equiv., 190. Found: C, 63.21; H, 3.31; neut. equiv., 188.

The large clusters, m. p. 197° (dec.), 7.0 g., were *o*-phthalic acid.

3-Methylenephthalide.—*o*-Acetobenzoic acid, 3.28 g. (0.02 mole), and 5.0 ml. of acetyl chloride were refluxed gently for one and one-half hours. An external bath temperature of 50° was maintained while the excess acetyl chloride was removed under reduced pressure. The oily residue was treated with 10 ml. of water and enough 10% aqueous ammonia to make the mixture alkaline to litmus. At this point the oil had partially solidified. The mixture was extracted with ether and the ether extracts dried over anhydrous sodium sulfate. The ether was distilled *in vacuo* leaving a semi-solid residue, 2.2 g. This was dissolved in 4.0 ml. of acetone, centrifuged and the clear acetone solution decanted. When diluted with 10 ml. of water an oil separated and soon solidified, 1.5 g., m. p. 50–55°. It was sublimed at 1–2 mm. with a bath at 45–50° and 0.65 g., m. p. 57°, of product was obtained. Gabriel[2] reported a m. p. of 58–60°. The sublimed material could be crystallized from hexane.

Anal. Calcd. for $C_9H_6O_2$: C, 73.97; H, 4.11. Found: C, 73.38; H, 4.21.

The aqueous ammoniacal solution was evaporated to dryness. From the residue there was obtained 0.5 g. of *o*-acetobenzoic acid.

The yield of 3-methylenephthalide was 26.2%.

THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH
DIVISION OF MEDICINAL CHEMISTRY
NEW BRUNSWICK, N. J. RECEIVED FEBRUARY 7, 1947

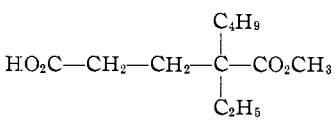
COMMUNICATIONS TO THE EDITOR

REARRANGEMENT IN PREPARATION OF ESTER ACID CHLORIDES

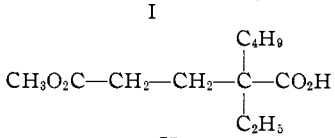
Sir:

In conversion of the half ester of a dibasic acid to the ester acid chloride, it has been assumed that the chlorine becomes attached to the carbon originally present as carboxyl. Thus, Bardhan[1] prepared acid chlorides from the two half esters of trimethylsuccinic acid, and treated each with methylzinc iodide. In each case there was obtained a "similar" mixture of ethyl α,α,β-trimethyllevulinate and ethyl α,β,β-trimethyllevulinate. This was ascribed to the half esters used as starting materials being a similar mixture of isomers, in spite of convincing evidence[2] that half esters so obtained are largely a single isomer.

We have obtained the isomeric half esters, I and II, of α-butyl-α-ethylglutaric acid.[3] Here the



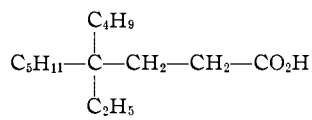
I



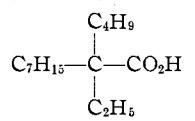
II

hindrance around one carboxyl is so great that the essential homogeneity of the isomers is assured. Esterification of the acid with a large excess of methanol in presence of sulfuric acid gave a high yield of II after one hour under reflux, whereas a 10% yield of II remained after one hundred forty hours under reflux. Each isomer was converted to the acid chloride with thionyl chloride and these heated with tribromoaniline in xylene. From each isomer was obtained a poor yield of a tribromoanilide, m. p. 127–128°, no depression on mixing the two. *Anal.* Calcd. for $C_{18}H_{24}NO_3Br_3$: C, 39.88; H, 4.45. Found: C, 39.94; H, 4.50. Thus, a mixture of ester acid chlorides must have been obtained from each isomer, and there was isolated only the tribromoanilide resulting from reaction with the unhindered acid chloride.

Further, the acid chloride from each isomeric half ester was treated with dibutylcadmium,[4] and the resulting mixture of keto esters was reduced by the modified Wolff–Kishner procedure.[5] There was obtained in the two cases nearly identical mixtures of acids of the expected equivalent weight and b. p. 148.5–149.5° (1.5 mm.). This mixture was separated into the acids, III (*ca.* 25%) and IV



III



IV

(*ca.* 75%), by virtue of the rapid esterification of III and the very slow esterification of IV. When the esterification procedure used was repeated on the residual IV, no ester was detected. *Anal.* Calcd. for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48; eq. wt., 242.4. Found for III: C, 74.09; H, 12.39; eq. wt., 245.7. Found for IV: C, 74.17; H, 12.01; eq. wt., 241.5; $n^{27}D$ for III, 1.4533; for IV, 1.4472. *p*-Bromoanilide of III, m. p. 88.5–89.0°; of IV, m. p. 121.5–122°. *Anal.* Calcd. for $C_{21}H_{34}NOBr$: C, 63.62; H, 8.65. Found for deriv. of III: C, 64.11; H, 8.42. Found for deriv. of IV: C, 63.51; H, 8.72.

CHEMICAL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF. JAMES CASON

RECEIVED MAY 26, 1947

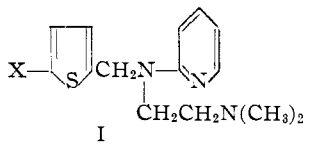
(1) Bardhan, *J. Chem. Soc.*, 2604 (1928).
(2) Bone, Sudborough and Sprankling, *ibid.*, **85**, 534 (1904).
(3) Bruson and Riener, THIS JOURNAL, **66**, 56 (1944).
(4) Cason, *ibid.*, **68**, 2078 (1946).
(5) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

HALOGENATED THIOPHENE DERIVATIVES AS ANTIHISTAMINE AGENTS

Sir:

The preparation of N,N-dimethyl-N′-(2-pyridyl)-N′-(2-thenyl)-ethylenediamine (I, X = H) and its antihistamine activity have been reported recently.[1] This compound is the thiophene analog of N,N-dimethyl-N′-(2-pyridyl)-N′-benzylethylenediamine (Pyribenzamine).[2]

Prior to the publication of these results,[1] we had also prepared this compound and pharmacological tests had been carried out in these Laboratories.[3] The results obtained confirm those reported earlier,[1] in that the compound is of the same order of activity as is Pyribenzamine *in vivo* and of the same order of acute toxicity.



I

In addition, however, we have prepared N,N-dimethyl - N′ - (2 - pyridyl) - N′ - (5 - bromo - 2-thenyl)-ethylenediamine (I, X = Br) and N,N-dimethyl - N′ - (2 - pyridyl) - N′ - (5 - chloro - 2-thenyl)-ethylenediamine (I, X = Cl). In tests using the isolated guinea pig ileum, these halogenated compounds were more active than Pyribenzamine. Preliminary tests in animals indicate that they have at least twice the antihistamine activity, twice the duration of action, and one-half the acute toxicity of Pyribenzamine.

These compounds were prepared by the reaction of 5-bromo-2-thenyl chloride and 5-chloro-2-thenyl chloride with N,N-dimethyl-N′-(2-pyridyl)-ethylenediamine.[2,4] 5-Bromo-2-thenyl chloride, b. p. 82–83° at 1 mm., was obtained in 70–80% yield from the chloromethylation of 2-bromothiophene by the method used previously with thiophene.[5] *Anal.* Calcd. for C_5H_4BrClS: Cl, 16.8. Found: Cl (by hydrolysis), 16.9%. 5-Chloro-2-thenyl chloride, b. p. 67–68° at 1 mm., was prepared similarly by the chloromethylation of 2-chlorothiophene. *Anal.* Calcd. for $C_5H_4Cl_2S$: Cl (by hydrolysis), 21.2%. Found: Cl, 21.1.

The condensation of 5-bromo-2-thenyl chloride and N,N - dimethyl - N′ - (2-pyridyl) - ethylenediamine using sodium[2] or potassium amide gave N,N - dimethyl - N′ - (2 - pyridyl) - N′ - (5-bromo - 2 - thenyl) - ethylenediamine (I, X = Br), b. p. 173–175° at 1 mm., in 54% yield. The monohydrochloride melted at 124–126°. *Anal.* Calcd. for $C_{14}H_{19}BrClN_3S$: C, 44.6; H, 5.1; N, 11.1; S, 8.5. Found: C, 44.9, 44.8; H, 5.3, 5.1; N, 11.0, 11.0: S, 8.7, 8.6. N,N-Dimethyl-N′-(2 - pyridyl) - N′ - (5 - chloro - 2 - thenyl) - ethylenediamine (I, X = Cl), b. p. 155–156° at 1 mm., was obtained similarly in 62% yield. The monohydrochloride of this compound melted at 106–108°. *Anal.* Calcd. for $C_{14}H_{19}Cl_2N_3S$: C, 50.6; H, 5.8; N, 12.6. Found: C, 50.8, 50.9; H, 6.0, 6.2; N, 12.3, 12.3.

These compounds will be described more fully in a further publication along with other compounds prepared in the course of this study.

CHEMOTHERAPY DIVISION
STAMFORD RESEARCH LABORATORIES
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R. C. CLAPP
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RECEIVED MAY 17, 1947

(1) A. W. Weston, THIS JOURNAL, **69**, 980 (1947).

(2) Huttrer, Djerassi, Beears, Mayer and Scholz, *ibid.*, **68**, 1999 (1946).

(3) Litchfield, Goddard, Adams and Jaeger, *Bull. Johns Hopkins Hosp.*, in press.

(4) Whitmore, Mosher, Goldsmith and Rytina, THIS JOURNAL, **67**, 393 (1945).

(5) Blicke and Leonard, *ibid.*, **68**, 1934 (1946).

STREPTOMYCIN. V.[1] DEGRADATION OF STREPTOMYCIN B TO STREPTIDINE, STREPTOBIOSAMINE AND D-MANNOSE

Sir:

Streptomycin B[1] has been degraded to derivatives of streptidine, streptobiosamine and D-mannose. It appears to be a triacidic base of the formula $C_{27}H_{49}O_{17}N_7$.

Methanolysis of streptomycin B with 1.3 *N* methanolic hydrogen chloride for five days at room temperature followed by acetylation afforded methyl tetraacetyl streptobiosaminide dimethyl acetal,[2] m. p. 124–125° (cor.); $[\alpha]^{25}D$ −122° (*c*, 0.56 in chloroform) and α-methyl tetraacetyl D-mannopyranoside, m. p. 65–66° (cor.) unchanged on admixture of an authentic specimen; $[\alpha]^{25}D$ +49° (*c*, 1.1 in chloroform).

Anal. Calcd. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.12; OCH_3, 8.56; CH_3CO, 47.5. Found: C, 50.01; H, 6.08; OCH_3, 8.98; CH_3CO, 47.7.

Treatment of streptomycin B with ethylmercaptan and concentrated hydrochloric acid for eighteen hours at room temperature and subsequent acetylation of the vacuum-dried residue afforded streptidine octaacetate, m. p. 255–257° (cor. dec.), β-thioethyl tetraacetyl streptobiosaminide diethyl mercaptal,[3] m. p. 112–113° (cor.); $[\alpha]^{25}D$ −30° (*c*, 0.95 in chloroform), and two isomeric thioethyl tetraacetyl hexosides: A, m. p. 107–108° (cor.), $[\alpha]^{25}D$ +94° (*c*, 1.06 in chloroform); and B, m. p. 161–162° (cor.), $[\alpha]^{25}D$ −67° (*c*, 0.51 in chloroform).

Anal. Calcd. for $C_{16}H_{24}O_9S$: C, 48.98; H, 6.17; S, 8.16; CH_3CO, 43.84; mol. wt., 392.4. Found for A: C, 48.91; H, 6.04; S, 8.17; CH_3CO, 44.2; mol. wt. (Rast), 378. Found for B: C, 49.16; H, 6.28; S, 8.41; CH_3CO, 43.3.

The hitherto undescribed β-thioethyl tetraacetyl D-mannoside was prepared from D-mannose by

(1) Paper IV of this series: J. Fried and E. Titus, *J. Biol. Chem.*, **168**, 391 (1947).

(2) N. G. Brink, F. A. Kuehl, Jr., and K. Folkers, *Science*, **102**, 506 (1945).

(3) I. R. Hooper, L. H. Klemm, W. J. Polglase and M. L. Wolfrom, THIS JOURNAL, **68**, 2120 (1946).

a similar procedure and shown to be identical with the higher-melting isomer B from streptomycin B by melting point (161–162°, no depression on admixture of isomer B), rotation ($[\alpha]^{25}D$ −65° (*c*, 1.1 in chloroform)), and analysis (C, 49.19; H, 5.98; S, 8.41; CH_3CO, 44.7). The dextrorotatory isomer A from streptomycin B presumably represents the previously unknown anomeric α-thioethyl-tetracetyl-D-mannoside.

Dihydrostreptomycin B trihydrochloride[1], m. p. 194–5° (cor. dec.), $[\alpha]^{25}D$ −55° (*c*, 0.9 in water), on treatment with 3% methanolic hydrogen chloride for forty hours at room temperature and subsequent acetylation yielded α-methyl pentaacetyl dihydrostreptobiosaminide[4,5] m. p. 192–3° (cor.). $[\alpha]^{25}D$ −119° (*c*, 0.49 in chloroform) and β-methyl tetraacetyl D-mannopyranoside, $[\alpha]^{25}D$ −50° (*c*, 0.69 in chloroform), m. p. 160–161° (cor.), unchanged on admixture of an authentic specimen.

Anal. Calcd. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.12; OCH_3, 8.56; CH_3CO, 47.5. Found: C, 49.61; H, 6.08; OCH_3, 8.35; CH_3CO, 48.5.

These results together with analytical data previously reported[1] for the reineckate[1] and hydrochloride of streptomycin B indicate that streptomycin B is made up of streptidine, streptobiosamine and D-mannose joined glycosidically to form a triacidic base of the composition $C_{27}H_{49}O_{17}N_7$.

Anal. Calcd. for $C_{27}H_{49}O_{17}N_7 \cdot 3HCr[(NH_3)_2(SCN)_4] \cdot 2H_2O$: C, 26.97; H, 4.29; N, 20.15; S, 22.11; Cr, 8.98. Found[1] (after drying *in vacuo* at 80° for two hours): C, 26.89; H, 4.24; N, 20.1; S, 22.2; Cr, 8.70. Calcd. for $C_{27}H_{49}O_{17}N_7 \cdot 3HCl \cdot H_2O$: C, 37.26; H, 6.24; N, 11.25; Cl, 12.23. Found (after drying *in vacuo* at 140° for two hours): C, 36.85; H, 6.11; N, 11.3; Cl, 12.83.

(4) J. Fried and O. Wintersteiner, THIS JOURNAL, **69**, 79 (1947).

(5) Q. R. Bartz, J. Controulis, H. M. Crooks, Jr., and M. C. Rebstock, *ibid.*, **68**, 2163 (1946).

DIVISION OF ORGANIC CHEMISTRY JOSEF FRIED
THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH
NEW BRUNSWICK, NEW JERSEY HOMER E. STAVELY

RECEIVED MAY 19, 1947

THE REACTION OF IODONIUM SALTS WITH THIOL COMPOUNDS

Sir:

In the interesting paper by Freedlander and French[1] on the chemotherapy of certain iodonium compounds, they have suggested tentatively that the activity of the iodonium compounds may, in some cases, be due to a reaction with certain thiol groups essential to the microörganisms.

For some time we have been engaged in the study of the reactions which occur between iodonium salts and sulfhydryl compounds. We have found, for example, that diphenyliodonium chloride reacts in an aqueous solution with thioglycolic acid (kept neutral with sodium carbonate) to produce phenyl iodide and S-phenylthioglycolic acid (21% yield), m. p. 58–60° (lit. 61–63°[2]); sparingly soluble in water, soluble in benzene. This reaction is a rapid one at the boiling point of the solution. It also proceeds at room temperature but at a reduced rate. When thioglycolic acid dissolved in water is shaken with diphenyliodonium chloride, sodium carbonate, tellurium and ether at room temperature, diphenyltellurium is formed. The latter compound can be isolated from the ether layer as the yellow dibromide, m. p. 199–200°. The reaction with tellurium is an interesting one because of the possibility of a free radical mechanism, although other interpretations are possible.[3]

It has also been found that diphenyliodonium chloride reacts with other thiol compounds, such as thiophenol and cysteine. In the latter case the product is S-phenylcysteine, m. p. 200° (lit. 201–202°)[4]; calcd. for $C_9H_{11}O_2SN$: S, 16.3. Found: S, 16.2. All the iodonium reactions show a characteristic transient yellow color or precipitate.

The above reactions should be of interest from the standpoint of enzyme studies. Further work is in progress and we hope to communicate full details at a later date. We are very grateful to the Alberta Branch of the Canadian Cancer Society for financial aid in support of this work.

DEPARTMENT OF CHEMISTRY REUBEN B. SANDIN
ROBERT G. CHRISTIANSEN
UNIVERSITY OF ALBERTA ROBERT K. BROWN
EDMONTON, CANADA SAMUEL KIRKWOOD[5]

RECEIVED MAY 14, 1947

(1) Freedlander and French, *Proc. Soc. Exptl. Biol. Med.*, **63**, 319 (1946); *C. A.*, **41**, 2115 (1947).

(2) Gilman and Webb, THIS JOURNAL, **62**, 987 (1940).

(3) Sandin, McClure and Irwin, THIS JOURNAL, **61**, 2944 (1939); Sandin and Brown, unpublished work.

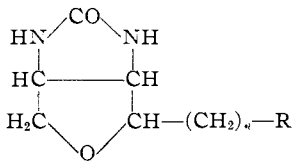
(4) Clarke and Inouye, *J. Biol. Chem.*, **94**, 541 (1931).

(5) Present address: 201 Prospect Avenue, Princeton, New Jersey.

FURAN AND TETRAHYDROFURAN DERIVATIVES. VIII. THE SYNTHESIS OF THE SULFONIC ACID ANALOGS OF OXYBIOTIN AND HOMOOXYBIOTIN

Sir:

In connection with our studies on the relationships of chemical structure and biological activity in the biotin and oxybiotin series,[1] we became interested in *dl*-oxybiotin sulfonic acid (I) and *dl*-homoöxybiotin sulfonic acid (II), the sulfonic acid analogs of *dl*-oxybiotin (III) and *dl*-homoöxybiotin (IV), respectively. In this communication we wish to record the synthesis of these two compounds.



	n	R
(I)	4	SO_3H
(II)	5	SO_3H
(III)	4	COOH
(IV)	5	COOH

(1) Hofmann, Chen, Bridgwater and Axelrod, THIS JOURNAL, **69**, 191 (1947).

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.

DEPARTMENT OF CHEMISTRY
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KLAUS HOFMANN
ANNA BRIDGWATER
A. E. AXELROD

RECEIVED MAY 9, 1947

(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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JACK GOLD
R. E. VAN STRIEN

RECEIVED MAY 13, 1947

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.

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

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

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

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

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 $[\eta] = \lim_{c\to 0} \frac{\ln \eta_{rel}}{c} = \sim 10$. 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 $\bar{n} \geqslant 10{,}000$.[1]

(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