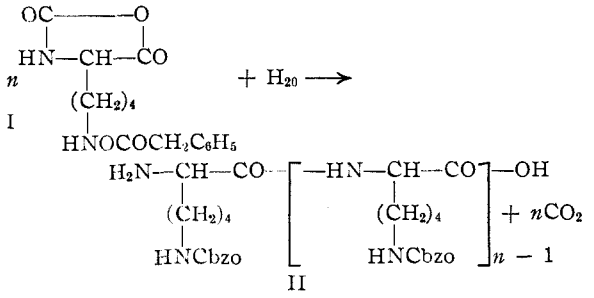
undergoes polymerization similarly to that of N-carboxyl-anhydrides of other amino acids studied previously.[3]

(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.

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RECEIVED AUGUST 8, 1947

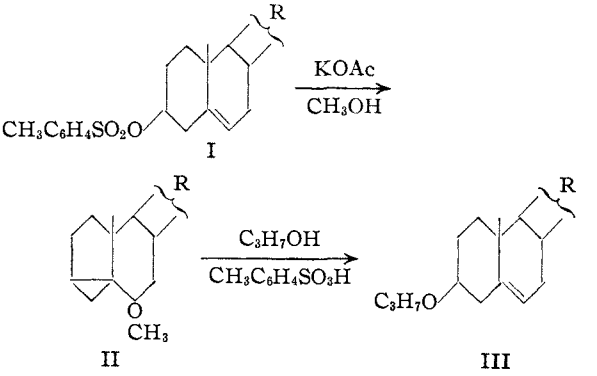
(3) *Cf.* Meyer and Go, *Helv. Chim Acta*, **17**, 1488 (1934); Go and Tani, *Bulletin Chem. Soc.*, Japan, **14**, 510 (1939).

(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-

(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[3] 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[3c] 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.

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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 (Br_2O) 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 Br_2O in 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 (Br_2O), 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 toluquinone failed.

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

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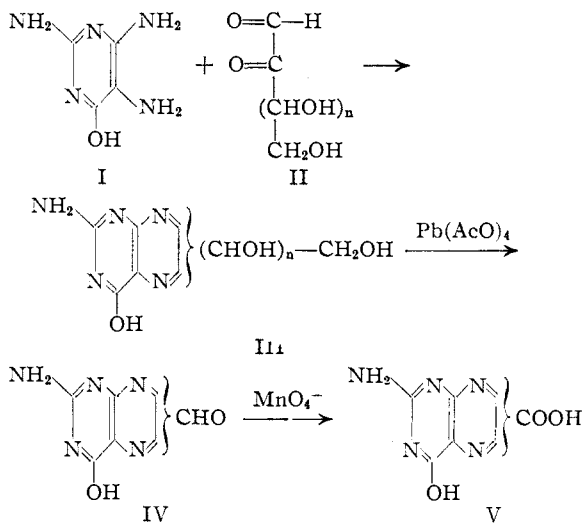
RECEIVED OCTOBER 6, 1947

A NEW SYNTHETIC METHOD FOR PTERINES

Sir:

In view of the recent publication of Karrer, *et al.*,[1] on the synthesis of polyhydroxypterines by the condensation of sugars with 2,3,5-triamino-6-hydroxypyrimindine (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**, 1031 (1947).