

The results of the distillation of a single batch of the above preparation is shown in Fig. 1. The fraction which boiled at 78° is believed to be ethanol present in the ordinary ether used to decompose the excess lithium aluminum hydride. An azeotrope probably consisting of 1-methylcyclopropanemethanol and water distilled at 94°.

The yield of alcohol, b. p. 124.5–128.0°, is 56% based upon the ester used. The physical constants for the intermediate cut taken between 75.6 and 85.2 ml. are presented in Table I. The alcohol reacts slowly with bromine in carbon tetrachloride.

The  $\alpha$ -naphthylurethan was prepared and recrystallized three times from petroleum ether.

*Anal.* Calcd. for  $C_{16}H_{17}O_2N$ : C, 75.27; H, 6.71; N, 5.49. Found<sup>2</sup>: C, 75.23; H, 6.66; N, 5.82.

The 3,5-dinitrobenzoate was prepared both in the presence and absence of pyridine. The products were the same, as indicated by the melting point and mixed melting point. The 3,5-dinitrobenzoate after three recrystallizations from alcohol had a m. p. of 85.5–85.7°.

*Anal.* Calcd. for  $C_{12}H_{12}O_6N_2$ : C, 51.43; H, 4.32. Found<sup>2</sup>: C, 51.92; H, 4.36.

**Oxidation of 1-Methylcyclopropanemethanol.**—The alcohol (100 mg.) was dissolved in 5 ml. of water, 1 ml. of 10% sodium hydroxide was added, and potassium permanganate was added in small amounts so that after refluxing for thirty minutes the solution retained the permanganate color. The solution was acidified with 5 *N* sulfuric acid after filtering off the manganese dioxide, and then steam distilled. Titration of the distillate indicated 44 mg. of acid (38% yield). This was converted to the *p*-bromophenacyl ester without isolating the acid from the aqueous solution. After recrystallization from alcohol, 32 mg. of ester was obtained, m. p. 62.5–63.0° (23% yield from the acid). The mixed melting point with an authentic sample of the *p*-bromophenacyl ester of 1-methylcyclopropanecarboxylic acid was 60–62°. The mixed melting point with the corresponding ester of tiglic acid was 49–59°.

**The Detection of Unsaturated Isomers.**—This was attempted by an analysis of a 0.02 *M* solution of the carbinol in 0.1 *N* sulfuric acid with a bromide-bromate mixture (0.05 *M* in bromine), adding an excess of potassium iodide at definite time intervals and back titrating with standard sodium thiosulfate. The values for the degree of unsaturation were found to increase from 38% after one minute to 86% after seven minutes. Unpublished work by the present authors indicates that a 0.05 *M* solution of cyclopropanemethanol (homolog of the alcohol described in this paper) in 0.1 *N* hydrochloric acid rearranges to an unsaturated isomer to the extent of 23% in 44 hours at 100° so it would appear highly desirable to avoid the use of acids in working with alcohols of this type.

The degree of unsaturation was determined by the titration of 100–200-mg. samples of product taken by intercepting the distillate at the experimental points. The titration was carried out with a 0.05 *M* solution of bromine in carbon tetrachloride and the end-point arbitrarily set as the point at which the bromine color was still visible one minute after adding the bromine solution in 0.04-ml. increments. This technique proved satisfactory for the analysis of 3-butene-1-ol. In a series of experiments involving the reaction of 0.042 molar 1-methylcyclopropanemethanol (of a less carefully purified sample than that reported in Table I) and 0.025 *N* bromine in carbon tetrachloride, the degree of unsaturation was found to increase in a regular manner from 9% after one minute to 54% after 128 min. This suggests that, under the conditions of the analysis, bromine will add to the cyclopropane ring. This would result in low titration values for the purity of the carbinol so it is felt that the values given indicate the minimum purity with respect to any unsaturated isomer.

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## A Synthesis of Cyanamide from Barium Carbonate Applicable to Use of Isotopic Carbon

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In preparing cyanamide containing  $C^{14}$ , it is desirable to use radioactive carbonate as starting material. Reported methods for carrying out this conversion are associated with rather difficult conditions of reaction or with only moderate yields, especially when done in semimicro amounts.<sup>1,2,3</sup>

It was found by us that barium carbonate reacts readily with ammonia in the presence of sodium azide to give cyanamide, the reaction being easily carried out in one step with greater than 94% yield based on carbon. This contrasts with more difficult conditions of reaction when no sodium azide is used.<sup>1</sup> The experimental evidence reported below applies to barium carbonate of normal isotope content. The reaction also has been used in the synthesis of cyanamide from 124 mg. of barium carbonate of which the carbon included 1 mc. of  $C^{14}$ . Since the work below was completed, another method of cyanamide synthesis from carbonate with high yield has been reported.<sup>4</sup>

The technique of the condensation was that described by Adamson,<sup>5</sup> except that anhydrous ammonia (passed over potassium hydroxide) was passed briskly into the open end of the test-tube which contained 200 mg. of isotopic barium carbonate and 4 g. of sodium azide. After sixty minutes of heating, the tube was cooled while under the stream of ammonia, and after cautiously destroying the sodium, the content was dissolved in 150 ml. of water and filtered. The clear filtrate was poured slowly into 50 ml. of 0.1 *N* silver nitrate containing 2% ammonia and after twelve hours the yellow-green precipitate was centrifuged off, dissolved in 30 ml. of 3.0 *N* nitric acid, then made up to 50 ml. with water and filtered. Twelve hours after adding 10 ml. of 0.1 *N* silver nitrate to the filtrate, it was made alkaline slowly with 5% ammonia, the centrifuged precipitate then was washed with water until the filtrate was free of silver ion, finally the precipitate was washed with methanol and ether and dried in the desiccator. The precipitate was identified as the silver salt of cyanamide by the following: it was clear yellow, insoluble in water and dilute ammonia, easily soluble in dilute nitric acid.<sup>6</sup> It had no melting point but decomposed violently at about 200°.<sup>3</sup> An analysis for the silver content<sup>7</sup> was made by dissolving the disilver salt in dilute nitric acid and titrating it with ammonium thiocyanate, ferric alum being used as indicator. Calcd. for  $CN_2Ag_2$ : Ag, 84.4. Found from three separately synthesized preparations: Ag, 83.5, 83.2, and 83.3. The silver salt was converted to *O*-methyl isourea monohydrochloride as part of

(1) German Patent 139,456; *Chem. Zentr.*, **74**, I, 6777 (1903); Franklin, *THIS JOURNAL*, **44**, 495 (1922); Calvin, Heidelberger, Reid, Tolbert and Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 158.

(2) Bloch and Schoenheimer, *J. Biol. Chem.*, **138**, 167 (1941); Aroll, *J. Chem. Soc.*, Pt. 2, 1534 (1948); Ullmann, "Enzyklopädie der technischen Chemie," 2nd edit., Vol. II, 109 (1928); German Patent 108,971; *Chem. Zentr.*, **71**, I, 1120 (1900); German Patent 163,320; *Chem. Zentr.*, **76**, II, 1059 (1905).

(3) Bellstein and Geuther, *Ann.*, **108**, 88 (1858).

(4) Murray and Ronzio, *THIS JOURNAL*, **71**, 2245 (1949).

(5) Adamson, *ibid.*, **69**, 2584 (1947).

(6) Dreschel, *J. prakt. Chem.*, **11**, 301 (1876).

(7) Pink, *Ind. Eng. Chem.*, **17**, 459 (1925).

the arginine synthesis; yield based on cyanamide was 90%, m. p. 126° uncor. (reported<sup>8</sup> m. p. 127–128°, uncor.).

In a control experiment, using no carbonate, no trace of the yellow-green silver precipitate appeared.

(8) Kapfhammer and Müller, *Z. physiol. Chem.*, **225**, 1 (1934).

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## Tenulin. II.<sup>1</sup> Anhydrotenulin and Pyrotenulin

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Tenulin (I),  $C_{17}H_{22}O_5$ , loses water when it is heated for a short time at 300°. The dehydration product, anhydrotenulin (II)  $C_{17}H_{20}O_4$ , has been purified and analyzed by Clark.<sup>5</sup>

Further investigations have shown that (II) has an ultraviolet absorption spectrum identical with that of tenulin and isotenulin<sup>1,5a</sup> (Fig. 1) which is indicative of an  $\alpha,\beta$ -unsaturated carbonyl group. Such a function is confirmed by the in-

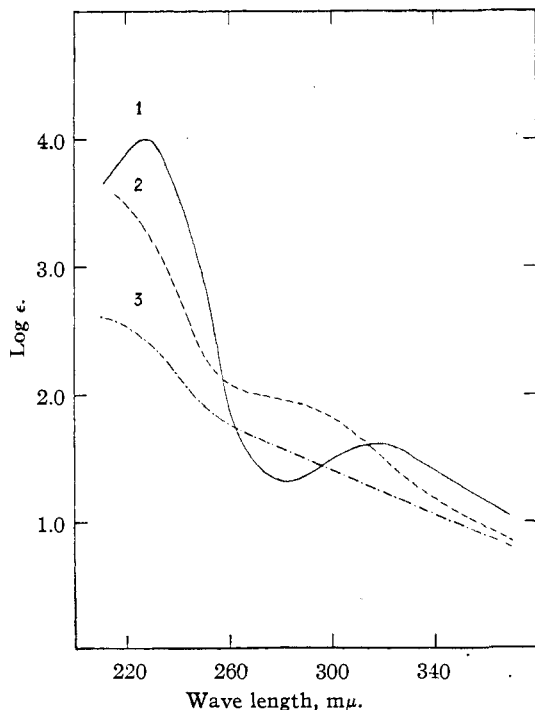


Fig. 1.—Ultraviolet absorption spectra in 95% alcohol: 1, anhydrotenulin (0.000753 mole per liter); 2, pyrotenulin (0.003559 mole per liter); tenulinic acid (0.00263 mole per liter).

(1) Paper I, *THIS JOURNAL*, **70**, 3921 (1948).

(2) Chemistry Department, New Mexico Highlands University, Las Vegas.

(3) In part from the Ph.D. thesis of E. C. Hendley.

(4) In part from the master's thesis of W. Dunkel.

(5) Clark, *THIS JOURNAL*, **61**, 1836 (1939).

(5a) Ungnade, *ibid.*, **71**, 4163 (1949).

frared spectra of the compounds which show bands at 5.89–5.92  $\mu^6$  ( $C=O$ ) and 6.37  $\mu^7$  ( $C=C$ , conjugated with  $C=O$ ) (Fig. 2).

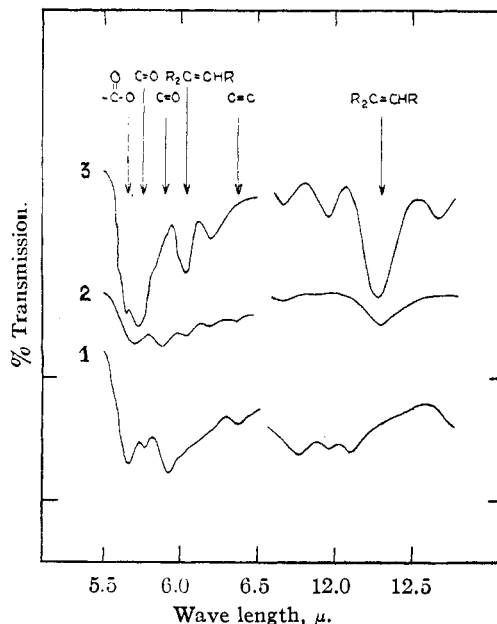


Fig. 2.—Infrared absorption spectra in nujol: 1, tenulin; 2, anhydrotenulin; 3, pyrotenulin.

The oxidation of anhydrotenulin with potassium permanganate yields acetyltenulinic acid ( $C_{17}H_{22}O_8$ ) while hydrogen peroxide oxidation furnishes tenulinic acid in good yields. The same acids are also obtained from tenulin and isotenulin under identical conditions.<sup>8</sup> Since tenulinic acid does not absorb appreciably in the ultraviolet, the  $\alpha,\beta$ -unsaturated carbonyl group is destroyed in these oxidation reactions. The oxidation results with anhydrotenulin are tentatively explained on the basis that the dehydration of tenulin is reversible, *i. e.*, that anhydrotenulin adds a molecule of water during the oxidation.

The infrared spectrum of anhydrotenulin shows new bands at 6.04, 6.20 and 12.30  $\mu$  which are regarded as evidence for unsaturation. The bands at 6.04 and 12.3  $\mu$  are associated with double bonds of the type  $R_2C=CHR$ .<sup>6b,9</sup>

Anhydrotenulin consumes two moles of alkali on heating with aqueous alcoholic alkali. It contains therefore in addition to the acetoxy group also the lactone grouping which has been suggested for tenulin.<sup>1</sup>

Strong heating of tenulin causes decomposition beyond simple dehydration. Pyrotenulin (III)  $C_{13}H_{16}O_3$  can be isolated from the pyrolysis products in 11% yield. Clark's molecular

(6) (a) Cromwell, Miller, Johnson, Frank and Wallace, *ibid.*, **71**, 3339 (1949); (b) Gunthard and Ruzicka, *Helv. Chim. Acta*, **32**, 2130 (1949).

(7) Adams and Herz, *THIS JOURNAL*, **71**, 2547 (1949).

(8) Clark, *ibid.*, **62**, 598 (1940).

(9) The band at 6.20  $\mu$  is thus far unexplained.