The specific volume was obtained from density, which was measured by flotation in carbon tetrachloride. The percentage increase in crystallinity was calculated using the values given by H. Mark[1] for the density of crystalline cellulose, 1.59 g./ml. (Sp V = 0.629). The density of amorphous cellulose was taken to be 1.50 g./ml. (Sp. V = 0.667) as estimated by P. H. Hermans.[2] The following relation was used to calculate the increase in crystallinity

$$\frac{\text{Sp. } V \text{ of untreated sample} - \text{Sp. } V \text{ of treated sample}}{\text{Difference in Sp. } V \text{ of amorphous and crystalline cellulose}}$$

A rayon of specific volume 0.653 showed a weight loss of 10% when treated with the reagent for five minutes. The specific volume of the treated sample was 0.647, indicating an increase of 16% in the crystallinity.

If the only process involved in the initial stages of this treatment is the attack and removal of the amorphous portion of the fiber, the density increase should predict a change of crystallinity of the same order of magnitude as the weight of material lost. However, the actual increase in density is much larger. This may indicate that with the rupture of a cellulose chain in an amorphous portion of the fiber a process of crystallization is initiated.

(1) H. Mark, "Physik und Chemie der Cellulose," Berlin, 1932.
(2) P. H. Hermans, "Contribution to the Physics of Cellulose Fibres," Elsevier Publishing Co., Inc., 1946.

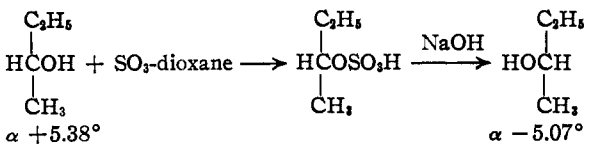
INST. OF POLYMER RESEARCH
POLYTECHNIC INST. OF BROOKLYN
BROOKLYN, N. Y.
F. C. BRENNER
V. FRILETTE
H. MARK

RECEIVED DECEMBER 9, 1947

A NEW WALDEN INVERSION

Sir:

The following reaction sequence constitutes a new Walden inversion



The second step resembles the displacement of *p*-toluenesulfonate ion from secondary alkyl esters of the sulfonic acid by ethoxide or acetate ions, a reaction which has been shown to invert the configuration of the carbinol carbon.[1]

We previously[2] prepared (+)*s*-butylsulfuric acid by action of Suter's sulfur trioxide–dioxane reagent on (+)*s*-butyl alcohol and found that upon its acid hydrolysis a (+)alcohol was recovered whose rotation was 30% of that of the starting material. We had assumed that the racemization was confined to the hydrolytic step and that the formation of the alkylsulfuric acid proceeded with little if any racemization. This is now confirmed.

Since the action of chlorosulfonic acid and of sulfuric acid upon (+)alcohol gave (+)*s*-butylsulfuric acid, and since it was difficult to see how all these methods could involve breaking the carbon–oxygen bond of the alcohol, it was considered that the alkylsulfuric acid had the same configuration as the alcohol. If this is true, and its plausibility is increased by our finding that the sulfur trioxide–pyridine complex[3] also gives a (+)alkylsulfuric acid, then the saponification involves the displacement of a sulfate ion by a hydroxide ion with inversion of configuration. Since this reaction is one between two ions of like charge it is comparatively slow.

The alkylsulfuric acid was prepared by action of the sulfur trioxide–dioxane complex upon an alcohol of α +5.38. In one saponification, 8 g. of (+)sodium *s*-butylsulfate (from neutralizing the alkylsulfuric acid reaction mixture with sodium hydroxide, evaporating and extracting the sodium alkylsulfate with methanol) and 10 g. of sodium hydroxide were dissolved in 50 cc. of water. At 100° the reaction required two days for substantial completion. Alcohol was recovered in 54% yield with a rotation 6% below that of the starting alcohol and of opposite sign. About 8% of gas, apparently butylene, was evolved. A similar alcohol was obtained from the barium salt in a more concentrated potassium hydroxide solution, but several times as much butylene resulted.

Further investigation now under way at this laboratory should reveal the degree to which this reaction is common to secondary alcohols.

(1) This work of Kenyon, Phillips and co-workers is reviewed by Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 160–163.
(2) Burwell, THIS JOURNAL, **67**, 220 (1945).
(3) Sobel, Drekter and Natelson, *J. Biol. Chem.*, **115**, 381 (1936).

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILL.
ROBERT L. BURWELL, JR.
HOWARD E. HOLMQUIST

RECEIVED DECEMBER 18, 1947

FORMYLFOLIC ACID, A FUNCTIONAL DERIVATIVE OF FOLIC ACID

Sir:

Previous studies from this Laboratory have indicated that a coenzyme containing *p*-aminobenzoic acid is involved in combining a single carbon unit into the pyrimidine ring of purines[1] and that folic acid functions in the biosynthesis of purines.[2] Seeking functional derivatives which could act as "carriers" of formate, we prepared *p*-aminobenzoylhistidine and condensed it with α,β-dibromopropionaldehyde and 2,4,5-triamino-6-hydroxypyrimidine to obtain pteroylhistidine. No pronounced activity was obtained with either of these histidine derivatives. The announcement of the structure of rhizopterin[3] which is *p*-[N-(2-amino-4-hydroxypyramido-[4,5-b]pyrazin-6-ylmethyl)-formamido]-benzoic acid gave a clue as

(1) Shive, *et al.*, THIS JOURNAL, **69**, 725 (1947).
(2) Rogers and Shive, *J. Biol. Chem.*, in press.
(3) Wolf, *et al.*, THIS JOURNAL, **69**, 2753 (1947).