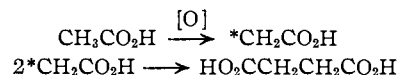


oxide; presumably the formation of carbon dioxide must also be accompanied by the formation of water. By approximate measurement the amount of carbon dioxide was that which should be expected from the amount of selenium dioxide used in excess of that required for the condensation reaction.

This reaction resembles those which Kharasch<sup>2</sup>

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

has carried out with peroxides and it appears likely that it proceeds by a similar mechanism



RESEARCH AND DEVELOPMENT LABORATORIES  
UNIVERSAL OIL PRODUCTS COMPANY  
RIVERSIDE, ILLINOIS

RECEIVED MAY 10, 1947

## COMMUNICATIONS TO THE EDITOR

### A RAPID METHOD OF PREPARING $\text{NaC}^{14}\text{N}$ FROM $\text{BaC}^{14}\text{O}_3$

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.<sup>1,2</sup> 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.<sup>3</sup> 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.<sup>2</sup>

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.

(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.

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  $78 \pm 2\%$ . In addition, two runs were made with added  $\text{BaC}^{14}\text{O}_3$ .<sup>4</sup> 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.

(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<sup>1</sup> to basic amino acids, we succeeded in preparing poly-lysine. This polymer represents the first synthetic basic  $\alpha$ -poly-amide and as it is water soluble, it may serve as a useful model in protein research.

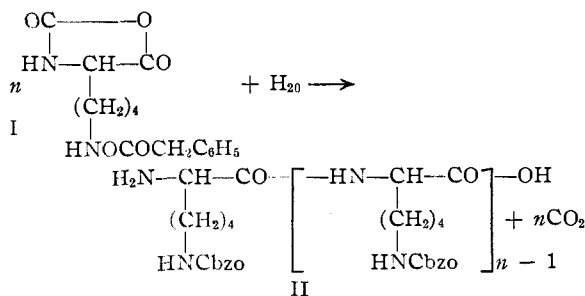
A suitable monomer was found in  $\epsilon$ -carboxybenzoxy- $\alpha$ -carboxyl-1-lysine anhydride (I)<sup>2</sup> which

(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.<sup>3</sup>

(I) carefully dried *in vacuo* undergoes at 105° melting and rapid polymerization, yielding polycarbobenzoxy-lysine (II). Its average chain length was calculated from the determination of the free NH<sub>2</sub>-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.<sup>4</sup> On coupling (III) with 2,4-dinitrofluorobenzene, at room temperature, the amino groups of (III) were converted to 2,4-dinitrophenylamino 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  $\alpha, \epsilon$ -di-2,4-dinitrophenyl-lysine (IV), derived from the terminal lysine units of (III) containing two free amino groups and  $\epsilon$ -2,4-dinitrophenyl-lysine (V). The two dinitrophenyl derivatives were purified chromatographically<sup>4</sup> 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)

(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).

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.

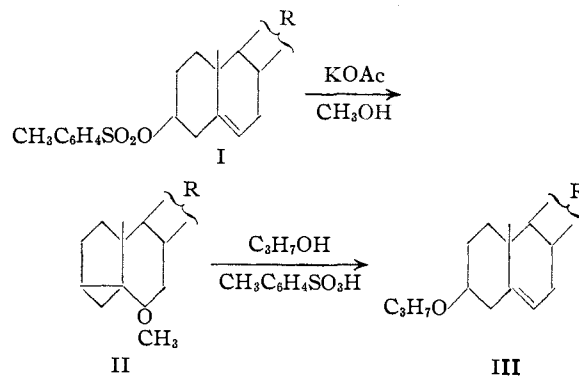
LABORATORY OF HIGH MOLECULAR CHEMISTRY  
EPHRAIM KATCHALSKI  
HEBREW UNIVERSITY  
ISAAC GROSSFELD  
JERUSALEM, PALESTINE  
MAX FRANKEL

RECEIVED AUGUST 8, 1947

### THE CHOLESTERYL-*i*-CHOLESTERYL ISOMERIZATION<sup>1</sup>

*Sir:*

In a previous study<sup>2</sup> 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<sup>3</sup> 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<sup>3a,4</sup> (II) which upon treatment with acid catalyst and parent alcohol are converted to normal ethers.<sup>2,5</sup>



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<sub>2</sub>O 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-

(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).

ered unchanged in quantitative yield. The second crop of crystals from the reaction of the *i*-ether had the properties of a mixture, indicating incomplete conversion and/or competition between methoxyl and propoxyl groups.

The preparation of cholesteryl halides from the *i*-ether and hydrogen halides under mild conditions<sup>3</sup> is not without analogy to the above. Wallis and co-workers, who have presented the currently most reasonable structure for the *i*-cholesterol compounds, considered<sup>3c</sup> that the interesting formation of the *i*-cholesterol compounds from the tosyl ester of cholesterol could best be described by a formulation which involves a molecular rearrangement. The essential nature of the reaction would now appear to involve an electronic shift between rings A and B with carbon atom no. 5 as the pivot.

A detailed description of the work which assumes interest as a preparative method as well as a presumptive route to the introduction or removal of labels in biochemical work will be reported later.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY  
THE JOHNS HOPKINS UNIVERSITY  
SCHOOL OF MEDICINE HERBERT MCKENNIS, JR.  
BALTIMORE 5, MARYLAND

RECEIVED AUGUST 21, 1947

#### FORMATION OF QUINONE BY THE ACTION OF BROMINE OXIDE ON BENZENE

Sir:

In an attempt to elucidate the mechanism of the effect of oxygen in accelerating the bromination of hydrocarbons, the effect of bromine oxide ( $\text{Br}_2\text{O}$ ) on the bromination of toluene and cyclohexane was investigated. This substance proved to be a powerful inhibitor for the photobromination of toluene (one mole per cent. of  $\text{Br}_2\text{O}$  in  $\text{Br}_2$  reduced the rate of bromination to one-half; two and a half mole per cent. reduced the rate to 1/30). It showed no similar effect on cyclohexane. By comparing the total bromine content of the solution with its oxidizing power as determined by a titration with sodium arsenate, it has been shown that when bromine oxide ( $\text{Br}_2\text{O}$ ), dissolved in carbon tetrachloride is mixed, in the light or in the dark, with toluene or cyclohexane, it is decomposed within one or two minutes. Attempts were then made to isolate the compounds formed by the reaction of bromine oxide with the hydrocarbons. When the unreacted bromine and excess solvent were removed from the reaction mixture containing toluene, a yellow concentrate was obtained which acted as an inhibitor in the bromination of toluene. It liberated iodine from acidified potassium iodide and reduced Tollens reagent instantaneously at room temperature. This behavior suggested a quinone. However, all attempts to isolate toluoquinone failed.

When benzene was used, the yellow oil (which remained after the removal of the solvent and un-

reacted materials) liberated iodine from potassium iodide, reduced Tollens reagent, and had a characteristic quinone odor. The material was molecularly distilled at reduced pressure. The yellow crystals, thus obtained, melted at 111–113°, and did not depress the melting point of an authentic sample of *p*-benzoquinone. The residue still reduced Tollens reagent and liberated iodine from potassium iodide. It was moderately soluble in water in which it formed a pink solution, suggestive of *o*-benzoquinone; but attempts to isolate this compound have thus far met with no success.

The direct formation of quinone from benzene is most remarkable. It is one of the few instances known to the authors, whereby, in a single reaction, benzene is converted to quinone. The study of other halogen oxides is contemplated.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CHICAGO  
CHICAGO, ILLINOIS

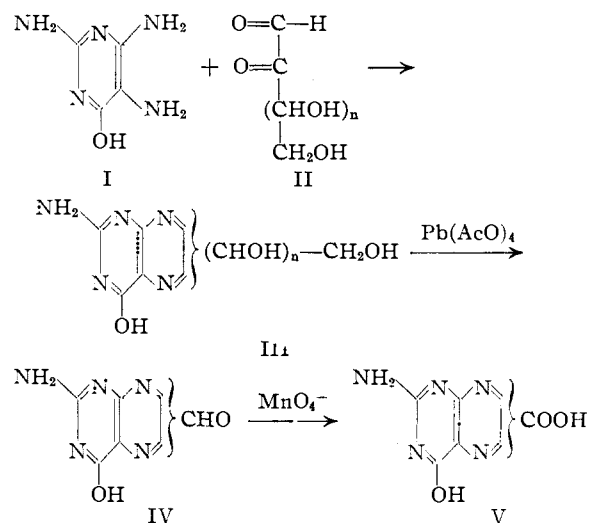
M. S. KHARASCH  
PERCY B. POLEN  
W. H. URRY

RECEIVED OCTOBER 6, 1947

#### A NEW SYNTHETIC METHOD FOR PTERINES

Sir:

In view of the recent publication of Karrer, *et al.*,<sup>1</sup> on the synthesis of polyhydroxypterines by the condensation of sugars with 2,3,5-triamino-6-hydroxypyrimidine (I) we wish to report our observations on the same reaction and on a new synthesis for similar compounds which is outlined below.



In our hands the condensation of D-glucose with I under the conditions of Karrer, *et al.*, yields 7-tetrahydroxybutylpterine, while the condensation of D-glucose with I-bisulfite or I-bisulfate under strongly acidic conditions yields primarily 6-tetrahydroxybutylpterine. The type of isomer obtained is determined by the physical properties of III or the carboxy-pterine (V) obtained from it.

(1) Karrer, Schwyzer, Erden and Siegwart, *Helv. Chim. Acta.* **30**, 1081 (1947).

Since the yield of 6-tetrahydroxypterine by the above procedure was small, our attention was centered on the more direct synthesis of III by the condensation of I with osones (II). The reaction of I with II is rapid and yields III in good quantity. The conditions for obtaining the preferred isomer appear to be reversed from that described above—*i. e.*, I and II at pH 5–9 yield the 6-isomer, while the condensation of I-bisulfite and II in strongly acidic solution yields a mixture richer in the 7-isomer.

Although details of work on pure isomers will be published later it is deemed worthy to report the synthesis of the isomeric mixture of III and the preparation of the isomeric mixture of formylpterine (IV) from III by the method outlined.

D-Glucosone was heated with an equivalent amount of 2,4,5-triamino-6-hydroxypyrimidine bisulfite in 75% acetic acid at 75° for forty-five minutes. The mixture was cooled and the precipitate collected. The product was exhaustively extracted with hot alcohol and dried. Yield of III was 60%,  $[\alpha]_{D}^{25}$ , -70.9° (169.2 mg. per 100 ml. of *N* NaOH). Absorption spectrum in 0.1 *N* NaOH showed maxima at 252 m $\mu$  and 360–362 m $\mu$  with  $\epsilon$  of 19,000 and 7940, respectively.

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>N<sub>5</sub>O<sub>5</sub>: C, 42.39; H, 4.62; N, 24.71. Found: C, 42.17; H, 4.92; N (Kjeldahl), 25.11.

III was oxidized with lead tetraacetate to IV, an isomeric mixture, obtained in 85% yield. IV contained ash which was hard to remove. It exhibited strong carbonyl activity forming oximes, hydrazones and Schiff bases readily. IV treated with a slight excess of barium permanganate gives V, identity of which was established by its ultraviolet absorption, titration curve and analysis.

*Anal.* Calcd. for C<sub>7</sub>H<sub>5</sub>N<sub>5</sub>O<sub>2</sub>H<sub>2</sub>O: C, 40.2; N, 33.5. Found: C, 38.8; N (Kjeldahl), 31.5 (cor. for 4.90% ash).

THE UPJOHN COMPANY  
KALAMAZOO, MICHIGAN

H. G. PETERING  
D. I. WEISBLAT

RECEIVED AUGUST 18, 1947

#### ANTAGONIST FOR PTEROYLGLUTAMIC ACID

Sir:

We wish to report the synthesis of a potent pteroylglutamic acid antagonist, N-[4-{{(2,4-diamino-6-pteridyl)-methyl}-amino}-benzoyl]-glutamic acid. In the course of an investigation of analogs of pteroylglutamic acid, this compound was prepared from 2,4,5,6-tetraminopyrimidine sulfate,<sup>1</sup> 2,3-dibromopropionaldehyde, and *p*-aminobenzoylglutamic acid under the conditions described for the synthesis of pteroylglutamic acid.<sup>2</sup> Purification of the crude product was accomplished by a method very similar to that used for pteroylglutamic acid.<sup>3</sup>

(1) Traube, *Ber.*, **37**, 4545 (1904).

(2) Angier, *et al.*, *Science*, **103**, 667 (1946).

(3) Waller, *et al.*, *THIS JOURNAL*, **69**, in press (1947).

The purified product was obtained crystalline as clusters of yellow needles, and in 0.1 *N* sodium hydroxide solution it shows ultraviolet absorption maxima at 260, 284 and 370 m $\mu$ , and minima at 239, 271 and 333 m $\mu$ . *Anal.* Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>5</sub>N<sub>8</sub>·2H<sub>2</sub>O: C, 47.9; H, 5.1; N, 23.5. Found: C, 47.3; H, 5.18; N, 23.4. Magnesium salt: Calcd. for C<sub>19</sub>H<sub>18</sub>O<sub>5</sub>N<sub>8</sub>Mg·3H<sub>2</sub>O: C, 44.2; H, 4.7; N, 21.7; Mg, 4.7. Found: C, 44.6; H, 4.85; N, 21.4; Mg, 4.82. The biological properties have been examined by Dr. B. L. Hutchings and Dr. E. L. R. Stokstad of the Lederle Laboratories Division, American Cyanamid Company, Pearl River, New York. The inhibition ratio for half-maximum inhibition of the growth of *Streptococcus faecalis* R is 1.9, 0.7 and 0.4 at concentrations of pteroylglutamic acid of 0.003, 0.005 and 0.01 microgram per 10 ml., respectively.

Details of the synthesis and properties of this and related compounds will be the subject of subsequent communications.

CALCO CHEMICAL DIVISION

DORIS R. SEEGER

AMERICAN CYANAMID COMPANY

JAMES M. SMITH, JR.

BOUND BROOK, NEW JERSEY

MARTIN E. HULTQUIST

RECEIVED SEPTEMBER 19, 1947

#### BIOSYNTHESSES INVOLVING PANTOTHENIC ACID

Sir:

In *Escherichia coli* cysteic acid appears to prevent competitively the decarboxylation of aspartic acid to  $\beta$ -alanine which results in pantothenic acid becoming a limiting growth factor.<sup>1</sup> Under our testing conditions the rate of pantothenic acid synthesis is determined by the ratio of cysteic to aspartic acid, and exogenous substances allowing growth to occur at a lower rate of pantothenic acid synthesis produce an increased antibacterial index.<sup>2</sup>

Such an effect is obtained with citric, *cis*-aconitic or  $\alpha$ -ketoglutaric acids. The antibacterial index over a thirty-fold range in aspartic acid concentrations was 300 in the medium containing these substances but only 30 in their absence. Oxalacetic and pyruvic acid were inactive alone, but a mixture of both necessitated a slight increase in the concentration of cysteic acid to obtain the same growth inhibition. Acetate alone possessed some activity. Pantoic acid was inactive. The apparent "sparing action" of *cis*-aconitic acid on the pantothenic acid requirement of *E. coli* is not equaled by its precursors; hence, it appears that pantothenic acid deficient cells are unable to convert effectively pyruvate and oxalacetate to *cis*-aconitate (or ketoglutarate). This datum explains the previously reported<sup>1</sup> enhanced activity of glutamic over aspartic acid in preventing the toxicity of cysteic acid. The transamination reaction produces both aspartic and  $\alpha$ -ketoglutaric acids, the latter having a

(1) Ravel and Shive, *J. Biol. Chem.*, **166**, 407 (1946).

(2) Molar ratio (analog to metabolite) just necessary for maximum inhibition of growth.

"sparing action" on the product of the blocked reaction. Previous evidence<sup>3</sup> involving pantothenate in the oxidation of pyruvate can also be explained on the basis of pantothenate mediating *cis*-aconitate synthesis.

That the above effect directly involves pantothenic acid was demonstrated by the reversing effect of both pantothenic and  $\alpha$ -ketoglutaric acids on a pantothenic acid antagonist, *N*- $\alpha$ , $\gamma$ -dihydroxy -  $\beta$ , $\beta$  - dimethylvaleryl -  $\beta$  - aminobutyric acid, for *E. coli*. Further, the pantothenic acid requirement of *Proteus morgani* in a medium of inorganic salts, glucose, nicotinamide and cystine was appreciably decreased by  $\alpha$ -ketoglutaric acid.

With *Lactobacillus arabinosus*, an oleic acid source ("Tween 80") or sodium glycocholate increased the antibacterial index from approximately 3,000 to 30,000 for the competitive inhibition of *N*-pantoyl-*n*-butylamine<sup>4</sup> of pantothenic acid functioning. Both substances added simultaneously did not enhance the effect. Since this organism presumably requires acetate for synthesis of sterols and fatty acids, this inhibitor appears to prevent the conversion of acetate to an intermediate common to both sterol and oleic acid synthesis.

The reported involvement of pantothenic acid in the conversion of glycine to threonine,<sup>5</sup> the demonstration by Lipmann, *et al.*,<sup>6</sup> of the presence of pantothenic acid in the coenzyme for acetylation of sulfanilamide and choline, and the results of the above *inhibition analyses* tend to indicate that many of the enzymatic reactions in which pantothenic acid functions involve the hypothetical "active" acetyl radical.

(3) Dorkman, *et al.*, *J. Biol. Chem.*, **144**, 393 (1942).

(4) Snell and Shive, *ibid.*, **160**, 287 (1945).

(5) Rossi and Cennamo, *Chem. Abstr.*, **40**, 6543 (1946).

(6) Lipmann, *et al.*, *J. Biol. Chem.*, **167**, 869 (1947).

BIOCHEMICAL INSTITUTE AND THE WILLIAM SHIVE  
CHEMISTRY DEPARTMENT OF THE W. W. ACKERMANN  
UNIVERSITY OF TEXAS, AND THE JOANNE MACOW RAVEL  
CLAYTON FOUNDATION FOR RESEARCH  
AUSTIN, TEXAS JUDITH ELIOTT SUTHERLAND

RECEIVED SEPTEMBER 19, 1947

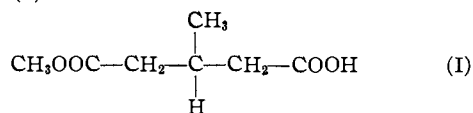
#### REARRANGEMENT IN THE PREPARATION OF ESTER ACID CHLORIDES

Sir:

Cason<sup>1</sup> has recently drawn attention to the fact that during the preparation of the ester acid chlorides of the isomeric half esters of dibasic acids such as  $\alpha$ -ethyl- $\alpha$ -butylglutaric acid by means of thionyl chloride rearrangement may occur, the derivatives obtained from the ester acid chlorides being mixtures derived from both isomers.

The writer has studied the conditions under which this type of rearrangement occurs when preparing the ester acid chlorides of the two

enantiomorphs<sup>2</sup> of methyl hydrogen  $\beta$ -methylglutarate (I)



Rearrangement leads in this case to racemization and can be detected simply by pouring the ester acid chloride into water and measuring the rotation of the recovered half ester. In this way it has been found that no rearrangement takes place when the ester acid chloride is prepared by the action of oxalyl chloride in benzene solution. In case of thionyl chloride the occurrence and extent of rearrangement depend on the purity of the reagent and on the reaction temperature. If pure thionyl chloride (Kahlbaum "reinst, wasserhell") is used no rearrangement occurs if the reaction takes place at 30° and excess reagent is removed under reduced pressure on a water-bath kept at 50°. Use of less pure thionyl chloride (Kahlbaum, "purum") leads under the conditions just described to rearrangement, the extent of which increases if the reaction temperature is raised. (The ester acid chlorides have not been distilled.)

It is well known that anhydrides may be formed during the action of thionyl chlorides on acids and that the yield of acid chloride is lower if impure thionyl chloride is used or if the reaction temperature is too high.<sup>3</sup> With dibasic acids of the succinic and glutaric acid series thionyl chloride gives the cyclic anhydrides only. It appears likely that the rearrangement observed in the preparation of the ester acid chlorides occurs via the anhydrides.

That rearrangement may be avoided during the preparation of the ester acid chloride of (I) is evident from the fact that lengthening of the chain of the dextrorotatory enantiomorph of (I) by the Arndt-Eistert synthesis has given (+)- $\beta$ -methyladipic acid identical with that derived from natural products.<sup>2</sup> Furthermore, the two enantiomorphs of (I) have been used as starting material for the synthesis of *d*(+)- and *l*(-)-3-methyltetracosanoic acids. The intermediate ester acid chloride was in case of one enantiomorph prepared by means of oxalyl chloride and in case of the other by means of pure thionyl chloride. The enantiomorphic long chain  $\beta$ -methyl substituted acids both melted sharply at 65.5° (cor.), and showed numerically equal optical rotations,  $[\text{M}]^{25\text{D}}$  13.2° (chloroform, *c*, 5.78). Mixed in equal proportions the acids gave a racemic compound melting sharply at 68.6° (cor.).

INSTITUTE OF MEDICAL CHEMISTRY  
UNIVERSITY OF UPPSALA STINA STÄLLBERG-STENHAGEN  
UPPSALA, SWEDEN

RECEIVED SEPTEMBER 11, 1947

(2) S. Ställberg-Stenhagen, *Arkiv Kemi, Min., Geol.* **25A**, No. 10 (1947).

(3) "Organic Syntheses," Coll. Vol. I, 2nd ed., p. 147.

(1) J. Cason, *THIS JOURNAL*, **69**, 1548 (1947).

**PEROXIDE-CATALYZED ADDITION OF IODOFORM TO OLEFINS**

*Sir:*

In a recent publication<sup>1</sup> Kharasch and co-workers described the peculiar observation that in the peroxide-catalyzed addition of chloroform to olefins the carbon-hydrogen bond of the former is broken and the  $\cdot\text{CCl}_3$ -radical attached to the terminal carbon atom of the olefin, whereas bromoform is split at a carbon-bromine linkage. Therefore, in the addition of bromoform the  $\cdot\text{CHBr}_2$ -group attacks the terminal methylene group of the olefin.

We wish to report analogous observations which we have made during the last year on the behavior of iodoform. Limonene and iodoform, in a molar ratio of 2:1, reacted under the influence of acetyl peroxide to yield a 1:1-addition product in 35% yield, b.p.  $75^\circ$  (25 mm.).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{17}\text{I}_3$ : C, 24.9; H, 3.2; I, 71.8. Found: C, 24.6; H, 3.2; I, 72.1.

That iodoform added as  $\text{CHI}_2$ - and I-radicals is indicated by the presence of *one* iodine atom which can be titrated with alcoholic silver nitrate and which can be removed by reduction over

(1) Kharasch, Jensen and Urry, *THIS JOURNAL*, **69**, 1100 (1947).

Adams catalyst to give a di-iodo compound of b.p.  $70^\circ$  (30 mm.).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{20}\text{I}_2$ : C, 32.5; H, 4.9. Found: C, 32.7; H, 4.6.

Hydrolysis experiments of the iodoform-addition product gave, however, complex and unexpected results, which will be reported in a comprehensive paper in *THIS JOURNAL*.

Allyl benzoate likewise forms with iodoform a 1:1-addition product, which cannot be purified but which can be hydrolyzed by refluxing with ethanolic sodium hydroxide. Under these conditions the benzoyl group remains untouched, but all the iodine atoms are removed to yield an aldehyde, b.p.  $70^\circ$  (10 mm), characterized by formation of a crystalline 2,4-dinitrophenylhydrazone of m.p.  $193$ – $194^\circ$ .

*Anal.* of the aldehyde. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}_3$ : C, 69.5; H, 5.3; mol. wt., 190. Found: C, 69.0; H, 5.3; mol. wt., 182.

*Anal.* of the 2,4-dinitrophenylhydrazone. Calcd. for  $\text{C}_{17}\text{H}_{14}\text{O}_6\text{N}_4$ : N, 15.1. Found: N, 14.9.

DEPARTMENT OF ORGANIC  
CHEMISTRY  
THE HEBREW UNIVERSITY  
JERUSALEM, PALESTINE

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## NEW BOOK

**Nuclear Physics Tables**, by J. MATTAUCH, Kaiser Wilhelm-Institut für Chemie, Berlin-Dahlem, and **An Introduction to Nuclear Physics**, by S. FLUEGGE, Kaiser Wilhelm-Institut für Chemie, Berlin-Dahlem. Translated from the German by EUGENE P. GROSS and S. BARGMANN. Published and Distributed in the Public Interest with the Consent of the Alien Property Custodian under License No. A-1136. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y., 1946. 173 pp. + 28 figs. + 8 plates.  $20 \times 28$  cm. Price, \$12.00.

This volume is an authoritative survey of the properties of stable and radioactive nuclei and of the phenomena associated with nuclear transformation. About two-thirds of the space is devoted to Fluegge's concise textbook presentation of the main features of nuclear science with emphasis on experiment and its interpretation. The remainder of the space is devoted to Mattauch's comprehensive tables of nuclear properties and nuclear reactions, with more than a thousand references giving complete literature coverage until the middle of 1941.

The textbook on nuclear physics is an outstanding contribution to the modern technical literature. The approach is distinctive, and the point of view fresh and modern. Understandable qualitative coverage is given to a large number of relevant topics in the small monograph, with a judicious choice of quantitative derivations and correlations. Some difficult concepts are presented effectively with the aid of an appeal to scientific intuition rather than with the esoteric theoretical development so often used in texts on the subject.

The properties of stable nuclei are presented first, with adequate coverage of mass spectrography, packing fraction, and mass defects, and of the role of nuclear mass, spin, magnetic moment, and electrical dipole moment in nuclear and atomic physics. The phenomena associated with nuclear reaction are presented from a general standpoint with good sections on the yields of nuclear reactions with high speed charged projectiles (Gamow factor) and with slow neutrons. The section on unstable nuclei is brief but generally to the point. The application of the Gamow theory to the phenomenon of alpha decay is good, as is the qualitative picture of the Fermi theory of beta decay and the Yukawa extension to include meson interactions in the nucleus, and the pictures of K-capture and of isomeric transition. Chemists will be interested in the last section on Systematics of Stable Nuclei for the existence rules, abundance rules, and the general equation for binding energy as a function of mass number and nuclear charge.

Quantitative discussion of the distribution of energies in beta decay is missing in the section on radioactivity, as is a discussion of range-energy relations of electrons or beta rays, treatment of specific problems of alpha, beta, and gamma counting, the problem of internal conversion of gamma rays, and the use of nuclear energy equations to predict decay energies of nuclei. Since the text was not designed to serve as a detailed introduction to laboratory investigations in nuclear science, similar omissions will be noted in the other sections. No literature citations or general references are given, and an index is lacking.

The specific data of nuclear physics are given in six