

1930) with an inflection at 272 $m\mu$ (ϵ 1670) and a shoulder at 285.5 $m\mu$ (ϵ 1160). The infrared spectrum of the material was similar to that of 1-(β -hydroxyethyl)-6-methoxy-1,2,3,4-tetrahydroisoquinoline, but had a number of additional absorption bands in the finger-print region. One gram of this material was chromatographed on 170 g. of Florisil which had been washed with methanol and air dried briefly to give a free-flowing powder (the Florisil contained about 35% methanol). Elution with benzene gave several fractions amounting to 0.49 g. which had ultraviolet spectra (λ_{\max} 271.5 and 278.5 $m\mu$) characteristic of the 8-methoxy isomer VI. Distillation of this material and crystallization of the distillate from hexane gave 0.27 g. of 1-(β -hydroxyethyl)-8-methoxy-1,2,3,4-tetrahydroisoquinoline (VI), m.p. 96–97°, $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 223 (ϵ 7200), 271 (ϵ 1600), and 278.5 $m\mu$ (ϵ 1700) with minima at 246 and 276 $m\mu$.

Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.50; H, 8.19; N, 6.98.

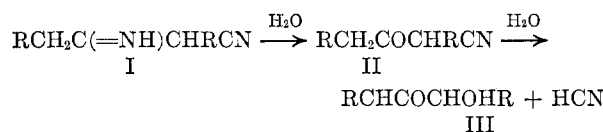
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The Decomposition of 11-Cyano-12-tricosanone

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Early investigations of the properties of low-molecular-weight dinitriles (I; diacetonitrile², R = H; dipropionitrile³, R = CH₃) have shown that upon boiling with water these substances slowly decompose with the formation of ammonia, hydrogen cyanide, and a substance which is easily oxidized by ammoniacal copper and silver solutions. It was postulated that the easily oxidizable material was an α -hydroxy ketone (ketol or acyloin) which was formed in the following manner:



In this Laboratory it has been observed that crystallized 11-cyano-12-tricosanone (II. R = C₁₀H₂₁) upon standing in air slowly evolves hydrogen cyanide leaving a liquid residue. Analysis of this residue by gas chromatography indicates that it is a mixture of equimolar amounts of undecanoic and dodecanoic acids. In an atmosphere of dry nitrogen the keto nitrile undergoes no change. Presumably moisture and oxygen are required to bring about the decomposition with formation of the mixture of acids although this has not been proved.

If 11-cyano-12-tricosanone were to decompose according to the reaction proposed above it would lead to the formation of 11-hydroxy-12-tricosanone (III. R = C₁₀H₂₁) which differs from the acyloin

13-hydroxy-12-tetracosanone (lauroin) by only one carbon atom. So far as we are aware the acyloins derived from higher fatty acids are not susceptible to decomposition upon exposure to the atmosphere. Mild oxidizing agents such as iodine in acetic acid⁴ or ferric chloride in acetic acid⁵ oxidize these compounds to the diketone. Strong oxidizing agents such as chromic oxide are required to effect cleavage to the fatty acid.⁵ We do not believe that the decomposition of the keto nitrile proceeds through the acyloin but do not have a reasonable alternative to offer.

EXPERIMENTAL

Dimeric lauronitrile. To 9.2 g. (0.2 g.-atom) of 50% sodium dispersion in xylene, in 200 ml. of dry ether was added over 0.5 hr., with stirring 45 g. (0.25 mole) of lauronitrile. The ether refluxed gently after a short induction period during the addition. When the exothermic reaction had subsided, the mixture was stirred and refluxed for 24 hr. The supernatant liquid was decanted from residual sodium into a separatory funnel. The sodium was destroyed with methanol and the alcoholic solution was added to the separatory funnel. The organic extracts were washed three times with water, dried over anhydrous sodium sulfate, the solvent removed, and the residue distilled to give 2.1 g. lauronitrile, b.p. 88–89°/0.25 mm.; 22.9 of dinitrile b.p. 220–240°/0.15 mm. and a significant residue. Redistillation of the dinitrile afforded 20.9 g. b.p. 208–212°/0.10 mm.

11-Cyano-12-tricosanone. A mixture of 5 g. of dinitrile, 100 ml. of 95% alcohol and 2 ml. of concd. hydrochloric acid was warmed until solution was effected, then chilled overnight in the icebox. The solid was filtered and dried under vacuum in a desiccator, m.p. 46–47°. The keto nitrile was stable in an atmosphere of dry nitrogen. Left standing open to the air, an odor of hydrogen cyanide was evolved and the material passed from solid through semisolid to liquid during 1 week. Gas chromatography of the liquid⁷ yielded two peaks of equal area, which were identical in position with those of a mixture of undecanoic and dodecanoic acids run under the same conditions. A sample sealed in an atmosphere of dry nitrogen underwent no change during a period of several years.

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(7) Through the courtesy of L. D. Metcalfe of this Laboratory. A phosphoric-acid-treated diethylene glycol-adipic acid polyester column was employed. Cf. L. D. Metcalfe, *Nature*, **188**, 142 (1960).

Preparation and Reduction of 3-Nitro-*p*-terphenyl

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Three of the four possible mononitro derivatives of *p*-terphenyl have been reported.^{1,2} The prepara-

(1) Address communications to this author.

(2) R. Holtzwarth, *J. prakt. Chem.*, **39**, 230 (1889).

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