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

$$HOOC\text{-}CH(R_1)\text{-}NH\text{-}(COCH(R_i)NH)_n\text{-}COCH(R_{n+2})NH_2$$
I

with very large values of n.