β - Chloro - β - (2,3,4,6 - tetramethylphenyl) - acrylic Acid.—Hydrogen chloride was added to 2,3,4,6-tetramethylphenylpropiolic acid under the conditions used in the preparation of β-chloro-β-(2,4,6-trimethylphenyl)-acrylic acid. From 1 g. of isodurylpropiolic acid was obtained 1.03 g. (90%) of the hydrogen chloride adduct. Recrystallization from petroleum ether gave large white needles, m. p. 185° (cor.).

Anal. Calcd. for $C_{13}H_{15}O_2Cl$: C, 65.41; H, 6.33. Found: C, 65.46; H, 6.46.

This same acid was obtained in 46% yield by treatment of 2,3,4,6-tetramethylbenzoylacetic acid with phosphorus oxychloride and phosphorus pentachloride.[2a] A mixed melting point of the two samples showed no depression.

β - Iodo - β - (2,3,4,6 - tetramethylphenyl) - acrylic Acid.—The general procedure used has been described by Michael.[10] From 7 g. of 2,3,4,6-tetramethylphenylpropiolic acid suspended in 10 cc. of constant boiling hydriodic acid for nine days at room temperature was obtained 1.24 g. of air-dried material. The acid was purified by recrystallization from carbon tetrachloride; white crystals m. p. 183–184° (cor.); yield 1.0 g. (90%).

Anal. Calcd. for $C_{13}H_{15}O_2I$: C, 47.29; H, 4.58. Found: C, 47.16; H, 4.53.

(10) Michael, *Ber.*, **34**, 3640 (1901).

Summary

1. Di-*ortho*-substituted phenylpropiolic acids have been shown to undergo similar addition reactions to phenylpropiolic acid though somewhat less readily. A method thus becomes available for preparing arylacrylic acids with restricted rotation in which the β-substituent can be varied.

2. Hydrogen chloride has been added to 2,4,6-trimethylphenylpropiolic acid with formation of β-chloro-β-(2,4,6-trimethylphenyl)-acrylic acid. Hydrogen bromide gives the corresponding brominated acrylic acid.

3. Hydrogen chloride has been added to 2,3,4,-6-tetramethylphenylpropiolic acid to give β-chloro-β-(2,3,4,6-tetramethylphenyl)-acrylic acid. Hydrogen iodide gives the corresponding iodinated acrylic acid.

4. The β-chloroacrylic acids mentioned in 2 and 3 are identical with those obtained by the action of phosphorus pentachloride on 2,4,6-trimethylbenzoylacetic acid and 2,3,4,6-tetramethylbenzoylacetic acid, respectively.

URBANA, ILLINOIS RECEIVED JULY 28, 1943

[CONTRIBUTION FROM NOYES LABORATORY, UNIVERSITY OF ILLINOIS, AND THE RESEARCH LABORATORIES, MERCK AND CO., INC.]

ω,ω'-Bimethionine

BY H. R. SNYDER, E. E. HOWE, GEORGE W. CANNON AND MELVIN A. NYMAN

The *dl*-methionine obtained by adaptation of the procedure of Barger and Weichselbaum[1] to the preparation of larger quantities has been found to be contaminated with a less-soluble material[2] which now has been identified as a mixture of the racemic and meso forms of ω,ω'-bimethionine, $HO_2CCH(NH_2)CH_2CH_2SCH_2CH_2SCH_2CH_2CH(NH_2)CO_2H$. Most of the impurity, originally called "pseudomethionine," could be removed by crystallization from water, but detectable amounts always remained in the methionine. These traces of the contaminant could not be removed by crystallization from acetic acid, aqueous methanol, aqueous ethanol, aqueous acetone or aqueous pyridine. Conversion of the methionine to the copper salt or the formyl derivative, followed by crystallization of the derivative and regeneration of the methionine, likewise failed to remove all the impurity.

The impurity may be detected by the use of a solution of anhydrous copper sulfate in concentrated sulfuric acid. A yellow color is produced when natural methionine or pure *dl*-methionine is added to this solution.[3] A green tint is distinguishable in the yellow solution when the contaminated methionine is tested.[2] A bright green color is produced when the isolated impurity is added to the test solution.

"Pseudomethionine" is a high-melting amphoteric solid. It can be recrystallized from a large volume of hot water and thus freed of methionine. Analyses of the substance and its acetyl and benzoyl derivatives indicated that its empirical formula is $C_5H_{10}O_2NS$. The molecular weight of the acetyl derivative indicated that the molecular formula of "pseudomethionine" is $C_{10}H_{20}O_4N_2S_2$. The neutral equivalent of the acetyl derivative indicated that the molecule contains two free carboxyl groups. A Dumas nitrogen determination and a Van Slyke amino-nitrogen determination indicated that two free amino groups are present. Tests for C-methyl, S-methyl, and disulfide groups were negative.

If the precursor of the substance is formed by alkylation of sodium ethyl phthalimidomalonate, the dichloride which leads to "pseudomethionine" either must be present in or must be formed from the monochloride, $CH_3SCH_2CH_2Cl$. The most likely mode of decomposition of β-chloroethyl methyl sulfide is through autoalkylation to form sulfonium salts. Sulfonium halides are known to decompose to sulfides and alkyl halides.[4]

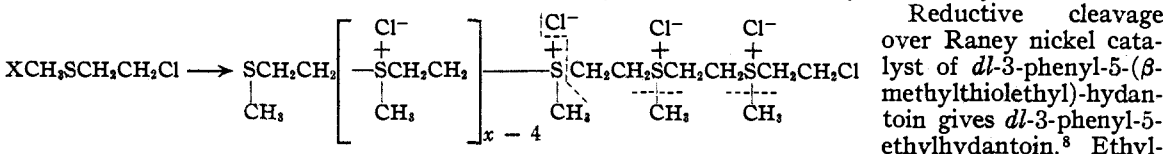
(1) Barger and Weichselbaum, "Organic Syntheses," Coll. Vol. II, p. 384 (1943); *Biochem. J.*, **25**, 997 (1931).

(2) Sofin, Rosenblum and Schultz, Merck and Co., Inc., private communication.

(3) Sofin, Rosenblum and Schultz, Merck and Co., Inc., *J. Biol. Chem.*, **147**, 557 (1943).

(4) Ray and Levine, *J. Org. Chem.*, **2**, 267 (1937); for other references, see Connor, "Organic Sulfur Compounds," Gilman's "Organic Chemistry," Chapter 10, John Wiley and Sons, Inc., New York, N. Y., 1942, ed. 2, Vol. 1, p. 868.

Since β-chloroethyl methyl sulfide is bifunctional, it may give rise to polysulfonium halides of the following structure.



The expected preferential mode of decomposition of such a polysulfonium chloride is that involving the loss of methyl chloride. However, if occasionally there were cleavage of the larger alkyl groups, as indicated by the dotted lines, then the dichloride $ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$ (I) would be formed.

The dichloride (I), by reaction with sodium ethyl phthalimidomalonate, would give rise to ω,ω′-bimethionine, the composition of which is identical with that of "pseudomethionine." The experimental conditions of the Barger–Weichselbaum synthesis of methionine—a long period of heating at temperatures of 160–165° in the absence of a solvent—are those which favor the formation and decomposition of sulfonium chlorides. In the preparation of β-chloroethyl methyl sulfide the distillation of the product is carried out at 30 mm. (b. p. 55–56°).[5] The authors have observed that distillation at higher pressures leads to the formation of large quantities of higher-boiling materials. These substances are probably the various sulfonium chlorides and their decomposition products.

To determine whether "pseudomethionine" has the proposed structure, the dichloride (I) was prepared[6] and allowed to react with ethyl acetaminomalonate[7]; hydrolysis and decarboxylation then gave ω,ω′-bimethionine. Color tests and the melting points (285–288°) of "pseudo-

$$(-CH_2SCH_2CH_2Cl)_2 + 2CH_3CONHC(CO_2C_2H_5)_2Na \longrightarrow [CH_3CONHC(CO_2C_2H_5)_2CH_2CH_2SCH_2]_2 \longrightarrow [-CH_2SCH_2CH_2CH(NH_2)COOH]_2$$

methionine" and the ω,ω′-bimethionine were indistinguishable. Derivatives of the two samples were prepared in an effort to confirm their identity. Benzoyl "pseudomethionine" (m. p. 157–160°) and benzoyl ω,ω′-bimethionine (m. p. 145–154°, after shrinking at 140°) were prepared; a mixture of the two began shrinking at 148° and melted at 155–160°. Formyl "pseudomethionine" (m. p. 114–154°) and formyl ω,ω′-bimethionine (m. p. 171–174°) were prepared; a mixture of the two melted at 160–168°. Analyses of each of these derivatives were in excellent agreement with the proposed structure. Their behavior suggests that the samples of both "pseudomethionine" and ω,ω′-bimethionine were mixtures of the *dl*- and the *meso*-forms, and that separation of an individual isomer did not occur during recrystallization of either the original compounds or their benzoyl and formyl derivatives.

Reductive cleavage over Raney nickel catalyst of *dl*-3-phenyl-5-(β-methylthiolethyl)-hydantoin gives *dl*-3-phenyl-5-ethylhydantoin.[8] Ethylene *bis*-[β-(3-phenyl-5-hydantoin)-ethyl sulfide] (II) was obtained by treating "pseudomethionine" with phenyl isocyanate and effecting ring closure with hydrochloric acid. The dihydantoin, although it was of analytical purity, melted over a nine-degree range. Obviously, it too was a mixture of *dl*- and *meso*-forms. Reductive cleavage of this dihydantoin gave *dl*-3-phenyl-5-ethylhydantoin (III) in 75% yield. The isolation of this

$$[-CH_2SCH_2CH_2\underbrace{CHCON(C_6H_5)CONH}]_2 \xrightarrow[Ni]{H_2} \underset{II}{} \; 2\underbrace{CH_3CH_2CHCON(C_6H_5)CONH}_{III}$$

substance demonstrates the presence of $-SCH_2CH_2CH(NH_2)COOH$ groups in "pseudomethionine."

Oxidation of "pseudomethionine" with hydrogen peroxide in acetic acid solution gave the expected disulfone, but oxidation in a mixture of acetic acid and acetic anhydride as a solvent gave a different compound. This substance could be recrystallized from water, and it dissolved more rapidly in base than in water or in acid. The difference in melting points indicated that it was not the acetyl derivative of "pseudomethionine." A Van Slyke amino nitrogen determination was negative.

Ethylene disulfones are less stable than the simple monosulfones and they undergo cleavage of a carbon-sulfur bond readily.[9] This suggested that the new compound might arise from the cleavage of the disulfone of "pseudomethionine" to produce a new amino acid. The absence of free amino-nitrogen and the fact that the compound could be titrated with alkali suggested that the amino group had been acetylated, and the analysis of the compound was in good agreement with the proposed structure (IV). Hydrolysis

$$[-CH_2SCH_2CH_2CH(NH_2)CO_2H]_2 \xrightarrow[H_2O_2]{AcOH\ (Ac)_2O} HOCH_2CH_2SO_2CH_2CH_2CH(NHCOCH_3)CO_2H \quad IV$$

with constant-boiling hydrochloric acid gave an

(5) "Organic Syntheses," Coll. Vol. II, p. 136 (1943).

(6) Bennett and Whincop, *J. Chem. Soc.*, **119**, 1860 (1921).

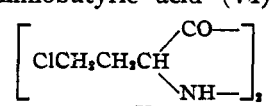
(7) The use of this substance in amino acid syntheses was first suggested to the authors by Dr. Max Tishler, Merck and Co., Inc.

(8) Mozingo, Wolf, Harris and Folkers, THIS JOURNAL, **65**, 1013 (1943).

(9) Otto and Damköhler, *J. prakt. Chem.*, [2] **30**, 171, 321 (1884); for other references, see Connor, "Organic Sulfur Compounds," Chapter 10, in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1942, ed. 2, Vol. I, p. 883.

amino acid whose analysis was in excellent agreement with the structure VI.

To establish this structure, the amino acid VI was synthesized: 3,6-*bis*-[β-(β-hydroxyethylthiol)-ethyl]-2,5-diketopiperazine was prepared by allowing 3,6-*bis*-(β-chloroethyl)-2,5-diketopiperazine (V) to react with the potassium salt of monothiolethylene glycol. Hydrolysis of the resulting dihydroxydiketopiperazine gave γ-(β-hydroxyethylthiol)-α-aminobutyric acid. Oxidation of this amino acid gave γ-(β-hydroxyethanesulfonyl)-α-aminobutyric acid (VI) which had



V

$HOCH_2CH_2SO_2CH_2CH_2CH(NH_2)CO_2H$

VI

properties identical with those of the amino acid obtained by hydrolysis of the "pseudomethionine" oxidation product. A mixed-melting point determination showed no depression, but this fact is not necessarily significant because of the decomposition of the samples below the melting point.

Consideration of all the evidence leaves no doubt but that "pseudomethionine" is a mixture of the racemic and meso forms of ω,ω'-bimethionine. It is probable that other similar by-products are produced also in the synthesis of methionine from β-chloroethyl methyl sulfide and sodium ethyl phthalimidomalonate.

Experimental

1. Isolation of "Pseudomethionine" from the Reaction of β-Chloroethyl Methyl Sulfide and Sodium Ethyl Phthalimidomalonate.[1]—*dl*-Methionine prepared by this procedure was dissolved in hot water and the solution was filtered and allowed to stand at room temperature for several days. Slow crystallization of "pseudomethionine" occurred. The material was collected by filtration and recrystallized from a large volume of hot water as a fine white powder, m. p. 285–288°. The amount was approximately 5% of the weight of crude methionine.

Anal. Calcd. for $C_{10}H_{20}O_4N_2S_2$: C, 40.5; H, 6.75; N, 9.45; S, 21.60. Found: C, 40.0; H, 6.93; N, 9.16; S, 21.9.

The acetyl derivative, prepared by the method of du Vigneaud and Meyer,[10] melted at 173–174°.

Anal. Calcd. for $C_{14}H_{24}O_6N_2S_2$: C, 44.30; H, 6.32; N, 7.37; S, 16.85; neut. equiv., 190; mol. wt., 380. Found: C, 44.43; H, 6.03; N, 7.26; S, 16.09; neut. equiv., 184; mol. wt., 312.

The benzoyl derivative, prepared by the method of Carter and Stevens,[11] melted at 157–160° after repeated recrystallization from ethanol–water.

Anal. Calcd. for $C_{24}H_{28}O_6N_2S_2$: C, 57.12; H, 5.59; N, 5.55. Found: C, 57.10; H, 5.76; N, 5.29.

The formyl derivative, prepared by the method of Clarke,[12] melted at 114–154° after repeated recrystallization from water.

Anal. Calcd. for $C_{12}H_{20}O_6N_2S_2$: C, 40.89; H, 5.72; N, 7.95. Found: C, 40.77; H, 5.72; N, 7.95.

(10) Du Vigneaud and Meyer, *J. Biol. Chem.*, **98**, 300 (1932).

(11) Carter and Stevens, *ibid.*, **138**, 627 (1941).

(12) Described by du Vigneaud and Meyer, *ibid.*, **98**, 302 (1932).

2. Synthesis of ω,ω'-Bimethionine.—A solution of 2.3 g. of sodium in 50 cc. of absolute ethanol was added to a solution of 7 g. of ethylene *bis*-(β-chloroethyl sulfide)[6] and 28 g. of ethyl acetaminomalonate in 150 cc. of absolute ethanol. This reaction mixture was heated under reflux with stirring for five hours, cooled in an ice-bath, and filtered. The solid collected on the funnel was extracted with boiling absolute ethanol until only sodium chloride remained. The combined alcoholic extracts were cooled and the product was separated by filtration: weight 4.5 g. (25.2%), m. p. 154–155°.

Anal. Calcd. for $C_{24}H_{40}O_{10}N_2S_2$: C, 49.64; H, 6.93. Found: C, 49.77; H, 7.08.

To a solution of 2 g. of sodium hydroxide in 25 cc. of water and 25 cc. of ethanol, 4.5 g. of the above ester was added. The mixture was heated under reflux for two hours and then evaporated to dryness under diminished pressure. The residue was dissolved in 100 cc. of concentrated hydrochloric acid and the solution was heated under reflux for three hours. It was then concentrated to dryness under diminished pressure. The residue was extracted three times with boiling ethanol, and the combined extracts were decolorized with charcoal. An excess of pyridine was added, and the solution was allowed to stand in a refrigerator overnight. The crude ω,ω'-bimethionine, collected by filtration, weighed 2.3 g. (96%). After two recrystallizations from water, it melted at 285–288°; a mixed-melting point determination with a sample obtained in (1) was not depressed.

Anal. Calcd. for $C_{10}H_{20}O_4N_2S_2$: C, 40.5; H, 6.75; N, 9.45. Found: C, 40.5; H, 7.06; N, 9.12.

The benzoyl derivative, prepared by the method of Carter and Stevens,[11] began shrinking at 140° and melted at 145–154°. A mixture with the benzoyl derivative prepared in (1) began shrinking at 148° and melted at 155–160°.

Anal. Calcd. for $C_{24}H_{28}O_6N_2S_2$: C, 57.12; H, 5.59. Found: C, 57.26; H, 5.56.

The formyl derivative, prepared by the method of Clarke,[12] melted at 171–174°. A mixture with the formyl derivative prepared in (1) melted at 160–168°.

Anal. Calcd. for $C_{12}H_{20}O_6N_2S_2$: C, 40.89; H, 5.72; N, 7.95. Found: C, 40.75; H, 5.75; N, 7.84.

3. Reductive Cleavage over Raney Nickel Catalyst.—Ethylene *bis*-β-(3-phenyl-5-hydantoin)-ethyl sulfide (II) was prepared from "pseudomethionine" and phenyl isocyanate in 69% yield using the method of Mozingo, Wolf, Harris and Folkers.[8] After three recrystallizations from ethyl acetate it melted with decomposition at 155–164°.

Anal. Calcd. for $C_{24}H_{28}O_4N_4S_2$: C, 57.83; H, 5.26; N, 11.24; mol. wt., 498.45. Found: C, 57.86; H, 5.43; N, 11.37; mol. wt. (cryoscopic in benzophenone), 517.5.

3-Phenyl-5-ethylhydantoin (III) was obtained from the dihydantoin derivative II in 75% yield by the method of Mozingo, Wolf, Harris and Folkers.[8] After three recrystallizations it melted at 121–122°. A mixed-melting point determination with an authentic sample of *dl*-3-phenyl-5-ethylhydantoin, obtained from *dl*-methionine, was not depressed.

Anal. Calcd. for $C_{11}H_{12}O_2N_2$: C, 64.69; H, 5.93; N, 13.71. Found: C, 64.82; H, 6.00; N, 13.68.

4. Oxidation of "Pseudomethionine."—The disulfone of "pseudomethionine" was prepared in 53% yield by oxidation according to the method of Gilman and Beaber[13] except that the reaction mixture was permitted to stand at room temperature for four days. After recrystallization from a large volume of hot water it decomposed without melting on a Maquenne block at 325–350°.

Anal. Calcd. for $C_{10}H_{20}O_8N_2S_2$: C, 33.34; H, 5.60; N, 7.77. Found: C, 33.30; H, 5.62; N, 7.93.

"Pseudomethionine" was oxidized in a glacial acetic acid–acetic anhydride solvent according to the method of Pomerantz and Connor.[14] After the reaction mixture had

(13) Gilman and Beaber, THIS JOURNAL, **47**, 1449 (1925).

(14) Pomerantz and Connor, *ibid.*, **61**, 3386 (1939).

stood at room temperature for six days, the product was collected by filtration. It was obtained in quantities of 61% of the theoretical [calculated as γ-(β-hydroxyethanesulfonyl)-α-acetaminobutyric acid (IV)] and could be recrystallized from water. It began darkening at 226° and melted with decomposition at 231–235°, depending upon the rate of heating.

Anal. Calcd. for $C_6H_{13}O_6NS$: C, 37.90; H, 5.94; N, 5.53; neut. equiv., 253. Found: C, 37.73; H, 5.83; N, 5.41; neut. equiv., 230.9; Van Slyke amino-nitrogen: negative.

A solution of 1.5 g. of this oxidation product and 50 cc. of concentrated hydrochloric acid was heated under reflux for two hours. The solution was concentrated under diminished pressure, and the gum was extracted with boiling 25% ethanol. The alcoholic extract was treated with an excess of pyridine and allowed to stand in a refrigerator overnight. The product was recrystallized from water. It darkened at 250° and decomposed without melting at 265–280°.

Anal. Calcd. for $C_6H_{13}O_5NS$: C, 34.12; H, 6.20; N, 6.63. Found: C, 34.12; H, 6.05; N, 6.72.

5. Preparation of γ-(β-Hydroxyethanesulfonyl)-α-aminobutyric Acid (VI).—3,6-*bis*-[β-(β-Hydroxyethylthiol)-ethyl]-2,5-diketopiperazine was prepared in the following manner. A mixture of 71.7 g. of 3,6-*bis*-(β-chloroethyl)-2,5-diketopiperazine (V)[15] and 600 cc. of ethanol was heated to reflux, and a solution of 36.9 g. of potassium hydroxide and 51.5 g. of monothiolethylene glycol[16] in 200 cc. of ethanol was added dropwise. The mixture was heated under reflux for a total of two hours, and the hot solution was filtered. The salt collected on the filter was extracted with a small amount of hot ethanol. The combined alcoholic extracts were cooled, and crystallization was initiated by scratching. The mother liquor was concentrated to a volume of 300 cc. and cooled. The total yield was 51.5 g. (53.3%). This material was recrystallized from ethanol several times; m. p. 148–149°.

Anal. Calcd. for $C_{12}H_{22}O_4N_2S_2$: C, 44.70; H, 6.79; N, 8.69. Found: C, 44.93; H, 6.89; N, 8.74.

By extraction of the reaction mixture with boiling chloroform there was obtained a small amount of solid, m. p. 171–178°, the analysis of which indicates that it is the monosubstituted product, 3-(β-chloroethyl)-6-[β-(β-hydroxyethylthiol)-ethyl]-2,5-diketopiperazine.

Anal. Calcd. for $C_{10}H_{17}O_3N_2SCl$: C, 42.70; H, 6.08; N, 10.0. Found: C, 42.42; H, 6.02; N, 9.81.

γ-(β-Hydroxyethylthiol)-α-aminobutyric acid was prepared in the following manner. A solution of 5 g. of the dihydroxydiketopiperazine in 100 cc. of concentrated hydrochloric acid was heated under reflux for two hours. The solution was concentrated under diminished pressure, and the residue was extracted with 100 cc. of boiling ethanol and filtered. The filtrate was treated with charcoal, and 20 cc. of pyridine was added to the warm filtrate. The solution was quickly decanted from a sticky flocculent solid. After cooling overnight in a refrigerator, the crude amino acid was collected by filtration; weight 3.5 g. (63%). It was recrystallized with difficulty from a water–ethanol mixture and melted with decomposition at 275–280°. However, it persisted in separating from the solution in an amorphous form and could not be rendered pure.

Anal. Calcd. for $C_6H_{13}O_5NS$: C, 40.28; H, 7.31; N, 7.82. Found: C, 39.85; H, 6.93; N, 8.82.

Attempts to oxidize the amino acid by the method of Barger and Coyne[17] were unsuccessful. It was oxidized by the method of Gilman and Beaber[18] modified as follows. Three grams of the amino acid was dissolved in 30 cc. of glacial acetic acid and cooled, and 6 cc. of 30% hydrogen peroxide was added in small portions. After standing at room temperature for six days, the reaction mixture was evaporated to dryness under an air jet at room temperature. Ethanol was added to the residue, and the procedure was repeated several times. After two recrystallizations from water the product weighed 1.5 g. (35.4%), m. p. 228° with decomposition. After repeated recrystallization from water it began darkening at 250° and decomposed without melting at 265–275°. A mixed-melting point determination with the amino acid obtained in (4) by hydrolysis of the unknown oxidation product was not depressed.

Anal. Calcd. for $C_6H_{13}O_5NS$: C, 34.12; H, 6.20. Found: C, 33.69, 33.72; H, 5.94, 6.07.

Summary

A by-product obtained when the Barger–Weichselbaum synthesis of methionine was adapted to large-scale preparations has been identified as a mixture of the racemic and meso forms of ω,ω′-bimethionine. The identification rests on the following evidence: (a) conversion of the unknown amino acid to the *bis*-phenylhydantoin and hydrogenolysis over Raney nickel catalyst to give 3-phenyl-5-ethyl-hydantoin; (b) oxidation of the unknown substance with hydrogen peroxide in acetic acid-acetic anhydride solution to produce the acetyl derivative of γ-(β-hydroxyethanesulfonyl-α-aminobutyric acid and comparison of this amino acid with a sample synthesized by another method; and (c) comparison of the unknown amino acid with ω,ω′-bimethionine synthesized from ethylene *bis*-(β-chloroethyl sulfide) and acetaminomalonic ester. A possible mode of formation of ω,ω′-bimethionine from β-chloroethyl methyl sulfide and sodium phthalimidomalonate is proposed.

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(15) Snyder, Andreen, Cannon and Peters, THIS JOURNAL, **64**, 2082 (1942).

(16) Bennett, *J. Chem. Soc.*, **119**, 418 (1921).

(17) Barger and Coyne, *Biochem. J.*, **22**, 1417 (1928).