ticularly interesting in view of the fact that the work of Erlenmeyer, Schoenauer and Schwarzenbach[3] indicates that all three hydrogen atoms of hypophosphorus acid exchange rapidly with deuterium oxide. Apparently in the deamination reaction a hydrogen atom was extracted from another aromatic nucleus, since that is the only source of hydrogen which is not equilibrated with deuterium.

(3) Erlenmeyer, Schoenauer and Schwarzenbach, *Helv. Chim. Acta*, **20**, 732 (1937); see also Franke and Mönch, *Ann*, **550**, 1 (1941).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS ELLIOT R. ALEXANDER
URBANA, ILLINOIS ROBERT E. BURGE

RECEIVED DECEMBER 22, 1947

CAUSE OF EXPLOSIONS OCCASIONALLY OBSERVED DURING EVAPORATION OF SOLUTIONS OF ALUMINUM HYDRIDE AND RELATED COMPOUNDS

Sir:

In experiments involving dimethyl ether solutions of aluminum hydride, as well as of lithium and sodium aluminum hydrides, explosions have occasionally occurred. The details to be described have demonstrated that the explosions were caused by carbon dioxide present as an impurity in some samples of the ether.

Explosions have occurred toward the end of distillations undertaken to remove the solvent from dimethyl ether solutions of lithium aluminum hydride. That the explosions were due to an impurity more volatile than dimethyl ether was indicated by the facts (1) that later samples of the ether taken from a cylinder caused less violent explosions than the first few samples, and (2) ether taken from another cylinder at no time caused these explosions. These facts, as well as chemical tests to prove their absence, excluded aldehydes, alcohols or peroxide as the offending impurity. Considerable carbon dioxide was present in the cylinders whose contents led to explosions; its removal by fractionation *in vacuo* rendered the contents harmless. After carbon dioxide was reintroduced into the purified sample, the explosions recurred. It was then found that diethyl ether solutions of lithium aluminum hydride, which can ordinarily be safely evaporated, may also cause explosions if first treated with carbon dioxide in considerable amount.

Evaporation of dimethyl ether solutions of aluminum hydride and subsequent slow heating of the residue may result in a very rapid reaction in which, at slightly above 40°, relatively large quantities of gaseous material are suddenly released, but which is not accompanied by detonation, unless a large excess of aluminum chloride is present. But carbon dioxide-free ether leads to a residue which begins to decompose *slowly* above 70°, if aluminum chloride is not present in large amount; even in the presence of a large excess of the latter (2.5 moles/l.), the decomposition above 40° is sudden but without detonation. Other experiments have shown that aluminum chloride accelerates the decomposition of aluminum hydride.

On one occasion a violent explosion occurred when the residue resulting from evaporation of a dimethylcellosolve solution of aluminum hydride was warmed. The aluminum hydride was contaminated with aluminum chloride, which is known to decrease the stability of the former, and the dimethylcellosolve was impure. No explosion resulted when the experiment was repeated with purified materials.

Lithium aluminum hydride is considerably more stable than aluminum hydride. Approximately two hundred different reactions using the former reagent have been carried out in this Laboratory without untoward results although no precautions were taken to exclude carbon dioxide. We are, therefore, convinced that it may be used with perfect safety if the precautions suggested by the facts herein reported are followed. In other words, we recommend that in the reduction of organic compounds the normal procedure of hydrolyzing the initial reaction product before evaporation of the solvent be employed. If, as would rarely be the case, it is desired to evaporate the solvent before hydrolysis of the initially produced organic salts, the safety of the procedure should first be tested by use of a small sample.

GERALDINE BARBARAS
DEPARTMENT OF CHEMISTRY GLEN D. BARBARAS
THE UNIVERSITY OF CHICAGO A. E. FINHOLT
CHICAGO 37, ILL. H. I. SCHLESINGER

RECEIVED DECEMBER 15, 1947

CRYSTALLINITY OF HYDRO-CELLULOSES

Sir:

Hydrolytic methods are being used at present for evaluating the intramolecular structure of cellulose. It has been suggested in a paper to be published in THIS JOURNAL that such methods might possibly cause additional crystallization in the initial stages of hydrolysis. We have succeeded in obtaining data which indicate that such changes do occur. Consequently, it would seem necessary to reinterpret accessibility measurements based on hydrolysis rates in terms of two competing processes: hydrolysis and further crystallization.

The data in Table I were obtained on a beechwood pulp that had been digested in boiling 2.5 *N* hydrochloric acid–0.6 *M* ferric chloride solution constantly saturated with air.

TABLE I

Time treated, minutes	Percentage of samples destroyed	Specific vol. of bone-dry hydrocellulose, ml./g.	Percentage increase in crystallinity from Sp *V.* change, %
0	0	0.652	
10	4.8	.647	15
19	6.0	.646	18
28	39.0	.645	19

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.

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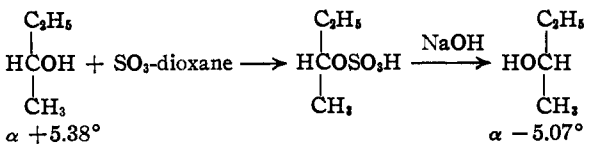
H. MARK

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
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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).