NEW COMPOUNDS

p-Benzyloxy-α-methylbenzyl Alcohol

To 113 g. (0.5 mole) of *p*-benzyloxyacetophenone,[1] dissolved in 500 cc. of methanol, was added 2 g. of copper chromite catalyst. The reduction mixture was shaken at 100° under 1500 pounds pressure for one and one-half hours, when no more hydrogen was absorbed. The catalyst was filtered off and the methanol removed under reduced pressure. On recrystallization of the crude product from ethanol, a 92% yield of white crystals, m. p. 83–84°, was obtained.

Anal.[2] Calcd. for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02; active hydrogen, 1. Found: C, 78.47; H, 7.38; active hydrogen (Zerewitinoff), 0.97.

(1) Prepared according to the directions of Suter and Ruddy, THIS JOURNAL, **66**, 747 (1944).

(2) Analyses by Miss F. B. Durkee and J. B. Dunphy.

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Characterization of Dibutylamine

The derivatives listed in the accompanying table have been prepared for the characterization of N,N-dibutylamine. They were obtained in substantially quantitative yields as follows: The sulfonamides by the reaction of the amine with benzenesulfonyl chloride or a derivative in the presence of a slight excess of an aqueous solution of 10% sodium hydroxide; the ureas by the reaction of the amine with phenyl isocyanate or phenyl isothiocyanate, and the amine hydrochloride with α-naphthyl isocyanate, treatment of the resulting solids with petroleum ether (b. p. 60–70°) and recrystallization from ethanol.

TABLE I

Derivative	M. p., °C. (cor.)	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Benzenesulfonamide[a]	[b]	$C_{14}H_{23}NSO_2$	62.5	62.3	8.55	8.55	5.20	5.20
p-Bromobenzenesulfonamide	60.5–60.6	$C_{14}H_{22}NBrSO_2$	48.3	48.3	6.36	6.35	4.02	4.06
Phenylurea	85.4	$C_{15}H_{24}N_2O$	72.5	72.6	9.74	9.78	11.3	11.1
α-Naphthylurea	73.6	$C_{19}H_{26}N_2O$	76.4	76.0	8.78	8.79	9.39	9.55
Phenylthiourea	85.5–86.0	$C_{15}H_{24}N_2S$	68.1	68.3	9.15	9.19	10.6	10.6

[a] $n^{25}D$ 1.5054. [b] B. p. 211–211.5° (17 mm.) and 202.5–203° (12 mm.).

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2-Thio-6-cyclopropyl-uracil

2-Thio-6-cyclopropyl-uracil was prepared by the condensation of ethyl β-keto-β-cyclopropylpropionate with thiourea in sodium ethylate solution. The intermediate, ethyl β-keto-β-cyclopropylpropionate was prepared from cyclopropyl methyl ketone and diethyl carbonate according to the method for synthesis of β-keto esters described by Wallingford, Homeyer and Jones[1] with a few minor variations.

(1) Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2252 (1941).

Ethyl β-Keto-β-cyclopropylpropionate.—To a slurry of two moles of sodium ethylate in 1400 ml. of diethyl carbonate, 168 g. of methyl cyclopropyl ketone was added at 120 mm. pressure over a ten-minute period at a bath temperature of 50°. The bath temperature was raised to 60° and maintained between 60–70° for two hours, during which time stirring was continued, the sodium ethylate slowly dissolved and 340 ml. of distillate was collected, mainly ethanol, at a boiling range of 40–50°. The cooled reaction mixture was treated in the usual manner, fractionation giving a yield of 81 g. (58%) of ethyl β-keto-β-cyclopropylpropionate, b. p. 74–78° (4 mm.).

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.51; H, 7.74. Found: C, 60.88; H, 7.73.

2-Thio-6-cyclopropyl-uracil.—A solution of 48.3 g. of sodium in 950 ml. of dry ethanol was prepared in a 3-liter, 3-necked flask fitted with a mercury sealed stirrer, reflux condenser and dropping funnel. To the solution at room temperature was added 80 g. of thiourea with stirring, followed by 164 g. of ethyl β-keto-β-cyclopropylpropionate over a period of five minutes. The mixture was then heated to gentle reflux, with stirring, for five hours, after which the flask was fitted with a downward condenser and the alcohol removed by distillation. The residue was dissolved in 1100 ml. of water, filtered to remove insoluble material and the cooled filtrate acidified by the addition of glacial acetic acid. The white precipitate was filtered, washed with water and dried to give 109 g. (61%) of crude product, m. p. 221–226°. After two crystallizations from water the product weighed 76.7 g. (43.4%) and melted at 239–240°.

Anal. Calcd. for $C_7H_8N_2OS$: N, 16.65; S, 19.06. Found: N, 16.86; S, 19.39.

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RECEIVED APRIL 9, 1947

Thiocyanation of Kojic Acid

Fourteen and two-tenths grams (0.1 mole) of finely powdered kojic acid was added to a cooled mixture of 38.8 g. (0.4 mole) of powdered potassium thiocyanate in 100 ml. of glacial acetic acid. The resulting mixture was placed in an ice–water-bath and stirred mechanically while 32 g. (0.2 mole) of bromine in 25 ml. of acetic acid was added over a period of one-half hour. After all the bromine had been added the stirring was continued for another half hour. The material at this point was deep yellow-orange and most of the reaction compound had separated.

The reaction mixture was diluted with 300 ml. of water and filtered. The yellow-orange precipitate was washed repeatedly with water and then air dried. The crude yield was 13.3 g.

The impure thiocyanate addition product (kojic acid hexathiocyanate) was purified by refluxing it for five minutes in 200 ml. of 95% ethanol, and filtering off the compound from the hot alcohol.

The kojic acid derivative was only sparingly soluble in methanol, ethanol and in boiling water. The compound was almost insoluble in ether and cold water. It was remarkably stable, decomposing at 309–320°.

Anal. Calcd. for $C_6H_6O_4(CNS)_6$: N, 17.14. Found: N, 17.05.[1]

The synthesis of this addition compound of kojic acid was the result of an attempt to prepare the 6-thiocyanokojic acid.

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RECEIVED MARCH 18, 1947

(1) Analysis by Dr. Carl Tiedcke.

COMMUNICATIONS TO THE EDITOR

INFRARED SPECTRA AND STRUCTURE OF NATURAL AND SYNTHETIC POLYPEPTIDES

Sir:

We wish to report the main features of the infrared spectrum that we have obtained of a synthetic polypeptide recently prepared by Woodward and Schramm.[1] There is a very close resemblance between this spectrum and that of a film of denatured keratin,[2] as can be seen from Fig. 1.

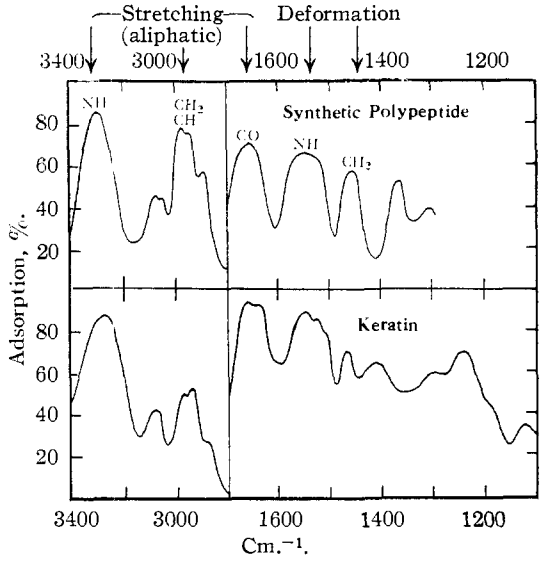

Fig. 1.—Infrared aborption spectra of Woodward and Schramm: synthetic polypeptide, and of keratin, 3400–1100 cm.$^{-1}$.

The interpretation of the principal bands is indicated on the curves. At the high frequency end of the spectrum the strong band at 3300 cm.$^{-1}$ arises from the stretching vibration of the NH bond. Its position and width show that the hydrogen atom is loosely bonded, presumably to the oxygen atom of the C=O group in a neighboring chain. The group of bands between 2970 and 2880 cm.$^{-1}$ arise from stretching vibrations of the CH groups in the methylene group and the "lone" CH of the side chain. The band at 1650 cm.$^{-1}$ arises from the C=O of the peptide link, while that at 1550 cm.$^{-1}$ is due to the deformation vibration of the NH group. The band at 1450 cm.$^{-1}$ is due to a well-known deformation vibration of the CH_2 group. The weak band near 3060 cm.$^{-1}$ is partly due to the CH stretching frequencies of the phenyl group but is also connected either with the NH or the C=O since it is associated with hydrogen with hydrogen bonding effects in simple amides.

The great similarity with the spectrum of keratin is thus fully explained and the fact that differences begin to appear only at frequencies below 1450 cm.$^{-1}$ is just what might be expected since it is in this region that skeletal and other frequencies characteristic of the residues in the polypeptide chain will occur. Indeed this illustrates another very important aspect of the use of these new synthetic polypeptides for by comparison with the spectrum of the parent amino acid it should be possible to identify with certainty the frequencies characterizing the residue of a given amino acid in a protein. We have found that this is not feasible with the smaller polypeptides hitherto available (*e. g.*, leucylglycylglycine) where the end groups still dominate the spectrum.

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RECEIVED JULY 19, 1947

(1) Woodward and Schramm, THIS JOURNAL, **69**, 1551 (1947). We thank Professor H. Mark for a small sample of this material supplied to him by Professor Woodward.

(2) Kindly supplied by the Wool Industries Research Association.

SYNTHESIS AND STRUCTURE OF TETRAHYDROPYRETHROLONE

Sir:

LaForge and Soloway[1] assigned the α-ketol structure (Ia) to the synthetic hydroxydihydrocinerone not identical with natural *dl*-dihydrocinerolone and proposed the β-ketol structure (IIa) for the other synthetic isomer identical with racemic natural material. Assignment of these structures was based on reinterpretation of earlier experimental evidence and on rational interpretation of the reactions employed, with the belief that N-bromosuccinimide characteristically brominates on the allylic position.[2] N-

(1) LaForge and Soloway, THIS JOURNAL, **69**, 186, 979 (1947).

(2) Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).