



Table 1. Yields and Physical Properties of L- $\alpha$ -Aminonitrile Hydrochlorides

| $\alpha$ -Aminonitrile·HCl | Mp°C(decomp.) | Yield(%) <sup>a</sup> | $[\alpha]_D^{25}$ (deg.)         | $\nu_{C\equiv N}$ (cm <sup>-1</sup> ) <sup>b</sup> | Rf <sup>c</sup>         |
|----------------------------|---------------|-----------------------|----------------------------------|--|-------------------------|
| IIIa                       | 156-158       | 13                    | -15.3(c 0.708, H <sub>2</sub> O) | 2260   | 0.55(0.49) <sup>d</sup> |
| IIIb                       | 173-176       | 76                    | +13.5(c 0.487, H <sub>2</sub> O) | 2260   | 0.86(0.69) <sup>d</sup> |
| IIIc                       | 176-178       | 30                    | +5.8(c 0.790, H <sub>2</sub> O)  | 2250   | 0.84(0.70) <sup>d</sup> |

a) Calculated on the basis of I. b) Measured as KBr tablet. c) Paper chromatography was carried out on Toyo Filter Paper No. 50 using the solvent system of n-BuOH-AcOH-H<sub>2</sub>O(4:1:2 v/v). d) R<sub>f</sub> value of the corresponding amide.

Retention of configuration in the L- $\alpha$ -aminonitriles(IIIa-c) was examined by a gas chromatographic method.<sup>8)</sup> These compounds were transformed into the amino acid methyl esters by treatment with 9N HCl-methanol, followed by addition of a small amount of water. These methyl esters were transesterified in (+)-2-butanol saturated with anhydrous HCl to give the (+)-2-butyl esters, which were then trifluoroacetylated with (CF<sub>3</sub>CO)<sub>2</sub>O. The N-trifluoroacetyl(TFA)-amino acid (+)-2-butyl esters obtained were analyzed by gas chromatography on the capillary column coated with LB 550X. The N-TFA-DL and L-amino acid (+)-2-butyl esters which were derivatized from DL and L-amino acids(alanine, leucine and phenylalanine) respectively, were also analyzed.

Table 2. Steric Purity of L- $\alpha$ -Aminonitriles

| $\alpha$ -Aminonitrile | Retention time(min.)          |       | Apparent      | Apparent steric purity          |
|------------------------|-------------------------------|-------|---------------|---------------------------------|
|                        | of diastereomers <sup>a</sup> |       | steric purity | of standard sample <sup>b</sup> |
|                        | L-(-)                         | L-(+) | L/(D+L)       | L/(D+L)                         |
| IIIa                   | 12.2                          | 13.0  | 0.93          | 0.93(L-alanine)                 |
| IIIb                   | 21.8                          | 22.8  | 0.93          | 0.93(L-leucine)                 |
| IIIc                   | 64.0                          | 64.8  | 0.94          | 0.92(L-phenylalanine)           |

a) Gas chromatography were carried out with a Hitachi gas chromatograph 063 provided with a flame ionization detector. Column: 150 ftx0.01 in. stainless steel capillary column(LB 550X), temperature 100-170°C 1°C/min; carrier gas He, 4.1Kg/cm<sup>2</sup>; H<sub>2</sub>, 1.5Kg/cm<sup>2</sup>. b) The standard samples were prepared by derivatization of commercial L-amino acids(Guaranteed Reagent).

The diastereomers of N-TFA-DL-amino acid (+)-2-butyl esters had almost identical detector response. Since the (+)-2-butanol<sup>9)</sup> used in this work contained a small amount of (-)-isomer, the N-TFA-amino acid (+)-2-butyl ester derivatized from each L-amino acid was found to contain a small amount of L-(-) diastereomer. The N-TFA-amino acid (+)-2-butyl ester derivatized from each L- $\alpha$ -aminonitrile, also contained a small amount of L-(-) diastereomer. The gas chromatographic data are summarized in Table 2, which shows that the apparent steric purity of each L- $\alpha$ -aminonitrile is almost identical with that of the standard L-amino acid. This indicates that the optical purity of the L- $\alpha$ -aminonitriles(IIIa-c) is well retained. Though their yields are rather poor, the method described above may be useful for the synthesis of enantiomeric  $\alpha$ -aminonitriles.

## REFERENCES

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