dl - Hexahydro - 2 - oxo - 4 - (4 - hydroxybutyl)-1-furo-(3,4)-imidazole (V), m. p. 154–155° (*Anal.* Calcd. for $C_9H_{16}O_3N_2$: C, 53.98; H, 8.05; N, 13.99. Found: C, 54.12; H, 7.81; N, 13.80) was obtained from 2-furanbutanol[2] (α-naphthylurethan, m. p. 72–73°; *Anal.* Calcd. for $C_{19}H_{19}O_3N$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.82; H, 6.17; N, 4.71) by the procedures developed in these laboratories for the synthesis of similar compounds.[1,3] Treatment of (V) with thionyl chloride gave *dl*-hexahydro-2-oxo-4-(4-chlorobutyl)-1-furo-(3,4)-imidazole (VI), m. p. 124–126° (*Anal.* Calcd. for $C_9H_{15}O_2N_2Cl$: C, 49.38; H, 6.90; N, 12.80; Cl, 16.22. Found: C, 49.16; H, 6.84; N, 12.54; Cl, 16.27), which on reaction with sodiobenzyl mercaptide was converted into the corresponding benzyl thioether (VII), m. p. 76–79° (*Anal.* Calcd. for $C_{16}H_{22}O_2N_2S$: C, 62.73; H, 7.24; N, 9.14; S, 10.46. Found: C, 62.54; H, 6.96; N, 9.31; S, 10.32). Reductive cleavage of (VII) yielded *dl*-hexahydro-2 - oxo - 4 - (4 - mercaptobutyl) - 1 - furo - (3,4)-imidazole (VIII), which on oxidation with barium permanganate was converted into the crystalline barium salt of oxybiotin sulfonic acid (I). (*Anal.* Calcd. for $C_9H_{15}O_5N_2S$ Ba/2: C, 32.53; H, 4.55; N, 8.44; S, 9.66; Ba, 20.69. Found: C, 32.58; H, 4.74; N, 8.18; S, 9.43; Ba, 20.33.) The configuration of (I) must be identical with that of *dl*-oxybiotin (III), since (VI) upon reaction with potassium cyanide followed by hydrolysis gave (III).

Similarly, *dl*-homoöxybiotin sulfonic acid (II) was prepared from *dl*-hexahydro-2-oxo-4-(5-chloropentyl)-1-furo-(3,4)-imidazole[1] through the corresponding benzyl thioether (IX), m. p. 66–68° (*Anal.* Calcd. for $C_{17}H_{24}O_2N_2S$: C, 63.73; H, 7.55; N, 8.74; S, 10.00. Found: C, 63.24; H, 7.36; N, 8.89; S, 10.30), and the mercaptopentanol (X). As in the case of the lower homolog (II) was also isolated in the form of its crystalline barium salt. (*Anal.* Calcd. for $C_{10}H_{17}O_5N_2SBa/2$: C, 34.70; H, 4.95; N, 8.10; S, 9.27; Ba, 19.86. Found: C, 34.37; H, 5.20; N, 8.14; S, 9.30; Ba, 19.60.) Compounds (I), (VII), (VIII), (IX), and (X) were found to have pronounced antibiotin and antioxybiotin activity for a number of microörganisms, in contrast to substance (II), which had a slight stimulatory effect. A detailed description of the synthesis and microbiological activity of these compounds will be presented in the near future.

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[2] Hofmann, Bridgwater and Axelrod, unpublished results.

[3] Hofmann, THIS JOURNAL, **67**, 1459 (1945).

FISSION OF BETA-OXYGENATED ORGANOSILICON COMPOUNDS

Sir:

Gilman and Clark in THIS JOURNAL, **69**, 967 (1947), quite naturally assume that the formation of acetone from the reaction product of triethylchlorosilane and sodioacetoacetic ester proves the absence of $Et_3SiCH(COCH_3)CO_2Et$. While that substance is likely absent, many studies in progress in this Laboratory on related β-oxygenated silicon compounds convince us that their reasoning is unsafe. Thus, we find that reactions expected to form $R_3SiCH_2COCH_3$ and $R_3SiCH_2CO_2H$ actually give acetone and acetic acid, respectively. Moreover, $R_3SiCH_2CHOHCH_3$ is sensitive to acid, giving propylene readily. In each case most of the silicon appears as $(R_3Si)_2O$.

Acetyl chloride and the Grignard reagent (I) from chloromethyltrimethylsilane[1] gave a yellow solid which, on decomposition with water, formed a variety of products including acetone. The latter was identified by conversion to dibenzalacetone, m. p. and mixed m. p. 111–113°.

Addition of carbon dioxide to (I) formed a colorless gel which, on steam distillation, gave hexamethyldisiloxane. The residue was acidified with dilute sulfuric acid and steam distilled. The distillate smelled strongly of acetic acid. This was identified as the *p*-phenylphenacyl derivative, m. p. 110–111°.

Acetaldehyde and (I) gave β-hydroxypropyltrimethylsilane, b. p. 48° at 10 mm., $n^{20}D$ 1.4281. *Anal.* Calcd. for $C_6H_{16}SiO$: Si, 21.2. Found: Si, 2.4. Warming with a few drops of 10% sulfuric acid gave a stream of gas which was converted to propylene dibromide, b. p. 139° at 728 mm., $n^{20}D$ 1.5196.

Other studies point to similar conclusions on the sensitivity to hydrolytic agents of the grouping Si—C—C—O in which the last two atoms may be singly or doubly bound in alcohols, ketones, acids, esters and the like. The resulting fissions are not surprising in view of the ease with which silicon can give an electron pair to an electronically deficient carbon atom in the position beta to it.[2]

[1] Whitmore and Sommer, THIS JOURNAL, **68**, 481 (1946).

[2] *Cf.* Whitmore, *ibid.*, **54**, 3277 (1932); **55**, 4153 (1933); Sommer, *et al.*, *ibid.*, **68**, 1083 (1946).

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SYNTHESIS OF PROTEIN ANALOGS

Sir:

We wish to record what we believe to be the first successful synthesis of molecules having, like fibrous proteins, the structure

$$\text{HOOC-CH}(R_1)\text{-NH-}(\text{COCH}(R_i)\text{NH})_n\text{-COCH}(R_{n+2})\text{NH}_2 \qquad \text{I}$$

with very large values of *n*.

We have used an ionic chain-polymerization reaction which has been observed before inadvertently (*cf.* Leuchs and Geiger, *Ber.*, **41,** 1721 (1908); Curtius and Sieber, *ibid.*, **55,** 1543 (1922); Wessely and John, *Z. physiol. Chem.*, **170,** 38 (1927)) but whose scope and generality do not appear to have been realized hitherto. Our monomers are the anhydrides (II) of N-carboxy-α-amino acids, and the initiator is water (in the experiments described here) or any substance XH, in which H is an active hydrogen atom. The reaction proceeds in the sense

$$\mathrm{H_2O} + \overline{\mathrm{COCH(R)NHCOO}}\ \mathrm{(II)} \longrightarrow \mathrm{HOOCCH(R)NHCOOH}$$

$$\xrightarrow{-\mathrm{CO_2}} \mathrm{HOOCCH(R)NH_2} \xrightarrow{+\mathrm{(II)}} \mathrm{HOOCCH(R)NHCOCH(R)NHCOOH}$$

$$\xrightarrow{-\mathrm{CO_2}} \mathrm{HOOCCH(R)NHCOCH(R)NH_2} \xrightarrow{+\mathrm{(II)}} \text{etc.}$$

Thus, each time a new peptide link is formed by the reaction of the active center ($-NH_2$) with a monomer molecule, a new, like, active center is generated by the (spontaneous) loss of carbon dioxide from the unstable grouping (—NHCOOH). The products of the reaction have the general formula (I), and the value of $\bar{n}$ is determined by (a) the supply of monomer molecules (which may be augmented after any particular value of $\bar{n}$ has been reached), (b) the relative concentrations of monomer and initiator and (c) the relative rates of the initiation and propagation reactions.

When N-carboxy-*l*-leucine anhydride (m. p. 76.5–78°; Found: C, 53.70; H, 7.01; N, 8.70. Calcd. for $C_7H_{11}O_3N$: C, 53.49; H, 7.06; N, 8.91) and N-carboxy-*dl*-phenylalanine anhydride (Leuchs and Geiger, *loc. cit.,*) were copolymerized in ordinary reagent benzene (the very small amount of water present in the solvent serving as initiator), the solution gradually became more viscous as reaction proceeded. After two weeks at room temperature, such solutions, when cast, left optically clear, tough, mechanically stable films (Found: C, 68.6; H, 8.5. Calcd.: C, 68.6; H, 7.9). Solutions of such films in benzene had $[\eta] = \lim\limits_{c \to 0} \frac{\ln \eta_{rel}}{c} = \sim 10$. Though it is impossible to assign with confidence values of K and α in the equation $[\eta] = KM^\alpha$ for this high polymeric species, the use of the extreme values of the parameters for all known polymers leads to the bracketing of the average molecular weight of the film-forming molecules within the limits 1,000,000–15,000,000. Careful osmotic measurements of 0.50% and 0.75% benzene solutions of the film in the sensitive Fuoss osmometer (Fuoss and Mead, *J. Phys. Chem.*, **47,** 59 (1943)) gave values of Δh not significantly different from 0; this result indicates a minimum average molecular weight of several million.

Thus, these synthetic molecules have the structure (I), with R_i variously $(CH_3)_2CHCH_2$- and $C_6H_5CH_2$-, and $\bar{n} \gtrless 10{,}000$.[1]

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[1] We wish to thank Mr. H. T. Wolosinski of Polaroid Corporation and Dr. Harry F. Herbrandson of these laboratories for assistance in carrying out physical measurements, and Eli Lilly and Co. for supplies of amino-acids and support of a fellowship for one of us (C. H. S.).

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NEW BOOKS

The Photography of the Reciprocal Lattice. By M. J. BUERGER, Massachusetts Institute of Technology, Cambridge, Massachusetts (ASXRED Monograph Number 1). Published by the American Society for X-Ray and Electron Diffraction, August, 1944. 37 pp. 18 figs. 16 × 24 cm. Copies obtainable at $1.50 each from The Murray Printing Company, 18 Ames St., Cambridge 42, Massachusetts.

In the analysis of complex crystal structures with the aid of X-ray diffraction data, it is convenient to deal with an imaginary "reciprocal lattice," in which each lattice point can be associated with a possible X-ray reflection. There is a direct correspondence between the locations of the diffraction spots on a Weissenberg photograph, for example, and the coördinates of the reciprocal lattice points. As shown by de Jong and Bouman, an X-ray photograph in which the diffraction spot pattern is a scale representation of a plane in the reciprocal lattice can be produced by making the crystal undergo the proper precessional motion. Such a photograph is somewhat simpler to interpret than a Weissenberg photograph, and has certain other advantages.

The present monograph describes the author's modification of de Jong and Bouman's apparatus, gives the basic theory underlying it, and outlines the interpretation of the resulting pictures. It is a useful addition to the literature dealing with crystal structure analysis methods.

MAURICE L. HUGGINS

Concise Chemical and Technical Dictionary. Edited by H. BENNETT, Technical Director, the Glyco Products Co., Inc., Editor-in-chief, *The Chemical Formulary; Practical Emulsions; Commercial Waxes*, etc. Chemical Publishing Co., Inc., Brooklyn 2, N. Y. 1947. xxx + 1055 pp. 15 × 23.5 cm. Price, $10.00.

For its handy size this volume contains an astonishing amount of definitive information, although it appears to be more suited to the needs of the technical user than to those of the teacher or student. The 50,000 terms listed include many trade names, such as Vel and Dreft of recent origin, 14 varieties of Nopco and eight of Pentaryl, as well as many of purely scientific use. Mineralogy, medicine, botany and many other special fields are represented with