AMINATION OF 7-CHLOROHEPTANENITRILE - PRODUCT
OF THE TELOMERIZATION OF ETHYLENE
WITH CYANOCYN CHLORIDE

(UDC 542.958.3)

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7,
pp. 1233-1236, July, 1964
Original article submitted November 26, 1962

ω-Chloroalkanenitriles have become widely accessible substances as a result of the detailed development of
the telomerization of ethylene with cyanogen chloride [1], which goes in accordance with the scheme:

\[
\text{ClCN} + n \text{CH}_2 = \text{CH} \rightarrow \text{Cl} (\text{CH}_2\text{CH}_2)_n \text{CN}.
\]

The reactions of these telomers have received little study. Like \(\alpha,\alpha,\alpha,\omega\)-tetrachloroalkanes, products of the
telomerization of ethylene with carbon tetrachloride, \(\omega\)-chloroalkanenitriles can be applied in the synthesis of vari-
ous \(\omega\)-substituted carboxylic acids. Recently, patents have been taken for the preparation of \(\omega\)-amino carboxylic
acids from \(\omega\)-chloroalkanenitriles [2]. Apart from this, \(\omega\)-chloroalkanenitriles may have special fields of application,
e.g., by the reduction of the nitrile group it is possible to pass to \(\omega\)-substituted amines.

In this work we studied the reactions of 7-chloroheptanenitrile with ammonia and with methylamine and also
further transformations of the \(\omega\)-cyanoalkylamines obtained. Ammonolysis was effected both by the action of solu-
tions of ammonia in water and alcohol and also by the action of liquid ammonia. The ammonolysis experiments are
summarized in the table, from which it will be seen that the composition and proportions of the products depend
greatly on the reaction conditions. Thus, when the reaction of 7-chloroheptanenitrile with ammonia was carried out
in water, mono-, bis-, and tris-6-cyanoheptylamines [7-amino-, 7,7'-iminodi-, and 7,7',7''-nitrilotri-heptanenitriles]
were isolated, but with alcoholic ammonia solution and with liquid ammonia the triply alkylated product was not
formed. As usual, the use of a large excess of ammonia favors the preferential formation of the primary amine. The
highest yield of primary amine was obtained in ammonolysis with excess of liquid ammonia.

The reaction of 7-chloroheptanenitrile was carried out with an alcoholic solution of methylamine under con-
tions favoring the formation of tertiary amine. However, together with 7,7''-(methylimino)diheptanenitrile, the
yield of which was 50%, we obtained a 34.9% yield of 7-(methylamino)heptanenitrile. By the reduction of 7,7''-(meth-
ylimino)diheptanenitrile with lithium aluminum hydride we obtained a satisfactory yield of 7,7''-(methylimino)bis-
heptylamine.

All \(\omega\)-aminoalkanenitriles synthesized were hydrolyzed quantitatively with concentrated hydrochloric acid into
the corresponding amino carboxylic acids.

EXPERIMENTAL

Ammonolysis of 7-Chloroheptanenitrile. With Aqueous Ammonia: A mixture of 39.9 g of 7-chloroheptanenit-
trile and 400 ml of 25% ammonia solution was heated in an autoclave for 5 h at 100°. The reaction mixture was ex-
tracted with ether (to remove unchanged chloronitrile), concentrated under reduced pressure, and treated with 40%
NaOH solution. The amines liberated were extracted with ether several times, the extract was dried with anhydrous
sodium sulfate, ether was driven off, and the residue was vacuum-distilled. We obtained 10.7 g (30.8%) of 7-amino-
heptanenitrile, b.p. 93-100° (3 mm) and \(\eta_{D}^{20}\) 1.4465; 7.3 g (22.5%) of 7,7''-iminodiheptanenitrile, b.p. 200-225° (3
mm) and \(\eta_{D}^{20}\) 1.4680. The substances were redistilled and then had the constants given below.
Cl\((\text{CH}_2)\text{CN}\) obtained, %

<table>
<thead>
<tr>
<th>Cl((\text{CH}_2)\text{CN}), g</th>
<th>Solvent, ml</th>
<th>NH(_3) content, g</th>
<th>Cl((\text{CH}_2)\text{CN}) solvent g/ml</th>
<th>React. time, h</th>
<th>obtained, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.9</td>
<td>H(_2)O</td>
<td>400</td>
<td>90</td>
<td>1:10</td>
<td>5.0</td>
</tr>
<tr>
<td>20.0</td>
<td>H(_2)O</td>
<td>400</td>
<td>90</td>
<td>1:20</td>
<td>4.0</td>
</tr>
<tr>
<td>40.0</td>
<td>H(_2)O</td>
<td>400</td>
<td>90</td>
<td>1:10</td>
<td>4.5</td>
</tr>
<tr>
<td>29.1</td>
<td>C(_2)H(_4)OH</td>
<td>120</td>
<td>20</td>
<td>1:4</td>
<td>5.0</td>
</tr>
<tr>
<td>10.0</td>
<td>C(_2)H(_4)OH</td>
<td>150</td>
<td>20</td>
<td>1:15</td>
<td>4.0</td>
</tr>
<tr>
<td>14.5</td>
<td>abs. C(_2)H(_4)OH</td>
<td>120</td>
<td>20</td>
<td>1:9</td>
<td>4.5</td>
</tr>
<tr>
<td>55.2</td>
<td>NH(_3)</td>
<td>600</td>
<td>460</td>
<td>1:10</td>
<td>2.0</td>
</tr>
<tr>
<td>40.3</td>
<td>NH(_3)</td>
<td>600</td>
<td>460</td>
<td>1:15</td>
<td>2.0</td>
</tr>
<tr>
<td>20.0</td>
<td>NH(_3)</td>
<td>600</td>
<td>460</td>
<td>1:30</td>
<td>2.0</td>
</tr>
<tr>
<td>20.2</td>
<td>NH(_3)</td>
<td>600</td>
<td>460</td>
<td>1:30</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\* R = \((\text{CH}_2)\text{CN}\).

† With addition of four molecular proportions of NH\(_4\)Cl.

7-Aminoheptanenitrile: b.p. 93° (3 mm); n\(_D\)\(^{20}\) 1.4482; d\(_4\)\(^{20}\) 0.8998; found MR 37.56; calculated MR 37.77. The literature [3] gives: b.p. 113-114° (9 mm); n\(_D\)\(^{20}\) 1.4510; d\(_4\)\(^{20}\) 0.8972. Hydrochloride, m.p. 102°. Found: N 17.18, 17.20%.

7-Aminoheptanenitrile was hydrolyzed quantitatively with concentrated hydrochloric acid to 7-aminoheptanoic acid, which was isolated from solution with the aid of the cation exchanger KU-2 [4] and had m.p. 193-194°. The literature [5] gives m.p. 195°.

7,7'-Iminodiheptanenitrile: b.p. 209-210° (3 mm); n\(_D\)\(^{20}\) 1.4620; d\(_4\)\(^{20}\) 0.9262. Found: C 71.56, 71.52; H 10.84, 10.76; N 18.09, 17.89%; MR 69.86. C\(_{14}\)H\(_{25}\)N\(_3\). Calculated: C 71.44; H 10.71; N 17.85%; MR 70.09. Hydrochloride, m.p. 136-137°. Found: N 15.74, 15.78%. C\(_{14}\)H\(_{26}\)ClN\(_3\). Calculated: N 15.46%. By the hydrolysis of this nitrile with concentrated hydrochloric acid we obtained a quantitative yield of 7,7'-iminodiheptanoic acid, m.p. 213-214°. The literature [6] gives m.p. 214°.

7,7',7''-Nitrilotriheptanenitrile: b.p. 267° (2 mm); n\(_D\)\(^{20}\) 1.4695; d\(_4\)\(^{20}\) 0.9425. Found: C 73.44, 73.38; H 10.53, 10.55; N 16.35, 16.41%; MR 101.90. C\(_{12}\)H\(_{16}\)N\(_4\). Calculated: C 73.20; H 10.53; N 16.26%; MR 102.57.

With Alcoholic Ammonia: A mixture of 29.1 g of 7-chloroheptanenitrile and 120 ml of ethanol containing 20 g of ammonia was heated in an autoclave for 5 h. Alcohol was driven off, and the reaction mixture was treated as in the preceding experiment. After fractionation we obtained 12.1 g (48.2%) of 7-aminoheptanenitrile, b.p. 101° (4 mm), and 8.0 g (34.3%) of 7,7'-iminodiheptanenitrile, b.p. 201° (2 mm).

With Liquid Ammonia: A mixture of 40.3 g of 7-chloroheptanenitrile and 600 ml of liquid ammonia was heated for 2 h at 100°. Ammonia was driven off, and the reaction mixture was diluted with water and treated as described above. We obtained 28.6 g (82.1%) of 7-aminoheptanenitrile, b.p. 96-99° (4 mm), and 2.15 g (6.6%) of 7,7'-iminodiheptanenitrile, b.p. 210-215° (4 mm).

Reaction of 7-Chloroheptanenitrile with Methylamine. A mixture of 40.3 g of 7-chloroheptanenitrile and 100 ml of alcohol containing 6.5 g of methylamine was heated for 5 h at 100°. Alcohol was driven off, and the reaction mixture was treated as described above. We obtained 12.3 g of the original chloro nitrile, 9.4 g (34.9% on the amount of the chloro nitrile that reacted) of 7-(methylamino)heptanenitrile [b.p. 86° (1 mm); n\(_D\)\(^{20}\) 1.4458; d\(_4\)\(^{20}\) 0.8691]. Found: C 68.34, 68.39; H 11.53, 11.49%; MR 42.52. C\(_{8}\)H\(_{15}\)N\(_2\). Calculated: C 68.52; H 11.50%; MR 42.56%. By the hydrolysis of this nitrile with concentrated hydrochloric acid and subsequent separation of the amino acid with the aid of a cation exchanger we obtained 7-(methylamino)heptanoic acid, m.p. 96-97° (from a mixture of alcohol and acetone). Found: C 54.16; 54.42; H 10.72; 10.88; N 8.05; 8.18%. C\(_{8}\)H\(_{17}\)NO\(_2\). Calculated: C 54.21; H 10.81; N 7.90%. By the hydrolysis of 7,7'- (methylamino)diheptanenitrile with concentrated hydrochloric acid and subsequent separation of the amino acid with the aid of a cation exchanger we obtained 7,7'-(methylamino)diheptanoic acid, m.p. 132-133°, undepressed by admixture of a known sample [5].