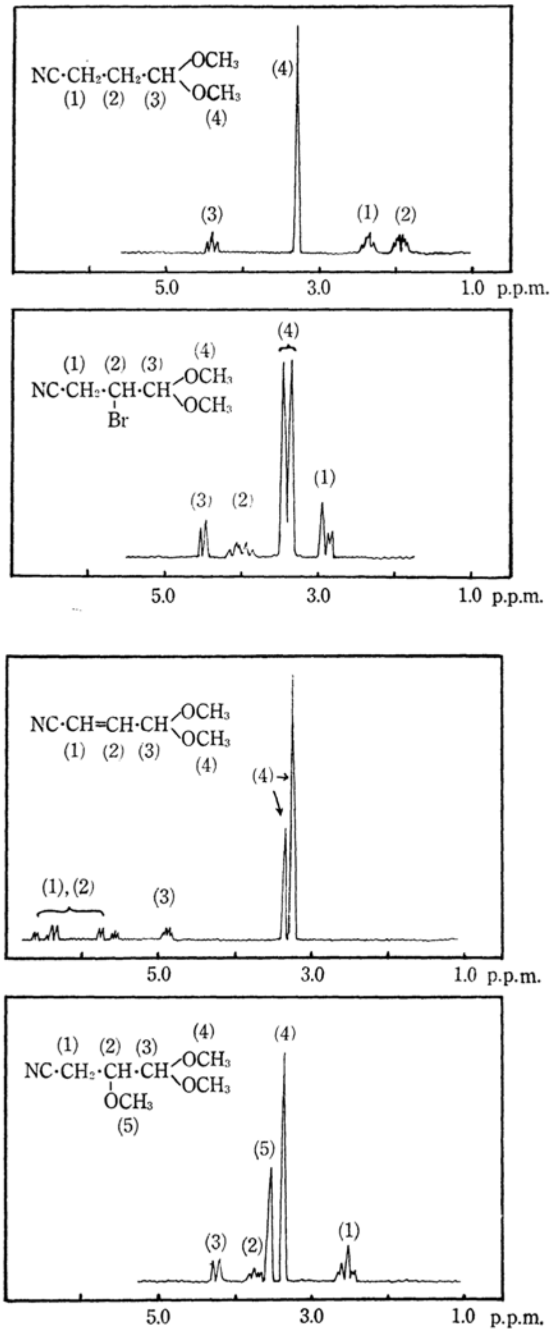

Fig. 2. A varian A-60 NMR spectrometer operating at 60 Mc./sec. was employed for all measurements.

reaction.[2] It was found, by means of a study of the NMR spectra (Fig. 2), that the bromine was introduced into the α-position of the aldehyde group; that is, the absorption of the protons of α-methylene group disappeared and the triplet of the aldehyde group changed to a doublet. Thus, the product was presumed to be α-bromo-β-cyanopropionaldehyde dimethyl acetal (IIIa). When IIIa was dehydrobrominated with 10% methanolic potash at −5 to 0°C, β-cyanoacrolein dimethyl acetal (IV) was obtained in high yield. The analytical values of the product were in accord with the calculated values of IV, and the infrared spectra showed the characteristic absorptions of methine at 3070 $\mathrm{cm^{-1}}$ and 3000 $\mathrm{cm^{-1}}$ and of carbon-carbon double bond at 1639 $\mathrm{cm^{-1}}$. Moreover, in the NMR spectrum, all the absorptions of methylene groups disappeared, while new absorptions of methine groups appeared.

In the dehydrobromination, the main product was α-methoxy-β-cyanopropionaldehyde dimethyl acetal (Va in Table I) when the temperature was elevated or when the concentration of alkali was increased. Under the same reaction conditions, the corresponding ethoxy derivative (Vb in Table I) was obtained in an ethanol solvent.

The dimethyl acetal (IV) was easily hydrolyzed by dilute hydrochloric acid to β-cyanoacrolein (VI) in a nearly quantitative yield. Though VI is a light green liquid which is a comparatively stable compound, it gradually becomes brown upon standing at room temperature for several days.

Halogenation was also carried out with chlorine instead of bromine. Chlorine gas was blown into the chloroform solution of β-cyanopropionaldehyde dimethyl acetal (II) in the presence of calcium carbonate. However, in this case, the chlorinated product did not show a definite boiling point. Therefore, the fraction (which had a b. p. of 88—93°C/5 mmHg) was collected; dehydrochlorination by alcoholic potash carried out in a similar manner gave a product, boiling at 65—66°C/6 mmHg, which was identified as IV. However, the yield was much less than with bromine.

Chlorination by sulfuryl chloride gave nearly the same results as when chlorine was used, and no single product could be obtained.

In the second method of the synthesis of VI, the direct dehydrogenation of β-CPA was examined. When β-CPA was allowed to react with selenium dioxide in a mixed solvent of water and dioxane, β-cyanoacrolein (VI) was obtained

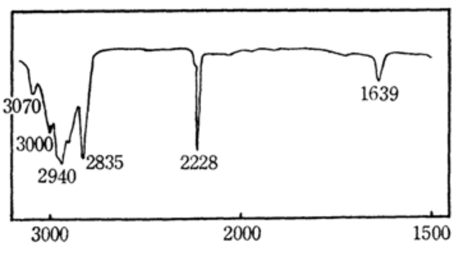

Fig. 3. The IR spectrum of β-cyanoacrolein dimethyl acetal.

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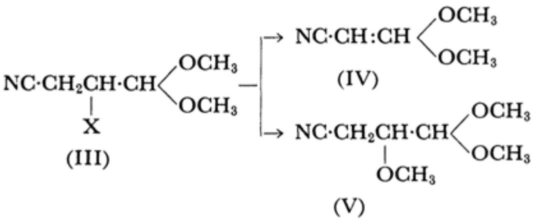
[2] W. H. Hartung and H. Adkins, *J. Am. Chem. Soc.*, **49**, 2517 (1927).

in a relatively good yield. As may be seen in Table II, the yield was highest when the proportion of dioxane to water was 100 : 20; the yield decreased as the amount of dioxane or of water increased.

Table I



Concn. of alkali, %	Temp., °C	Product	Yield, %
20	25—30	V	66.2
20	−5— 0	V	63.8
10	25—30	IV	68.0
10	−5— 0	IV	78.5
15	25—30	IV+V	29.1+40.9
15	−5— 0	IV+V	55.3+19.4

Table II

$$\underset{\text{(I)}}{2NC\cdot CH_2CH_2CHO} + SeO_2 \xrightarrow[70°C]{} \underset{\text{(VI)}}{2NC\cdot CH{:}CH\cdot CHO} + Se + 2H_2O$$

Solvent Dioxane : Water	Molar ratio I : SeO_2	Yield %
100 : 10	2 : 1	15.3
100 : 20	2 : 1	29.1
100 : 50	2 : 1	19.1
0 : 50	2 : 1	5.1
100 : 20	2 : 1.5	49.4

Experimental

α-Bromo-β-cyanopropionaldehyde Dimethyl Acetal (IIIa). — In a three-necked 1000 ml. flask, 65.5 g. (0.5 mol.) of II was dissolved in 300 g. of carbon tetrachloride, and then 30 g. (0.3 mol.) of powdered calcium carbonate was added. After the solution had been heated to boiling, vigorous stirring was started and 80 g. of bromine in 100 g. of carbon tetrachloride was added drop by drop, to the refluxing solution over approximately a two-hour period. After another one hour's stirring, the mixture was filtered and the filtrate was washed with water several times. The fractional distillation of the carbon tetrachloride solution gave 52.5 g. of pure IIIa; b. p. 87°C/2 mmHg; yield, 50.5%.

Found: C, 34.44; H, 4.97; N, 6.70; Br, 38.90. Calcd. for $C_6H_{10}O_2NBr$: C, 34.63; H, 4.87; N, 6.73; Br, 38.40%.

Care must be taken to stop the distillation when the contents of the flask become viscous and the temperature of the distillate begins to rise; otherwise, a vigorous decomposition of the contents will occur. The bromo-acetal thus obtained turned yellow or dark brown after standing at room temperature for several days.

β-Cyanoacrolein Dimethyl Acetal (IV).—The dehydrobromination of α-bromo-β-cyanopropionaldehyde dimethyl acetal was carried out with alcoholic potash in the usual manner. β-Cyanoacrolein dimethyl acetal, b. p. 62°C/4 mmHg.

Found: C, 56.40; H, 7.28; N, 11.14. Calcd. for $C_6H_9O_2N$: C, 56.68; H, 7.14; N, 11.02%.

α-Alkoxy-β-cyanopropionaldehyde dimethyl acetal was formed as a by-product. α-Methoxy-β-cyanopropionaldehyde dimethyl acetal (Va), b. p. 92°C/5 mmHg.

Found: C, 52.57; H, 8.37; N, 8.94. Calcd. for $C_7H_{13}O_3N$: C, 52.81; H, 8.23; N, 8.80%.

α-Ethoxy-β-cyanopropionaldehyde dimethyl acetal (Vb), b. p. 98°C/5 mmHg.

Found: C, 55.25; H, 8.89; N, 8.21. Calcd. for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09%.

The results are summarized in Table I.

The hydrolysis of the acetal (IV) with dilute hydrochloric acid gave β-cyanoacrolein (VI), b. p. 52°C/5 mmHg; yiled ca. 90%.

Found: C, 58.99; H, 3.92; N, 17.50. Calcd. for C_4H_3ON: C, 59.26; H, 3.73; N, 17.28%.

2, 4-Dinitrophenylhydrazone: m. p. 176°C.

β-Cyanoacrolein (VI) (The Dehydrogenation of β-CPA).—Into a solution of 16.6 g. (0.2 mol.) of β-CPA in 30 ml. of dioxane there was stirred a solution of 11.1 g. (0.1 mol.) of selenium dioxide in 20 ml. of water and 70 ml. of dioxane over a two-hour period, with the temperature maintained at about 70°C. After the solution had been refluxed for another three hours, the reaction mixture was extracted with ether, washed with water, and dried over anhydrous sodium sulfate. By fractional distillation, 8.0 g. of VI was obtained, b. p. 52—53°C/5 mmHg; yield 29.1%.

Found: C, 59.17; H, 3.91; N, 17.21. Calcd. for C_4H_3ON: C, 59.26; H, 3.73; N, 17.28%.

The yield of VI was raised to 49.4% when an excess of selenium dioxide was used.

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