oxide; presumably the formation of carbon dioxide must also be accompanied by the formation of water. By approximate measurement the amount of carbon dioxide was that which should be expected from the amount of selenium dioxide used in excess of that required for the condensation reaction.

This reaction resembles those which Kharasch[2] has carried out with peroxides and it appears likely that it proceeds by a similar mechanism

$$CH_3CO_2H \xrightarrow{[O]} {}^*CH_2CO_2H$$
$$2{}^*CH_2CO_2H \longrightarrow HO_2CCH_2CH_2CO_2H$$

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[2] M. S. Kharasch and M. T. Gladstone, THIS JOURNAL, **65**, 15 (1943).

RESEARCH AND DEVELOPMENT LABORATORIES
UNIVERSAL OIL PRODUCTS COMPANY
RIVERSIDE, ILLINOIS
RECEIVED MAY 10, 1947

COMMUNICATIONS TO THE EDITOR

A RAPID METHOD OF PREPARING $NaC^{14}N$ FROM $BaC^{14}O_3$

Sir:

Studies on the exchange of radiocyanide ion with cyanide complexes have been initiated recently in this Laboratory. Since radiocarbon is presently available only in the form of barium carbonate, it was necessary to investigate various means of converting it into a soluble cyanide.

A possible procedure is that of Cramer and Kistiakowsky.[1,2] This makes use of the reaction of gaseous ammonia and carbon dioxide with a potassium mirror. The procedure is somewhat elaborate and requires the use of a vacuum apparatus. For this reason, some simpler method of accomplishing the conversion would be highly desirable.

Several exploratory experiments were carried out on the use of electro-positive metals as reductants.[3] It was found that insignificant yields of cyanide resulted on heating zinc, aluminum, magnesium or sodium with barium carbonate, in a nitrogen atmosphere. This is in agreement with Loftfield's report.[2]

Preliminary results indicate, however, that yields of 75–80% can be obtained by heating sodium azide and barium carbonate in a nitrogen atmosphere. The method has the advantage of requiring only about thirty minutes and not necessitating the use of any special apparatus.

The procedure is: 0.1 g. of barium carbonate is mixed with 1 g. of sodium azide (Amend Drug and Chemical Co., N. Y.) in a six-inch test-tube, and a slow stream of nitrogen is directed into the mouth of the tube. The mixture is then heated carefully so as to maintain a steady but not too rapid decomposition of the azide. The fumes of sodium oxide may be drawn off into a hood or through a funnel connected to an aspirator. When the decomposition is complete, the test-tube is heated at a dull red heat for ten minutes. After cooling, water is added dropwise until all of the sodium present has reacted. The solution is then diluted, acidified with sulfuric acid, and the hydrogen cyanide distilled over into a slight excess of sodium hydroxide solution.

Four experiments were made with inactive barium carbonate. The resulting cyanide was determined by adding ammonia and potassium iodide and titrating with silver nitrate solution. The average yield was 78 ± 2%. In addition, two runs were made with added $BaC^{14}O_3$.[4] The specific gravity of the radiocyanide, counted as silver cyanide, was within experimental error of the calculated value, indicating that the radiochemical yield is the same as the analytical yield.

Much of the cyanide is formed during the final heating when no sodium azide is present. This suggests that the actual reaction may involve not the sodium azide, but the sodium nitride formed by its decomposition.

Support of this investigation by a grant-in-aid from The Research Corporation is gratefully acknowledged.

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[1] Cramer and Kistiakowsky, *J. Biol. Chem.*, **137**, 549 (1941).

[2] Loftfield, "The Preparation of Carbon-fourteen Labelled Hydrogen Cyanide, Alanine and Glycine," Circular C-3, Isotopes Branch, United States Atomic Energy Commission, June, 1947.

[3] A portion of these experiments was carried out by Mr. M. Volpe.

[4] Supplied by the U. S. Atomic Energy Commission.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA ARTHUR W. ADAMSON
RECEIVED SEPTEMBER 10, 1947

POLY-LYSINE

Sir:

On extending experiments concerning polymerization of amino acids[1] to basic amino acids, we succeeded in preparing poly-lysine. This polymer represents the first synthetic basic α-poly-amide and as it is water soluble, it may serve as a useful model in protein research.

A suitable monomer was found in ε-carbobenzoxy-α-carboxyl-l-lysine anhydride (I)[2] which

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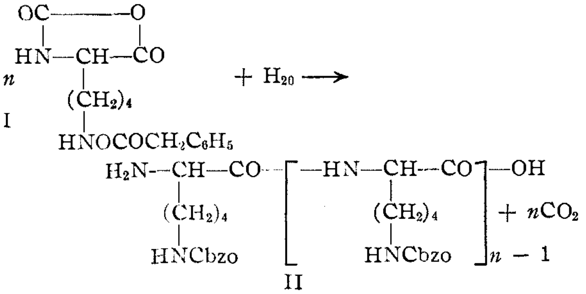
[1] Frankel and Katchalski, THIS JOURNAL, **64**, 2264 (1942); **64**, 2268 (1942).

[2] Bergmann, Zervas and Ross, *J. Biol. Chem.*, **111**, 245 (1935).

undergoes polymerization similarly to that of N-carboxyl-anhydrides of other amino acids studied previously.[3]

(I) carefully dried *in vacuo* undergoes at 105° melting and rapid polymerization, yielding poly-carbobenzoxy-lysine (II). Its average chain length was calculated from the determination of the free NH_2-end group (Van Slyke).



As illustration we give the following data concerning poly-lysine derivatives with an average chain length of 32 units.

Anal. Calcd. for (II) (n-average = 32 units): C, 64.0; H, 6.9; N, 10.6; amino N, 0.17. Found: C, 63.9; H, 7.1; N, 10.3; amino N, 0.17>.

On reduction with phosphonium iodide (II) yields poly-lysine hydriodide (III).

Anal. Calcd. for (III) (n-average = 32): C, 27.7; H, 5.0; N, 10.7; amino N, 5.5; I, 50.2. Found: C, 27.6; H, 5.2; N, 10.7; amino N, 5.3; I, 50.0.

(III) dissolves readily in water, gives positive ninhydrin and biuret reactions and negative picric acid test.

The Van Slyke ninhydrin method for determination of free amino acids showed that (III) contains practically no free lysine. Acid hydrolysis of (III), on the other hand, yielded lysine quantitatively.

Independent support for the constitution and average chain length of (III) was obtained by making use of Sanger's method.[4] On coupling (III) with 2,4-dinitrofluorobenzene, at room temperature, the amino groups of (III) were converted to 2,4-nitrophenylamino groups.

Anal. Calcd. (n-average = 32): N, 19.0; amino N, 0.0. Found: N, 19.0; amino N, 0.03.

Acid hydrolysis of the 2,4-dinitrophenylated polymer yields α,ϵ-di-2,4-dinitrophenyl-lysine (IV), derived from the terminal lysine units of (III) containing two free amino groups and ϵ-2,4-dinitropheny-lysine (V). The two dinitrophenyl derivatives were purified chromatographically[4] and each of them estimated colorimetrically. By taking into account the breakdown on hydrolysis of (IV) and (V) the following figures were obtained: Expected yield (from 100 mg. of the 2,4-dinitrophenyl derivative) of (IV) 4.98 mg.; of (V) 101 mg. Found: (IV) 4.80 mg.; of (V) 98 mg.

The constitution of poly-lysine seems thus to be proved. Finally, it may be mentioned that poly-lysine is split by glycerol extract of pancreatin as well as by crystalline trypsin.

LABORATORY OF HIGH MOLECULAR CHEMISTRY
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EPHRAIM KATCHALSKI
ISAAC GROSSFELD
MAX FRANKEL

RECEIVED AUGUST 8, 1947

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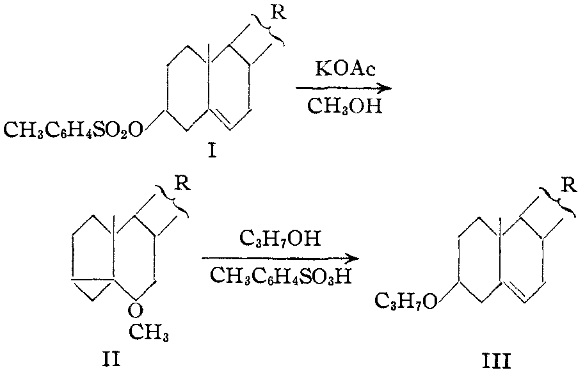
[3] *Cf.* Meyer and Go, *Helv. Chim Acta*, **17**, 1488 (1934); Go and Tani, *Bulletin Chem. Soc.*, Japan, **14**, 510 (1939).

[4] Sanger, *Biochem. J.*, **39**, 507 (1945).

THE CHOLESTEROL-*i*-CHOLESTEROL ISOMERIZATION[1]

Sir:

In a previous study[2] which describes the reaction of cholesteryl p-toluenesulfonate (I) with various alcohols, thiophenol and I were found to react with the formation of a compound which has been tentatively designated 3,5-bis-(phenylthio)-cholestane. The formation of this compound together with other data from the literature[3] suggests that in the production of cholesteryl ethers from I the cleavage of the carbon–oxygen bond occurs in the steroid rather than in the alcohol. I and alcohols react under basic conditions to form isomeric ethers[3a,4] (II) which upon treatment with acid catalyst and parent alcohol are converted to normal ethers.[2,5]



The conversion of *i*-cholesteryl methyl ether (II) into the normal n-propyl ether of cholesterol has now been effected in this laboratory by heating II and an excess of n-propanol with p-toluenesulfonic acid·H_2O as catalyst. The yield of cholesteryl n-propyl ether (III), constituting the first crop, was 77% of the calculated amount (m. p. 100°; not depressed by authentic material). Cholesteryl methyl ether does not react with n-propanol under these conditions and can be recov-

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[1] Aided by a grant from the John and Mary R. Markle Foundation.

[2] McKennis, THIS JOURNAL, in press.

[3] (a) Beynon, Heilbron, and Spring, *J. Chem. Soc.*, 907 (1936); (b) Wallis and co-workers, THIS JOURNAL, **59**, 137 (1937); (c) **59**, 1415 (1937); (d) **60**, 413 (1938).

[4] Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

[5] Wagner-Jauregg and Werner, *Z. physiol. Chem.*, **213**, 119 (1932).