Although the dehydration of methyl ethyl ketone cyanohydrin has been reported[2] to yield a mixture of isomers, it was believed that the pyrolysis of the acetate might afford a single product, α-ethacrylonitrile. However, pyrolysis of the acetate on pulverized clay plate at 420–480° afforded a mixture of the desired α-ethacrylonitrile and its isomer, α-methylcrotononitrile.[3]

The infrared spectrum of the main fraction of the pyrolysis product possessed bands at 11.90 and 9.60 μ. These bands were not present in the spectrum of a sample of α-ethacrylonitrile which was prepared by the dehydration of α-ethacrolein oxime.[4] Absorption near 11.90 μ has been attributed[5] to 1,1,2-trisubstituted ethylenes, hence the presence of α-methylcrotononitrile was indicated. Refractionation afforded a poor yield of pure α-ethacrylonitrile which was devoid of infrared absorption at 11.90 and 9.60 μ.

The α-methylcrotononitrile was not isolated, but its presence was also indicated by the isolation of tiglic acid from basic hydrolysis of a higher boiling fraction of the pyrolysate.

Only red viscous oils were obtained when attempts were made to polymerize the α-ethacrylonitrile by conventional procedures.[6]

Experimental

Methyl Ethyl Ketone Cyanohydrin.—This compound was obtained in 76% yield by the procedure described in "Organic Syntheses"[7] for the preparation of acetone cyanohydrin, b.p. 87–88° (17 mm.), $n^{24}\text{D}$ 1.4119.

Methyl Ethyl Ketone Cyanohydrin Acetate.—The cyanohydrin was acetylated by the slow addition (with stirring) to an equimolar quantity of acetic anhydride which contained a few drops of sulfuric acid. It was found necessary to neutralize the sulfuric acid with a few pellets of sodium hydroxide and distill the reaction mixture at reduced pressure as soon as the heat of reaction had subsided. The acetate was obtained in an 83% yield as a colorless oily liquid, b.p. 90–91° (16 mm.), $n^{24}\text{D}$ 1.4111.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.6; H, 7.9; N, 9.9. Found: C, 59.5; H, 7.9; N, 10.3.

Pyrolysis of Methyl Ethyl Ketone Cyanohydrin Acetate.—The pyrolysis chamber was constructed essentially as that described by J. Dvorak.[8] Pulverized clay plate was used as the packing and the temperature was measured by an iron–constantan thermocouple.

A slow stream of nitrogen was passed through the chamber and the acetate (800 g.) was pyrolyzed at 420–480° over a 12-hr. period. The pyrolysate was washed with excess aqueous sodium carbonate and distilled through a 30-cm. helix-packed column to obtain 321 g. (70%) of a mixture of α-ethacrylonitrile and α-methylcrotononitrile (b.p. 110–130°). This mixture was fractionally distilled through an electrically heated column (120 cm. × 20 mm.) which was packed with glass helices. Thirteen fractions were cut with a 7-1 reflux ratio and a constant rise in boiling point and refractive indices was observed. Infrared analyses of the main three cuts (total of 159.8 g., b.p. 111-114°) indicated contamination with α-methylcrotononitrile. This material (140 g.) was redistilled through an electrically heated, helix-packed column (120 cm. × 15 mm.). Employing a 15–1 reflux ratio, 68.0 g. of pure α-ethacrylonitrile was obtained, b.p. 111.9–112.9°, $n^{20}\text{D}$ 1.4118.

Anal. Calcd. for C_5H_7N: C, 74.0; H, 8.7; N, 17.3. Found: C, 73.9; H, 8.7; N, 17.3.

Hydrolysis of a 128–139° Pyrolysis Fraction.—The mixture (10 g.) was treated with a solution of 15 g. of sodium hydroxide, 20 cc. of water and 40 cc. of ethanol. Methanol was added to form a homogeneous solution and the reaction mixture was refluxed for 24 hr. The alcohol was removed by distillation and the residue was cautiously acidified with 50% sulfuric acid to yield a sharp smelling yellow liquid. The organic material was separated and the aqueous solution was extracted with 50 cc. of chloroform in small portions. Combination of the organic material and distillation of the chloroform yielded a yellow liquid which was dissolved in 250 cc. of boiling water. Ice cooling and scratching yielded 0.80 g. of tiglic acid, as white needles, m.p. 63–64° (uncor.), reported[9] m.p. 64.5°, neut. equiv. calcd. 100, found 103.

α-Ethacrylic acid is reported[10] as a liquid, m.p. $-16°$.

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[2] P. Bruylants, *et al.*, *Bull. sci. acad. roy. Belg.*, [5] **16,** 721 (1930).

[3] NOTE ADDED IN PROOF.—The referee has informed us that pyrolysis of this ester on glass helices affords a single pure product, α-ethacrylonitrile in 73% yield and has suggested that the formation of the two isomers which we have observed may be due to the acidic character of the clay plate. The selective pyrolysis is described in the Ph.D. thesis submitted in 1953 to the Graduate School of Wayne University by J. J. Hewitt

[4] C. S. Marvel, W. Miller and L. Chou, THIS JOURNAL, **72,** 5408 (1950).

[5] R. Rasmussen and R. Brattain, *J. Chem. Phys.*, **15**, 120, 130, 135 (1947).

[6] NOTE ADDED IN PROOF.—Since the receipt of this publication, our observation of the reluctance of α-ethacrylonitrile to readily homopolymerize has been corroborated by others who mention that this monomer would not readily polymerize with free radical or ionic initiators. This work is described by C. S. Marvel, *et al.*, *Ind. Eng. Chem.*, **46**, 804 (1954).

[7] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 7.

[8] J. Dvorak, *Collection Czech. Chem. Communs.*, **15**, 909 (1951).

[9] A. Michael and J. Ross, THIS JOURNAL, **55**, 3612 (1933).

[10] W. G. Young, R. T. Dillon and H. J. Lucas, **51**, 2532 (1929).

MONSANTO CHEMICAL COMPANY
PLASTICS DIVISION
SPRINGFIELD, MASS.

Preparation of Amines by Low Pressure Hydrogenation of Oximes

BY DON C. IFFLAND AND TEH-FU YEN

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Although the oximino group is reported to react with Raney nickel catalyst under milder conditions than most other groups,[1] the generality and usefulness of this conversion at low hydrogen pressures have not been established. Hydrogenation over Raney nickel at hydrogen pressures of 60 to 100 atmospheres has been widely employed[2–5] with numerous aliphatic and aromatic aldoximes and ketoximes. On the other hand, low pressure hydrogenation of oximes has been infrequently reported and limited to the hydrogenation of isobutyraldoxime and butanone oxime at 4 atmospheres by Campbell and co-workers[6] and 5-heptanone and 5-decanone oximes at one atmosphere by Buckley.[4]

In order to prepare authentic samples of aliphatic amines and to determine the general usefulness of low pressure hydrogenation, ten aliphatic ketoximes have been treated with hydrogen at two to three atmospheres pressure over Raney nickel catalyst. Primary amines were obtained in 43 to 85% yields and secondary amines were not encountered. In most cases, however, a neutral fraction was isolated and found to be the related ketone resulting from partial hydrolysis of the oxime.

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[1] C. F. Winans and H. Adkins, THIS JOURNAL, **5**, 2051 (1933).

[2] R. Paul, *Bull. soc. chim.*, [5] **4**, 1121 (1937).

[3] M. Harispe and J. Pernin, *ibid.*, 660 (1950).

[4] G. D. Buckley, *J. Chem. Soc.*, 1494 (1947).

[5] E. Rohrmann and H. A. Shonle, THIS JOURNAL, **66**, 1519 (1944).

[6] K. N. Campbell, A. R. Sommers, J. F. Kerwin and B. K. Campbell, *ibid.*, **68**, 1557 (1946).

TABLE I

YIELDS AND PHYSICAL CONSTANTS OF AMINES AND DERIVATIVES

Amine	Yield, %	B.p., °C.	n^{25}_{D}	M.p., °C.[a]	Derivative Nitrogen, % Calcd.	Found[b]
			Alkylphenylthioureas			
2-Aminopentane	85	88-90[c]	1.4010	66-67	12.60	12.71
3-Aminopentane	83	88-90[d]	1.4030	88-89	12.60	12.72
3-Amino-2-methylbutane	64	82-84[e]	1.4105	92-93	12.60	12.62
3-Amino-2,2-dimethylbutane	70	100-102[f]	1.4105	121-122	11.85	11.66
			N-Alkylbenzamides			
2-Aminohexane	63	115-117	1.4080	82-83	6.82	6.70
3-Aminohexane	55	115-116	1.4093	88-89	6.82	6.79
2-Aminoheptane	43	140-142[g]	1.4150	71-72	6.39	6.24
3-Aminoheptane	50	140-142[g]	1.4160	92-93	6.39	6.18
4-Aminoheptane	55	139-141[g]	1.4160[h]	109-110	6.39	6.22
2-Aminoöctane	51	56-57[i] (13 mm.)	1.4212	77-78	6.00	5.87

[a] All derivatives were crystallized from aqueous methanol. [b] Microanalysis by Galbraith Laboratories, Knoxville, Tenn. [c] A. N. Kost, *et al.*, *Izvest. Akad. Nauk, S. S. S. R., Otdel, Khim. Nauk*, 150 (1951), report 89-91° (*C. A.*, **45**, 10194 (1951)). [d] H. L. Bami, *et al.*, *Current Sci.* (*India*), **16**, 253 (1947), report 84-86°. [e] A. Michael and G. Carlson, *J. Org. Chem.*, **4**, 169 (1939), report 85-89°. [f] E. Schwoegler and H. Adkins, THIS JOURNAL, **61**, 3499 (1939), report 102°. [g] E. Rohrmann and H. A. Shonle, ref. 5, report the following values: 2-aminoheptane, b.p. 140-142.5°, n^{24}_{D} 1.4150; 3-aminoheptane, b.p. 139-140°; 4-aminoheptane, b.p. 139-140°, n^{24}_{D} 1.4172. [h] This value obtained for successive fractions in two runs. [i] F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 456 (1944), report 58-59° (13 mm.).

Adequate derivatives characterizing these amines have not been described previously. Although amine salts have been prepared for analytical purposes, the melting points admittedly were unsatisfactory for identification purposes.[5] Consequently, alkylphenylurea or N-alkyl benzamide derivatives were prepared in the conventional manner[7] for each amine.

The yields and physical constants of the amines and properties of the derivatives are collected in Table I.

Experimental

The following procedure describing the preparation of 2-aminohexane is representative and was used to obtain all of the amines indicated in Table I. Fifteen-hundredths of a mole of 2-hexanone oxime was dissolved in 125 ml. of 95% ethyl alcohol containing about 4 g. of Raney nickel catalyst[8] and shaken at room temperature with hydrogen at an initial pressure of three atmospheres in a Parr low pressure hydrogenation apparatus. The apparatus was recharged with hydrogen as needed to maintain the pressure between two and three atmospheres and the shaking was continued usually three to four hours until the theoretical amount of hydrogen was absorbed. With a larger amount of catalyst (five times) the reaction was more rapid but very exothermic. After completion of the reaction, the mixture was filtered, diluted with about 100 ml. of water and acidified with 0.25 equivalent of 20% sulfuric acid. The acid solution was steam distilled until 300-400 ml. of distillate was collected. This distillate was later examined for 2-hexanone. The residue from the steam distillation was treated with 0.3 mole of 25% aqueous sodium hydroxide solution and subjected to further steam distillation and distillate consisting of an aqueous suspension of 2-aminohexane was collected. After cooling, this distillate was extracted with four 50-ml. portions of 35-37° petroleum ether.[9] The combined extracts were dried over anhydrous sodium sulfate and distilled. Several fractions were collected during the distillation and the yield was calculated only on the fractions having constant refractive index. In this manner, 9.50 g. of 2-aminohexane was collected having the properties indicated in Table I.

The 2-aminohexane formed an N-alkylbenzamide when shaken with a mixture of benzoyl chloride and 10% sodium hydroxide and after two crystallizations from aqueous methanol gave the melting point and analysis shown in Table I.

The first steam distillate was repeatedly extracted with 35-37° petroleum ether. The extract was washed with water, dried and concentrated. Distillation of the residue gave 3.0 g. of 2-hexanone, boiling range 132-136°. The 2,4-dinitrophenylhydrazone was prepared, m.p. 106-107°.

DEPARTMENT OF CHEMISTRY
WEST VIRGINIA UNIVERSITY
MORGANTOWN, WEST VIRGINIA

A Synthesis of *dl*-α-Methylglutamic Acid and Some Derivatives

BY ANDREW E. GAL, SOUREN AVAKIAN AND GUSTAV J. MARTIN

RECEIVED APRIL 23, 1954

dl-α-Methylglutamic acid has been found to inhibit the enzymatic system concerned with the synthesis and subsequent utilization of glutamine.[1,2] The literature reports only the melting point[2] of *dl*-α-methylglutamic acid. Hence, for the biological studies conducted in our laboratories, it was necessary to devise a synthesis for this compound.

The observation of H. Meyer[3] that lactones derived from acids with a tertiary hydroxyl group form lactams when treated with ammonia suggested the synthesis employed by us which consisted of treating ethyl levulinate with ammonium cyanide in an ether-water medium to form γ-cyano-γ-valerolactone (I). This lactone was then treated with ammonia in an alcohol solution and the γ-cyano-γ-valerolactam (II) obtained was hydrolyzed to *dl*-α-methylglutamic acid (III).

The lactam (II) was also prepared directly by allowing ethyl levulinate to react with ammonium cyanide in an alcohol-water medium and then treating the reaction mixture with ammonium hydroxide.

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(7) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 178, 179.

(8) A. A. Pavlic and H. Adkins, THIS JOURNAL, **68**, 1471 (1946).

(9) Before extracting the aminopentanes, the corresponding steam distillate was nearly saturated with potassium carbonate.

(1) N. Lichtenstein, H. E. Ross and P. Cohen, *Nature*, **171**, 45 (1953); *J. Biol. Chem.*, **201**, 117 (1953).

(2) P. Ayengar and E. Roberts, *Proc. Soc. Exptl. Biol. Med.*, **79**, 76 (1952).

(3) H. Meyer, *Monatsh.*, **20**, 717 (1899).