1930) with an inflection at 272 mμ (ε 1670) and a shoulder at 285.5 mμ (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 mμ) 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°, $\lambda_{max}^{C_2H_5OH}$ 223 (ε 7200), 271 (ε 1600), and 278.5 mμ (ε 1700) with minima at 246 and 276 mμ.

Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.50; H, 8.19; N, 6.98.

Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Mass.

The Decomposition of 11-Cyano-12-tricosanone

C. C. Cochrane and H. J. Harwood[1]

Received December 1, 1960

Early investigations of the properties of low-molecular-weight dinitriles (I; diacetonitrile[2], R = H; dipropionitrile[3], R = CH_3) 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:

$$\underset{I}{RCH_2C(=NH)CHRCN} \xrightarrow{H_2O} \underset{II}{RCH_2COCHRCN} \xrightarrow{H_2O} \underset{III}{RCHCOCHOHR} + HCN$$

In this Laboratory it has been observed that crystallized 11-cyano-12-tricosanone (II. R = $C_{10}H_{21}$) 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 = $C_{10}H_{21}$) 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 acid[4] or ferric chloride in acetic acid[5] 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°[6] 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 liquid[7] 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.

Armour Industrial Chemical Co.
Chicago, Ill.

---

(1) Address communications to this author.

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

(3) E. von Meyer, *J. prakt. Chem.*, **39**, 188 (1889).

(4) V. L. Hansley, *J. Am. Chem. Soc.*, **57**, 2303 (1935).

(5) F. Bonquet and C. Paquot, *Bull. soc. chim. France*, 1165 (1948).

(6) M. R. McCorkle, *Iowa State Coll. J. Sci.*, **14**, 64 (1939); *Chem. Abstr.*, **34**, 6220 (1940), reports the m.p. 44-45°.

(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

Robert G. Splies

Received December 9, 1960

Three of the four possible mononitro derivatives of *p*-terphenyl have been reported.[1,2] The preparation of the remaining isomer, 3-nitro-*p*-terphenyl is reported in this study.

p-Terphenyl was nitrated using a modification of the method of Allen and Burness.[3] Slow addition of a dilute nitrating mixture apparently decreased dinitration and oxidation and gave an improved yield of the desired 4-nitro-*p*-terphenyl (I). Reduction of I was carried out in a high pressure bomb with a Raney nickel catalyst. The resulting 4 amino-*p*-terphenyl (II) was acetylated by treatment with acetic anhydride. The amide thus produced was nitrated directly without isolation, affording 3-nitro-4-acetylamino-*p*-terphenyl (III) in good yield. Hydrolysis of III in a warm dioxane solution was effected by aqueous potassium hydroxide. The brightly colored hydrolysis product proved to be the desired 3-nitro-4-amino-*p*-terphenyl (IV).[4]

A diazotized solution of IV was deaminated by refluxing with ethyl alcohol. The resulting 3-nitro-*p*-terphenyl (V), on oxidation, yielded the known 3-nitrodiphenyl-4′-carboxylic acid.[5] This is in accordance with the observation of France, Heilbron, and Hey[2] who reported that oxidation of I and 2-nitro-*p*-terphenyl yielded 4-nitrodiphenyl-4′-carboxylic acid and 2-nitrodiphenyl-4′-carboxylic acid respectively.

Catalytic hydrogenation of V gave 3-amino-*p*-terphenyl (VI). Acetylation of VI with acetic anhydride gave 3-acetylamino-*p*-terphenyl (VII).

EXPERIMENTAL[6]

4-Nitro-p-terphenyl (I). A suspension of 23.0 g. of *p*-terphenyl in 110 ml. refluxing glacial acetic acid was stirred vigorously while a mixture of 15 ml. of red fuming nitric acid and 25 ml. of acetic acid was added during 3.5 hr. After cooling in an ice bath the yellow solid was removed by filtration on a sintered glass funnel. The crude yield of I was 23.3 g. (85%). Recrystallization from nitromethane yielded I as a pale yellow solid, m.p. 210–211°.

4-Amino-p-terphenyl (II). A suspension of 11.0 g. of I in 130 ml. of dioxane was reduced by hydrogen under a cold pressure of 2200 p.s.i. The reduction was carried out with 1 teaspoon of Raney nickel catalyst in a 270-ml. void bomb. The reduction required 2 hr. at 90° after which the bomb was cooled and rinsed with a small amount of dioxane. The catalyst was removed by filtration and evaporation of the solvent under reduced pressure yielded 9.15 g. (94%) of II, m.p. 186–193°. Recrystallization from ethyl alcohol produced light tan crystals melting at 199.5–200.5°.

3-Nitro-4-acetylamino-p-terphenyl (III). A solution of 12.25 g. of II in 300 ml. of acetic acid was warmed and stirred while 10 ml. of acetic anhydride was added dropwise. Heating and stirring were continued for an hour. The reaction mixture was cooled to 70° and a mixture of 10 ml. of fuming nitric acid (*d.* 1.5) and 20 ml. of acetic acid was added during 20 min. Nitration was completed by warming to 90° for 0.5 hr. After chilling, the suspension was filtered and 13.24 g. (88%) of an orange solid was obtained, m.p. 202.5–205°. An analytical sample, m.p. 204.7–206°, was prepared by recrystallization from acetic acid.

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.27; H, 4.85; N, 8.42. Found: C, 72.38; H, 4.89; N, 8.42.

3-Nitro-p-terphenyl (V). A suspension of 3.24 g. of IV in 110 ml. of acetic acid was added to 30 ml. of cold, concentrated sulfuric acid containing 0.84 g. of sodium nitrite. The resulting deep red diazonium solution was added dropwise to a refluxing solution of 0.25 g. of copper sulfate and 20 ml. of water in 400 ml. of ethyl alcohol. The mixture, contained in a 1000-ml. flask, was stirred vigorously during the addition which required 2.5 hr. Refluxing and stirring were continued for 1 hr. after which the mixture was diluted with water. The solid was removed by filtration and dried by suction. After crystallization from petroleum ether (b.p. 110–120°) 2.69 g. (88%) of a light orange solid was obtained, m.p. 178–180°. Three recrystallizations from petroleum ether gave an analytical sample, m.p. 180–181.2°.

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.21; H, 4.83.

Oxidation of 3-nitro-p-terphenyl. The method of France, Heilbron, and Hey[2] was employed in the oxidation of 0.25 g. of V. The yield of 2-nitrodiphenyl-4′-carboxylic acid was 0.12 g., m.p. 308–312°. Two recrystallizations from absolute ethanol raised the m.p. to 312–312.3° (lit.,[5] m.p. 313–315.1°).

3-Amino-p-terphenyl (VI). A solution of 5.5 g. of V in 130 ml. of dioxane was reduced catalytically using the method reported above for the preparation of II. A cream-colored solid, 4.43 g. (91%), was obtained, m.p. 163–173°. Recrystallization from petroleum ether gave a solid, m.p. 181–181.9°.

Anal. Calcd. for $C_{18}H_{15}N$: C, 88.13; H, 6.16. Found: C, 87.68; H, 6.12.

3-Acetylamino-p-terphenyl (VII). A solution of 2.27 g. of VI in 150 ml. of refluxing benzene was stirred while 4 ml. of acetic anhydride and 5 drops of pyridine were added. After stirring at room temperature for 1 hr. the solvent was removed by warming on a steam bath in a current of air. The amide was crystallized from an alcohol-petroleum ether mixture. The fine, white needles weighed 2.08 g. (76%), m.p. 218–219°.

Anal. Calcd. for $C_{20}H_{17}ON$: C, 83.59; H, 5.97. Found. C, 83.36; H, 5.96.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MILWAUKEE 3, WIS.

---

(1) F. R. Bashford, *J. Chem. Soc.*, 1442 (1937).

(2) H. France, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 1364 (1938).

(3) C. F. H. Allen and D. M. Burness, *J. Org. Chem.*, **14**, 177 (1949).

(4) E. Sawicki and F. E. Ray, *J. Org. Chem.*, **19**, 1903 (1954).

(5) E. Berliner and E. A. Bloomers, *J. Am. Chem. Soc.*, **73**, 2479 (1951).

(6) Melting points are uncorrected.

α-Oximino Ketones. IX. The Synthesis of α,ω-Diamino Acids from Cyclic Ketones

ARTHUR F. FERRIS, FRANCIS E. GOULD, GRANNIS S. JOHNSON,[1] AND HUGO STANGE

Received December 12, 1960

In a series of publications from this laboratory several related routes for the conversion of cyclohexanone to DL-lysine have been described.[2–5]

---

(1) Present address: General Aniline and Film Corp., Linden, N. J.

(2) A. F. Ferris, F. E. Gould, G. S. Johnson, H. K. Latourette, and H. Stange, *Chem. & Ind.* (*London*), **1959**, 996.