as a base was determined by titration of a sample in acetonitrile with 0.1 *N* perchloric acid in dioxane using the conventional techniques discussed by Fritz.[6] The titration data and elemental analyses are in excellent agreement with the values required for a basic zinc double salt.

Anal. Calc'd for $C_{24}H_{55}O_7P_3S_6Zn_2$: P, 10.66; S, 22.07; Zn, 15.00; Neut. Equiv. (as a base), 872; Neut. Equiv. (as an acid), 291. Found: P, 10.7; S, 22.2; Zn, 15.1; Neut. Equiv. (as a base), 880; Neut. Equiv. (as an acid), 295.

This composition was substantiated further by synthesis, using the stoichiometric ratios of phosphorodithioic acid: $Zn^{++}:OH^- = 3:2:4$ as required by the proposed formula.

B. Synthesis. Purified O,O-di-*n*-butyl phosphorodithioic acid (24.4 g., 0.1 mole) was added to a solution of 5.5 g. (0.133 mole) of 97% sodium hydroxide in 200 ml. of water containing 50 g. of ice. A very small amount of insoluble oil was removed by filtration of the solution through filter aid. A solution of 9.1 g. (0.067 mole) of zinc chloride in 50 ml. of water was added slowly with manual stirring. The solid crystalline basic zinc double salt began to form immediately; there was no evidence of the liquid normal salt. The yield of air-dried product was 26.0 g. (89.5%). It was identical with the by-product material described previously.

Zinc O,O-diisopropyl phosphorodithioate. A solution of 15.2 g. (0.06 mole) of potassium O,O-diisopropyl phosphorodithioate[7] in 200 ml. of water was treated with 15.0 ml. of 2 *M* zinc chloride solution giving an 86.5% yield (12.7 g.) of crystalline product, m.p. 147–148°.

Anal. Calc'd for $C_{12}H_{28}O_4P_2S_4Zn$: P, 12.60; S, 26.07; Zn, 13.29; Neut. Equiv. (as an acid), 246. Found: P, 12.6; S, 25.9; Zn, 13.9; Neut. Equiv. (as an acid), 253.

No basicity was indicated by titration with perchloric acid.

Basic zinc double salt of O,O-diisopropyl phosphorodithioic acid. A solution of 15.2 g. (0.06 mole) of potassium O,O-diisopropyl phosphorodithioate in 200 ml. of water containing 0.02 mole of sodium hydroxide was treated with 20 ml. of 2 *M* zinc chloride solution. A 13.5 g. (86.0%) yield of crystalline solid was obtained. After recrystallization from cyclohexane it melted at 204–206°.

Anal. Calc'd for $C_{18}H_{43}O_7P_3S_6Zn_2$: P, 11.80; S, 24.42; Zn, 16.59; Neut. Equiv. (as a base), 788; Neut. Equiv. (as an acid), 263. Found: P, 11.7; S, 25.0; Zn, 17.0; Neut. Equiv. (as a base), 798; Neut. Equiv. (as an acid), 281.

Infrared spectra. The infrared absorption spectra of the normal zinc salts were compared with those of basic zinc double salts using a Perkin-Elmer Model 21 double-beam Infrared Spectrophotometer. The two series of salts, examined as Nujol mulls, exhibited essentially the same spectra, with minor exceptions. The normal salts show a shoulder at 1025 cm.$^{-1}$ on the side of the very strong P—O band at 980 cm.$^{-1}$.[8] The normal salts have a medium strong band at 785 cm.$^{-1}$ that the basic salts lack. A band at 1110 cm.$^{-1}$ in the basic salts is lowered 5 cm.$^{-1}$ in the normal salts, and a band at 665 cm.$^{-1}$ in the basic salts is not present in the normal salts. No O—H stretching frequency was observed in the spectrum of the basic salt.

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(6) Fritz, *Acid-Base Titrations in Non-aqueous Solvents*, G. F. Smith Chemical Company, Columbus, Ohio, 1952, p. 9 ff.

(7) Hoegberg and Cassaday, *J. Am. Chem. Soc.*, **73**, 557 (1951).

(8) Gore, *Faraday Society Discussion*, No. 9, 138 (1950), discusses the infrared absorption spectra of phosphorothioic acid derivatives.

The Synthesis of N-(2-oxoalkyl)-N-methylamides[1] from Sarcosine and Acyl Chlorides in Ethyl Acetate

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The synthesis of some high molecular weight acyl sarcosines was approached by applying the direct amino acid acylation procedure of Ronwin,[2] in which a heterogeneous mixture of amino acid and a solution of the acyl chloride in anhydrous ethyl acetate is heated at reflux temperature. The reactions of myristoyl and palmitoyl chlorides with sarcosine progressed slowly under these conditions, and reflux time was extended to 48 hours. The products from these two reactions (2:1 excess of acyl chloride) proved to be N-(2-oxoalkyl)-N-methylamides instead of acylated sarcosines.

$$2RCOCl + CH_3NHCH_2COOH \xrightarrow[\text{ethyl acetate}]{\text{48 hr. reflux in}} RCON(CH_3)CH_2COR$$

$$R = C_{13}H_{27};\ C_{15}H_{31}$$

A similar reaction of sarcosine, to form N-acetonyl-N-methylacetamide, has been reported.[3] This was the basis for determining that an azlactone is not necessarily an intermediate in the conversion of α-amino acids to "acylamido ketones" in basic solution, as had been proposed previously.[4] The synthesis of the amide compounds from sarcosine, reported here, (a) furnishes additional evidence in this respect, (b) extends the reaction to include high molecular weight acylating agents, and (c) is the first instance, to the authors' knowledge, of the formation of these compounds from an N-alkyl-α-amino acid in the absence of a basic solvent such as pyridine.

EXPERIMENTAL

N-(2-oxopentadecyl)-N-methylmyristamide (I). Sarcosine, 4.46 g. (0.05 mole), and a solution of 24.6 g. (0.10 mole) of myristoyl chloride in 80 ml. of anhydrous ethyl acetate were heated at reflux temperature for 48 hours. The reaction mixture was cooled, filtered, and the filtrate was evaporated to a crystalline residue with a stream of dry air. Recrystallizations from acetone, carbon tetrachloride, and ethanol gave a product melting at 72–73°;[5] further purification from ethyl acetate and from acetone gave I, melting sharply at 75°; 2.91 g. (12.5%); the compound was soluble in concen-

(1) Nomenclature as amides according to *Chem. Abstr.*, **39**, 5876 (1945); This type of compound is frequently referred to in the literature as an *acylamido ketone*.

(2) Ronwin, *J. Org. Chem.*, **18**, 127, 1546 (1953).

(3) Wiley, *Science*, 111, 259 (1950); Wiley and Borum, *J. Am. Chem. Soc.*, **72**, 1626 (1950).

(4) Dakin and West, *J. Biol. Chem.*, **78**, 91, 745 (1928); Cleland and Niemann, *J. Am. Chem. Soc.*, **71**, 841 (1949).

(5) All melting points are uncorrected.

trated sulfuric acid and in ether, insoluble in dilute hydrochloric acid and sodium hydroxide, and formed a hydrazone (not analyzed) rapidly with 2,4-dinitrophenylhydrazine in perchloric acid.[6]

Anal. Calc'd for $C_{30}H_{59}NO_2$: C, 77.35; H, 12.77; N, 3.01. Found: C, 77.87; H, 12.91; N, 2.85.

N-(2-oxoheptadecyl)-N-methylpalmitamide (II). The reaction, as above, of sarcosine and palmitoyl chloride gave 37.1% of II, melting sharply at 82°, after recrystallizations from 85% ethanol, ethyl acetate, and from acetone-water mixtures. The properties of II were analogous to those described for I.

Anal. Calc'd for $C_{34}H_{67}NO_2$: C, 78.24; H, 12.94; N, 2.68. Found: C, 78.53; H, 12.99; N, 2.85.

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(6) Neuberg, Grauer, and Pisha, *Anal. Chim. Acta*, **7**, 238 (1952).

The Mono-2,4-dinitrophenylhydrazones of Diacetyl and Glyoxal

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Diacetyl monodinitrophenylhydrazone can easily be prepared in aqueous hydrochloric acid, in chloroform-acetic acid, or by refluxing an alcoholic solution of the components. In order to avoid osazone formation it is advisable to use an excess of diacetyl. The monodinitrophenylhydrazone shows an infrared band at 5.97 μ (keto group) and an absorption maximum at 350 mμ. This maximum is at a wave-length 13 mμ shorter than in acetone dinitrophenylhydrazone (λ_{max} 363 mμ). A similar effect of an adjacent keto group was previously observed in the spectra of methyl propyl ketone dinitrophenylhydrazone and hexane-2,3-dione monodinitrophenylhydrazone.[1] In distinction from the dinitrophenylhydrazones of other ketones that of diacetyl dissolves with a red color in alcoholic sodium hydroxide solution.

Neither method mentioned above could be used for the preparation of glyoxal monodinitrophenylhydrazone.[2] In every case only glyoxal dinitrophenylosazone was obtained, although an excess of glyoxal was used. It was found, however, that an alcoholic solution of glyoxal reacts very readily with dinitrophenylhydrazine at room temperature to give a mixture of the osazone and the monodinitrophenylhydrazone. Since the latter is soluble in ethanol, it can easily be separated from the completely insoluble osazone. The great reactivity of glyoxal is best illustrated by a comparison with acetone which, under similar conditions, gives only 12% dinitrophenylhydrazone. The glyoxal monodinitrophenylhydrazone shows an infrared band at 5.95 μ (aldehyde group). Since it exhibits maximum absorption at 343 mμ, the shift to shorter wavelengths in comparison with formaldehyde dinitrophenylhydrazone (λ_{max} 347 mμ) amounts only to 4 mμ.

(1) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

(2) Glyoxal monophenylhydrazone was described by H. O. L. Fischer and C. Taube, *Ber.*, **59**, 856 (1926).

EXPERIMENTAL[3]

Diacetyl monodinitrophenylhydrazone. (*a*). A solution of 0.1 ml. of diacetyl (98 mg.) in 5 ml. of ethanol was added to a suspension of 113 mg. of 2,4-dinitrophenylhydrazine in 68 ml. of chloroform and 11.3 ml. of glacial acetic acid. After standing overnight, the clear yellow solution was washed to neutrality, dried, and evaporated. The residue was chromatographed on 5 g. of neutral aluminum oxide Woelm and eluted with hexane-benzene 1:1. Two recrystallizations from chloroform-ethanol gave small yellow prisms, m.p. 176–177°; λ_{max} 350 mμ (ϵ 26,260); infrared band at 5.97 μ. The substance dissolved with red color in alcoholic NaOH. Large crystals sometimes were orange in color.

Anal. Calc'd for $C_{10}H_{10}N_4O_5$: N, 21.05. Found: N, 21.22.

(*b*). A mixture of 113 mg. of dinitrophenylhydrazine, 0.1 ml. of diacetyl, and 15 ml. of ethanol was refluxed for two hours. The orange crystals which separated on cooling were washed with cold ethanol, dried, and chromatographed as described above. After recrystallization from chloroform-ethanol, 79 mg. of yellow prisms were obtained which proved to be identical with the product from procedure (*a*).

(*c*). Diacetyl (58.8 mg.) in 6 ml. of 2 *N* HCl was added to 67.6 mg. of dinitrophenylhydrazine in 16.9 ml. of 2 *N* HCl. The yellow crystals (89.5 mg.) were filtered after 5 minutes, washed with water, dried, and recrystallized from chloroform-ethanol; m.p. 176–177°.

Glyoxal monodinitrophenylhydrazone. A suspension of 200 mg. of dinitrophenylhydrazine in 25 ml. of ethanol and 1 ml. of glyoxal was stirred for two hours. The dinitrophenylhydrazine dissolved and the orange glyoxal dinitrophenylosazone precipitated. The mixture was kept in the refrigerator overnight, filtered, and diluted with 25 ml. of water. Upon renewed cooling, light-orange crystals appeared which were washed with 40% ethanol and dried (yield 113 mg.). They gave a red-brown color with alcoholic NaOH and melted at 190°; λ_{max} 343 mμ (ϵ 24,210); infrared band at 5.95 μ.

Anal. Calc'd for $C_8H_6N_5O_4$: N, 23.53. Found: N, 23.63.

This dinitrophenylhydrazone could neither be chromatographed nor recrystallized satisfactorily. A sample was dissolved in hot ethanol and cooled. Upon addition of a few drops of concentrated hydrochloric acid, glyoxal dinitrophenylosazone precipitated almost immediately.

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(3) The melting points were determined on a Fisher-Johns melting point block and are uncorrected. The ultraviolet spectra were taken in chloroform on a Cary recording spectrophotometer, the infrared spectra on a Baird double-beam spectrophotometer (KBr wafer technique). The microanalyses were carried out by Huffman Microanalytical Laboratories, Wheatridge, Colo.