[Contribution from Bell Telephone Laboratories]

Sebacic Acid Mononitrile

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Pyrolysis of sebacamide in the absence of excess ammonia has been found to yield in addition to sebaconitrile[1] a new product which has been identified as the half nitrile of sebacic acid. Similar results, differing only in relative proportions of the products, are obtained whether the pyrolysis is carried out on the pure diamide, the diammonium salt, or the crude diamide obtained by heating sebacic acid with urea.[2]

Sebacomononitrile cannot be distilled unchanged even under vacuum since it rearranges to some extent into the dinitrile and sebacic acid. Its purification was effected through the barium salt.

Sebacomononitrile methyl ester was prepared directly by the action of dimethyl sulfate on the sodium salt dissolved in methyl alcohol. For confirmation the ester was also prepared by orthodox methods from the monomethyl ester of sebacic acid through the ester-chloride and ester-amide.

Experimental

Typical Pyrolysis of Sebacamide.—231 grams of sebacamide was heated in a roomy distillation flask as rapidly as foaming would permit and until only a small residue was left. The oily distillate was shaken with ammonium hydroxide solution and the sebaconitrile layer separated; b. p. 204°, 16 mm.; yield 95 g. or 50%. The aqueous solution was heated to boiling, neutralized, and barium chloride solution added to precipitate barium sebacate. The barium salt of the mononitrile separated from the filtered solution on cooling. This salt was redissolved in water and acidified. The resulting oil was washed repeatedly with hot water and was dried *in vacuo* over calcium chloride. It crystallized to a white solid; m. p. 51.5–52°.

Anal. Calcd. for $C_{10}H_{17}O_2N$: C, 65.57; H, 9.26; N, 7.64. Found: C, 65.22; H, 9.11; N, 7.50.

Acidification of the original filtrate precipitated another crop of practically pure oil; total yield 75 g. or 35%. One mole of sebacic acid heated with 1.2 moles of urea at 160° for four hours and then distilled in the manner described above yielded 55% sebaconitrile and 35% mononitrile.

Methyl Ester of Sebacomononitrile (Methyl ω-Cyanopelargonate).—The methyl ester was prepared by heating a methyl alcohol solution containing equivalent amounts of mononitrile, sodium methoxide, and dimethyl sulfate. The product distilled at 178° (16 mm.), $n^{25}D$ 1.4398.

Anal. Calcd. for $C_{11}H_{19}O_2N$: C, 67.01; H, 9.64; N, 7.11. Found: C, 66.87; H, 9.59; N, 6.92.

Methyl Sebacamate.—Monomethyl sebacate was converted to the acid chloride with thionyl chloride and the product was poured into cold strong ammonium hydroxide. The amide was recrystallized from water; m. p. 77.4°; yield 90%.

Anal. Calcd. for $C_{11}H_{21}O_3N$: C, 61.39; H, 9.76; N, 6.51. Found: C, 61.56; H, 9.82; N, 6.43.

Methyl ω-Cyanopelargonate.—The above ester amide was dehydrated by a process similar to that of Wilcke,[3] the amide being mixed with an equal weight of phosphorus pentoxide, covered with *sym*-tetrachloroethane and heated to the boiling point of the solvent (146°) for one hour. The decanted liquid was distilled, the cyano ester being taken at 170°, 14 mm.; yield 64–71%; $n^{25}D$ 1.4398.

Anal. Calcd. for $C_{11}H_{19}O_2N$: C, 67.01; H, 9.64; N, 7.11. Found: C, 66.93, 66.92; H, 9.58, 9.39; N, 6.77.

Acknowledgment.—The authors are indebted to Mr. F. C. Koch for the analyses.

Summary

Processes are described which furnish practical yields of sebaconitrile and sebacic acid mononitrile. Sebacic acid mononitrile and its methyl ester are characterized.

Summit, N. J. Received December 20, 1940

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[1] Greenwalt and Rigby, U. S. Patent 2,132,849; *C. A.*, **33**, 178 (1939).

[2] General methods for the preparation of amides by heating acids with urea have been described by Bruson, U. S. Patent 1,989,968 (*C. A.*, **29**, 1833 (1935)) and by D'Alelio and Reid, U. S. Patent 2,109,941 (*C. A.*, **32**, 3419 (1938)).

[3] Wilcke, U. S. Patent 1,828,267.